Hybrid Nafion–inorganic oxides membrane doped with heteropolyacids for high temperature operation of proton exchange membrane fuel cell

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Abstract

Performance of the proton exchange membrane fuel cell (PEMFC) with composite Nafion–inorganic additives such as silicon oxide (SiO₂), titanium dioxide (TiO₂), tungsten oxide (WO₃), and SiO₂/phosphotungstic acid (PWA) has been studied for the operation of temperature of above 100 °C. These composite membranes are prepared by the way of blending of the inorganic oxides with Nafion solution by the recasting procedure. The physico-chemical properties studied by means of scanning electron microscopy (SEM) and X-ray diffraction (XRD) techniques have proved the uniform and homogeneous distribution of these oxides and the consequent enhancement of crystalline character of these membranes. The thermogravimetry analysis (TGA) results have indicated that the additives TiO₂ and WO₃ have accelerated decomposition of the membrane at an earlier temperature than that of the Nafion membrane. The modified membranes have shown higher uptake of water relative to that of the unmodified membranes. The proton conductivity of the modified membranes, except that of the Nafion/TiO₂, is found to be close to that of the native Nafion membrane at high temperature and at 100% relative humidity (RH), however, it was much higher at low RH. The performance of these modified membranes in the PEMFC operated at 110 °C and 70% RH is better than that of Nafion membrane and is found in the order of Nafion/SiO₂/PWA > Nafion/SiO₂ > Nafion/WO₃ > Nafion/TiO₂.

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1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are promising system for a wide spectrum of applications where high efficiency is required. The PEMFCs function best with high purity hydrogen gas as the fuel, but high purity hydrogen will unlikely be the fuel in the near future from the economic and storage point of view. Instead, hydrogen from reformed fuels will likely be the fuel for these fuel cells. The hydrogen from the reformed fuel contains trace amounts of CO which poisons the Pt catalyst. To reduce the effect of CO adsorption onto the Pt catalyst, high temperature operation of the PEMFC is required (above 100 °C) [1–4]. However, the typical membrane currently employed for the cell is perfluorosulfonic acid (PFSA), which significantly suffers from the problem of dehydration of water from the membrane at this elevated temperature. The hydration of the membrane is crucial for the performance of the PEMFC since proton conductivity decreases drastically with dehydration. In addition, the dehydration also causes shrinkage of the membrane which in turn makes a poor contact between the membrane and the electrodes. Therefore, dehydration at elevated temperatures can potentially offset any performance benefits that arise from high CO tolerance. A fully hydrated membrane at elevated temperature is desirable for efficient proton conduction in the membrane [5].

In recent years, organic–inorganic composites have been investigated for hydrogen PEMFCs with the main objective of increasing the proton conductivity of the membrane [6–11]. Among them, the incorporation of highly conductive (0.02~0.1 S/cm at room temperature) heteropolyacids such as phosphotungstic acid (PWA) and silicotungstic acid [8–11] has shown encouraging results. The inclusion of phosphates into the Nafion membrane also exhibits good results. For instance, the
addition of zirconium phosphates to Nafion enhances the water retention characteristics of the membrane at higher temperatures [12,13]. In addition, the incorporation of hydrophilic inorganic metal oxide particles produced promising results, because of their tendency to accommodate water in their interlayer region and turn out to be more hydrophilic or more permeable to water. Recently, Adjemian et al. [14] have prepared Nafion/SiO2 composite membrane by the sol–gel technique, which exhibited high water retention characteristics above 100 °C. Jung et al. [15] have studied the proton conductivity of Nafion with different content of SiO2 and they have concluded that the proton conductivity increases for the silicon oxide content of 12.4% at 125 °C. The nano-composite membrane consisting of SiO2 in different polymer hybrids synthesized through sol–gel process was found to offer the proton conductivities of 10 to 10−3 S/cm at 160 °C and at 100% relative humidity [16]. In the present investigation, with a view to improve the proton conductivity of the native Nafion 115, the four different types of inorganic additives such as SiO2, TiO2, WO3, and SiO2/PWA are impregnated into the Nafion membrane by the recasting procedure and their physico-chemical characteristics are studied. The performance of these modified membranes in the PEMFC is better than that of Nafion membrane and is found in the order of Nafion/SiO2/PWA > Nafion/SiO2 > Nafion/WO3 > Nafion/TiO2.

2. Experimental

2.1. Membrane preparation

PWA supported on silica gel has been prepared by using commercial PWA (Acros Chemical Company) and silica gel (Grade 643, 15 nm, Aldrich Chemical Company). An appropriate amount of PWA was mixed with SiO2 in a water solution (weight ratio, PWA:SiO2 = 3:7). Subsequently, it was stirred in an ultrasonic bath for 30 min. Then, the suspension was dried at room temperature. The resulting solid material was crushed in an agate-mortar to obtain a fine powder and then it was further dried at 50 °C for 2 h.

The composite membranes were prepared by the following procedure. An appropriate amount 5% Nafion solution (EW 1100, Electrochem, Inc.) was mixed with SiO2 or TiO2 (Degussa, P25) or WO3 (Aldrich) or SiO2/PWA powders (SiO2 or TiO2 or WO3 or SiO2 content is 10 wt.%) in an ultrasonic bath for 30 min. These solutions were cast in a glass tray and heated at 70 °C for 30 min. Then, the recast composite membranes were detached from the glass tray by adding some de-ionized water. In order to enhance the mechanical properties, the recast membranes were hot pressed between two Teflon films at 160 °C for 10 min. Finally, the membranes were purified by heating at 80 °C in the solution of 3% H2O2, de-ionized water, 0.5 M H2SO4 and in de-ionized water for 2 h, respectively.

2.2. Membrane-electrode assembly (MEA)

Gas diffusion electrodes (20 wt.% Pt on carbon, 0.4 mg Pt/cm2, E-TEK, Inc.) were impregnated with 0.8 mg/cm2 of Nafion (dry weight) and then dried at 70 °C for 1 h. The membranes were sandwiched between the two electrodes and then, they were hot pressed at 135 °C and 70 atm for 90 s. The geometrical area of the electrodes was 5 cm2.

2.3. Physico-chemical characterization

The morphology of the composite polymer membranes was investigated using a scanning electron microscope (SEM) (JEOL-6300F).

X-ray diffraction (XRD) measurements were carried out using Philips PW1830 X-ray diffractometer using a Cu-Kα source operated at 40 keV and at a scan rate of 0.05°/S. The instrumental resolution was determined by standard Pt sample under the same analysis condition.

Thermogravimetry analysis (TGA) of the composite membrane was performed on a TGA/DTA 92 Setaram system in a temperature range from 25 to 650 °C at the heating rate of 10 °C/min in a N2 atmosphere.

2.4. Hydration of membrane

The water uptake of the membrane was determined by the following procedure. The membranes were first hot pressed between two Teflon films at 135 °C and 70 atm for 90 s. This operation was to maintain consistency with the treatment of the membranes that employed in the PEMFC. Then, the membranes were dried in a vacuum oven at 70 °C for 24 h and equilibrated in boiling water for 24 h. After that, the total amount of water inside the membrane was calculated by weighing the membrane. These measurements were done at 25 °C.

2.5. Mechanical tensile measurements

Stress vs. strain tests were conducted at 25 °C using an Series IX Automated Material Testing System (Instron Corporation) at a strain rate of 2.5 mm/min on 3 mm wide × 10 mm long samples.

2.6. Proton conductivity measurements of the membrane and cell polarization testing

FCT-2000 fuel cell testing station (ElectroChem, USA) and Autolab potentiostat (Eco Chemie, Netherlands) with built in frequency response analyser were used for the cell polarization testing and the proton conductivity of the membrane. The gas flow of H2/O2 was fixed at 80/100 ml/min, respectively. The operating temperature of the cell was maintained to 20−115 °C. The resistance of the membranes was measured by impedance spectroscopy in the frequency range of 1−100 kHz at the open circuit potential. The RH was controlled by controlling the water temperature of the H2 and O2 gas humidification bottle. During the proton conductivity, for the measurement of every data point, the testing system was maintained stable for about 2 h to get a constant value. The results thus obtained in the form of resistance are normalized based on the geometric area and membrane thickness and then reported as conductivity.
3. Results and discussion

3.1. Microstructure of the composite membranes

Fig. 1 displays the electron micrographs of the recast composite Nafion membrane with 10 wt.% of SiO$_2$, TiO$_2$, WO$_3$ and 14.3 wt.% SiO$_2$/PWA (SiO$_2$ content is 10 wt.%), respectively. From Fig. 1a, it can be seen that the SiO$_2$ particles are embedded in the inomer matrix and the particles are of a size of 40 to 45 $\mu$m. Fig. 1b shows the membrane with TiO$_2$ particles, the distribution of these particles is relatively uniform, but it is clear from the figure that there are differences in the particles size of the additive (3–10 $\mu$m). The morphology of WO$_3$ impregnated membrane (Fig. 1c) indicates that the particles are spread over uniformly and the size of the particles are in the range of 2 $\mu$m. It can be seen that the solid SiO$_2$ and PWA are uniformly and well distributed over the membrane and do not form any agglomerated like structures (Fig. 1d). The SiO$_2$ and PWA particles are observed to be in the range of 40 $\mu$m. The diameter of the inorganic powders (15 nm for SiO$_2$, 25 nm for P25, and 20 nm for WO$_3$) is similar, but the morphology of the composite membranes incorporated with them is very different. It may be caused by their different compatibility with inomer matrix. From the Fig. 1, we can see that WO$_3$ can be incorporated uniformly into inomer matrix.

3.2. Phase analysis

The XRD patterns of recast Nafion membrane and recast composite Nafion membrane containing the additives SiO$_2$, TiO$_2$, WO$_3$, SiO$_2$/PWA are represented in Fig. 2. The patterns of composite membrane with TiO$_2$ and WO$_3$ show all the characteristics peaks of the respective inorganic additives, indicating that the formation of big enough crystallites on the outer surface of the membrane. The diffractogram of the SiO$_2$ and SiO$_2$/PWA impregnated membrane exhibits no peak characteristics of SiO$_2$ and PWA. This has demonstrated that the presence of SiO$_2$ and PWA in the membrane is amorphous nature. Furthermore, it is noted that the XRD peaks at about 18° 2$\theta$ become sharper by incorporation of the inorganic additives than that of recast Nafion membrane, indicating the enhancement of crystallinity of the incorporated membranes. Similarly, Stangar et al. [17] showed the increasing crystallinity of the
membrane for PWA impregnated membrane. The increasing crystallinity of the membrane in turn provides mechanical strength to the membrane.

3.3. Thermal analysis

The TGA thermograms of the pure Nafion and inorganic additive incorporated membranes are shown in Fig. 3. Initially, the weight loss between 75 and 250 °C is found in all the composite membranes, which is attributed to the loss of residual water in the membrane. It is seen that the decomposition temperature of the composite membranes shifts with the nature of inorganic content. The pure Nafion, Nafion/SiO₂, and Nafion/SiO₂/PWA started to decompose at temperatures of 320, 350 and 340 °C, respectively. Whereas, the TiO₂ and WO₃ composite membranes decompose relatively at lower temperatures, i.e. at 280 and 315 °C, respectively. This has indicated that the TiO₂ and WO₃ have accelerated the decomposition of the membrane at an early temperature than that of the pure Nafion membrane. On the other hand, the cross-linking silica frameworks in the hybrid membrane are temperature tolerant.

Fig. 3. TGA thermograms and associated derivative curves, taken at a heating rate of 10 °C/min, under N₂, for (a) Nafion, (b) Nafion/TiO₂, (c) Nafion/WO₃, (d) Nafion/SiO₂, and (e) Nafion/SiO₂/PWA.
3.4. Membrane hydration

The hydration of the membrane is closely related to the conductivity and the mechanical stability. The variations of the water uptake of the inorganic modified membranes with that of the recast and commercial Nafion 115 are given in Table 1. The water uptake of modified recast membranes is about 8–12% and 2–6% higher than the commercial and recast membranes, respectively. These results can be explained due to the factors such as hydrophilic character of the inorganic oxides and PWA, change in the crystallinity of the membrane and the stronger interactions between the absorbed water and the modified matrix. When the membrane absorbs higher amount of water, the number of exchange sites available per cluster increases; this results in the increase of the proton conductivity of the membrane. Zawodzinski et al. [18] reported that the proton conductivity of the Nafion membrane increases roughly linearly with the increase of water uptake in the membrane. The water uptake property of Nafion/SiO2/PWA impregnated membrane is found to be extremely good than the other membranes, it is expected to possess a higher proton conductivity.

3.5. Mechanical tensile measurements

The stress vs. strain results are shown in Fig. 4. The commercial Nafion 115 membrane and pure recast Nafion membrane are ductile in the same way as reported in the earlier studies [19]. In contrast, the inorganic oxide impregnated membranes become brittle, suggesting that the inorganic particles have a significant degree of interconnection with the membrane. Shao et al. [20] also observed a similar type of properties for the membrane that was impregnated by the TiO2 additive. The tensile strength of the membrane increases in the order of impregnation of SiO2, TiO2 and WO3, respectively. This result is consistent with their powder size in composite membrane (see Fig. 1). Big tensile strength of the membrane impregnated with WO3 may be caused by that WO3 has good compatibility with Nafion.

3.6. Proton conductivity

The proton conductivity of Nafion 115 and inorganic additives (SiO2, TiO2, WO3 and SiO2/PWA) impregnated Nafion composite membranes under 100% relative humidity environment is reported in Fig. 5. The proton conductivity of the inorganic impregnated membranes is lower than that of the Nafion 115 membrane in the lower temperature range. In contrast, the proton conductivity of the SiO2, WO3 and SiO2/PWA impregnated membranes is found to be close to that of the Nafion 115 at the high temperature range. On the other hand, the proton conductivity of TiO2 impregnated membrane is found to be low even at this high temperature range. The activation

<table>
<thead>
<tr>
<th>Membrane identification</th>
<th>Maximum water uptake (%)</th>
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<tr>
<td>Nafion 115</td>
<td>26</td>
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<tr>
<td>Recast Nafion</td>
<td>32</td>
</tr>
<tr>
<td>Recast Nafion/TiO2</td>
<td>34</td>
</tr>
<tr>
<td>Recast Nafion/SiO2</td>
<td>34</td>
</tr>
<tr>
<td>Recast Nafion/WO3</td>
<td>37</td>
</tr>
<tr>
<td>Recast Nafion/SiO2/PWA</td>
<td>38</td>
</tr>
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Fig. 4. Mechanical tensile measurements of Nafion 115, recast Nafion membrane, and recast composite membranes.

Fig. 5. Proton conductivity of Nafion 115, Nafion/TiO2, Nafion/WO3, Nafion/SiO2, and Nafion/SiO2/PWA composite membrane under 100% RH environment.

Fig. 6. Conductivity as a function of RH for Nafion 115, Nafion/SiO2, and Nafion/SiO2/PWA composite membranes at 100 °C.
energies of Nafion 115, Nafion/SiO2, Nafion/WO3, Nafion/TiO2, and Nafion/SiO2/PWA are calculated from the figure and are given as 8.3, 9.6, 11.0, 8.4, and 11.2 kJ/mol, respectively. The higher activation energy values observed for the composite membranes might be caused by the presence of inorganic additives in the membrane.

The proton conduction in the polymer electrolyte is an intimate function of crystallinity, equivalent weight (EW), and the RH (water content). The effect of RH on the proton conductivity of the membranes at 100 °C is shown in Fig. 6. From this figure, we can observe that the proton conductivity of the Nafion/SiO2 composite membrane is higher than that of Nafion 115 membrane under the low RH. This can be explained by the fact that the silica particles can retain water even at high temperature and at low RH; this property can help to prevent the drying of the membrane during the operation of the fuel cell. From Fig. 6, it can also be noted that the proton conductivity of the Nafion/SiO2/PWA composite membrane is higher than that of the Nafion/SiO2 composite membrane under low RH. Staiti et al. [21] also observed that the resistance of silica–PWA-modified recast Nafion membrane was lower than that of the silica-modified recast Nafion membrane under an operation at 140 °C for the liquid feed direct methanol fuel cell. It can be explained by the higher uptake of water by the Nafion/SiO2/PWA composite membrane.

3.7. Single cell performance

The performance of the single cell with all types of membranes operated at 110 °C and lower humidifying temperature (100 °C) is given in Fig. 7. The cells with composite membranes have shown better performances than that with Nafion 115 membrane. The cells with the recast composite membranes such as Nafion/SiO2, Nafion/WO3, Nafion/TiO2, and Nafion/SiO2/PWA have delivered current densities of 320, 300, 185 and 540 mA/cm² at 0.4 V, respectively. In a similar condition, the cell with Nafion 115 membrane only produces a current density value of 95 mA/cm² at 0.4 V. This lower performance of the cell with Nafion 115 membrane is attributed to higher membrane resistance caused by the lower water vapor pressure in the cell. The membrane area resistance and proton conductivity of the composite membranes and Nafion 115 are shown in Table 2. It is observed that the proton conductivities of the composite membranes are higher than that of the Nafion 115 membrane, and also can be found in the order of SiO2/PWA > SiO2 > WO3 > TiO2. This is consistent with their performance in PEMFC (Fig. 7). The proton conductivity of the Nafion/SiO2/PWA composite membrane is about three times higher than that of Nafion 115 membrane. This is attributed to the water retention and the proton conduction properties of the SiO2 and the PWA, respectively.

4. Conclusions

The inorganic composite membranes are prepared by the impregnation of Nafion 115 via recasting procedure, using Nafion solution mixed with SiO2, TiO2, WO3 and SiO2/PWA powders. The impregnation of these additives has produced uniform, homogeneous distribution of the oxides, which resulted in enhancement of crystallinity and mechanical strength of the membranes. The mechanical tensile strength study also confirmed the fact that these inorganic particles have a better interaction with the membranes. From the TGA results, it is concluded that the additives TiO2 and WO3 have accelerated decomposition of the membrane at an earlier temperature than that of the Nafion membrane. The water retention characteristics of these oxide impregnated membranes are found to be better than the unmodified membrane. These modified membranes with the exception of Nafion/TiO2 have exhibited proton conductivity close to the native Nafion membrane at high temperature and 100% relative humidity; however, it was much higher at low RH. The single PEMFC employed with the composite membranes viz. Nafion/SiO2, Nafion/WO3, Nafion/TiO2, and Nafion/SiO2/PWA has been able to deliver higher current density values (320, 230, 150, and 540 mA/cm² at 0.4 V, respectively) than that of the Nafion 115 membrane (95 mA/cm²), under the operating condition of 110 °C and at 70% RH condition. On comparing the performance among the modified membranes in the cell, the Nafion/SiO2/
PWA is found to be a most promising candidate electrolyte for high temperature operation of the PEMFCs.

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References