A new composite membrane is fabricated by incorporating tungsten trioxide hydrate into Nafion to be employed as a candidate electrolyte for proton exchange membrane fuel cells (PEMFCs) operated above 100°C. Thermal behavior and proton conductivity of the composite membrane are studied by means of thermogravimetric/differential thermal analysis (TG/DTA) and AC impedance measurements, respectively. These results demonstrate that the thermal stability of the composite membrane has no appreciable change when compared with the native Nafion membrane. The proton conductivity of the composite membrane is found to be better than that of the native Nafion membrane at high temperature and lower relative humidity. When the composite membrane is used as an electrolyte in H₂/O₂ PEMFC under the operating conditions of 110°C, 1.36 atm gas pressure, and 70% relative humidity, the observed current density value at 0.4 V is 1.5 times higher than that of the cell employing native Nafion membrane as an electrolyte.

Keywords  High temperature; Nafion membrane; PEMFC; Tungsten trioxide hydrate

Introduction

Proton exchange membrane fuel cells (PEMFCs) have been considered as one of the most important fuel cell systems because of their application in automobiles and portable devices. However, one of the major issues limiting the introduction of PEMFCs in applications is the poisoning of platinum-based anode catalysts by the trace amount of CO inevitably contained in reformed fuel. To overcome the problem of CO poisoning, normally the cell is subjected to operation at a high temperature (above 100°C) (Savinell et al., 1994; Alberti et al., 2001; Yang et al., 2001a; Costamagna et al., 2002). This high-temperature operation, in addition to minimizing the CO poisoning, can also help maintain thermal and water management of the stack and increase the kinetics of both the anode and cathode reactions.
However, the currently employed perfluorosulfonic acid (PFSA) membrane electrolytes in PEMFC are seriously affected in this high-temperature operation, that is, the high-temperature operation decreases the water content in the membrane in a remarkable manner. It is well known that the ability of the membranes to conduct protons is mainly dependent on the extent of their hydration (Kreuer, 1997). Increasing the operating pressure can raise the boiling point of water, but in order to get higher energy efficiency for the PEMFC system, the reactant gas pressure should not exceed 3 bars (corresponding to a boiling point about 134°C). Therefore, the existing PFSA membranes need to be modified in such a way that they would be able to retain the water content at high-temperature (above 100°C) operation or low water vapor pressure environment.

Some efforts have been made in previous studies to enhance the water retention property by modifying the PFSA membranes for high-temperature operations. These studies include the impregnation of heteropolyacids (Malhotra and Datta, 1997; Lin et al., 2005; Shao et al., 2004; Aparicio et al., 2005; Tazi and Savadogo, 2000) and incorporation of SiO$_2$ (Antonucci et al., 1997; Adjemian et al., 2002) and zirconium phosphate (Yang et al., 2001b; Costamagna et al., 2002) into the PFSA membranes (Jones and Roziere, 2001). Unfortunately, these studies have encountered some problems in the course of operating the cells. The impregnated heteropolyacids are found to be dissolved in water present in the membrane. The other incorporated additives such as silicon dioxide and zirconium phosphate tend to be poor proton conductors under lower relative humidity (Alberti and Casciola, 1997). In the 1970s and 1980s, tungsten oxide hydrates were reported as proton conductors (Nishimura, 1976; Slade, 1985). Recently, Li and coworkers (2000) have found that tungsten trioxide hydrates exhibited relatively high proton conductivity under various high temperature ranges and water vapor pressures. The high proton conducting property of tungsten trioxide hydrates reported in their work has motivated us to study the effect of incorporation of this material into the PFSA membranes for high-temperature operations. To this end, we have fabricated tungsten trioxide hydrate incorporated Nafion recast membrane and employed it as an electrolyte in PEMFC operated at high temperature and low water vapor pressure. The performance of the cell with this new composite membrane is found to be better than the cell where a conventional Nafion membrane is used.

**Experimental Section**

**Membrane Preparation and Characterization**

WO$_3$ powder was prepared according to the procedure given elsewhere (Freedman, 1959). Briefly, 20 mL of 1.0 M Na$_3$WO$_4$·2H$_2$O solution was added to 180 mL of 3 N HCl and cooled at temperature of 5°C. As a result of this, a white precipitate was formed at once and turned yellow after 30 mins. Then, the precipitate was filtered and washed with 100 mL of 0.1 N HCl. Finally, it was washed with deionized water for several times until all the chloride ions were removed. WO$_3$·xH$_2$O powder was thus obtained after the precipitate was dried at room temperature in a fume hood for two days.

The composite membrane was prepared by the following procedure. An appropriate amount of 5% Nafion solution (EW 1100, Electrochem. Inc.) was mixed with the WO$_3$·xH$_2$O powder and treated in an ultrasonic bath for 30 min. The weight ratio of Nafion (dry weight) to WO$_3$·xH$_2$O is 9:1. This solution was cast in a glass
tray and heated at 70°C for 30 min. The recast Nafion/WO$_3$10 wt% WO$_3$:xH$_2$O composite membrane was detached from the glass tray by adding some deionized water. In order to improve its mechanical properties, the recast membrane was hot pressed between two Teflon films at 160°C for 10 min. Then, the membrane was purified by heating at 80°C in a solution of 3% H$_2$O$_2$, 0.5 M H$_2$SO$_4$, and deionized water for 2 h.

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

Thermal analysis of the composite membrane was performed on a TG/DTA system (Setaram 92, France) in a N$_2$ atmosphere in a temperature range from 25°C to 650°C at the heating rate of 10°C min$^{-1}$.

**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 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.

**Membrane-Electrode Assembly (MEA)**

Gas diffusion electrodes (20% Pt on carbon, 0.4 mg Pt cm$^{-2}$, E-TEK, Inc.) were impregnated with 0.8 mg cm$^{-2}$ of Nafion (dry weight) and then dried at 70°C for 1 h. A membrane was sandwiched between the two electrodes and then hot pressed at 135°C and 70 atm for 90 s. The geometrical area of the electrodes was 5 cm$^2$.

**Proton Conductivity Measurements of the Membrane and Cell Polarization Testing**

The FCT-2000 fuel cell testing station (ElectroChem, USA) and Autolab potentiostat (Eco Chemie, Netherlands) with built-in frequency response analyser were used for testing cell polarization and the proton conductivity of the membrane. The gas flow of H$_2$/O$_2$ was fixed at 80/100 mL/min. The operating temperature of the cell was maintained at 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 relative humidity (RH) was controlled by controlling the water temperature of the H$_2$ and O$_2$ gas humidification bottle. During the proton conductivity test, 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.

**Results and Discussion**

The morphology of the composite Nafion/WO$_3$ recast membrane is shown in Figure 1. It can be seen that the solid WO$_3$ particles are uniformly and well
distributed over the membrane and do not form any agglomerated structures. The WO$_3$ particles are observed to be in the range of ~1 μm.

A thermal analysis for the composite membrane has been carried out to check the thermal stability, as shown in Figure 2. It can be seen that the composite membrane is able to retain more than 95% of its weight up to the temperature of about 330°C. The gradual loss of about 5% from the original weight of the membrane may be attributed to the slow evaporation of water molecules present in the membrane. Above 330°C, the composite membrane has started to decompose, mainly due to the loss of sulfonic acid groups associated with the membrane. The observed thermal behavior of the composite membrane is similar to that of the native Nafion

![Figure 1. SEM of recast Nafion/WO$_3$ composite membrane.](image)

![Figure 2. TG-DTA curves for the Nafion/WO$_3$ composite membrane from room temperature to 650°C at the heating rate of 10°C min$^{-1}$ under N$_2$ atmosphere.](image)
membrane reported by Samms et al. (1996). From these results, it is apparent that the thermal stability of recast Nafion membrane has not undergone any appreciable change below the temperature of 330°C even after the incorporation of tungsten trioxide. It should also be noted that during the membrane preparation procedure, in order to improve the mechanical properties of the membrane, the hot-press treatment (160°C for 10 min) is used. Therefore, only 1.5% water uptake is seen as a loss below 100°C in the TGA.

The hydration of the membrane is closely related to its conductivity and mechanical stability. The differences of the water uptake of tungsten trioxide modified membrane, recast Nafion, and commercial Nafion 115 are given in Table I. The water uptake of the modified recast membrane is about 11% and 6% higher than that of the commercial and recast membranes, respectively. These results can be explained due to factors such as the hydrophilic character of tungsten trioxide, 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, resulting in an increase of the proton conductivity of the membrane. Zawodzinski et al. (1993) reported that the proton conductivity of the Nafion membrane increases roughly linearly with the increase of water uptake in the membrane.

The proton conduction in the polymer electrolyte is an intimate function of crystallinity, equivalent weight (EW), and RH (water content). The effect of RH on the proton conductivity of the membranes at 100°C is shown in Figure 3. From this

<table>
<thead>
<tr>
<th>Membrane identification</th>
<th>Maximum water uptake (%)</th>
</tr>
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<tbody>
<tr>
<td>Nafion 115</td>
<td>26</td>
</tr>
<tr>
<td>Recast Nafion</td>
<td>32</td>
</tr>
<tr>
<td>Recast Nafion/WO₃</td>
<td>37</td>
</tr>
</tbody>
</table>

Figure 3. Conductivity as a function of relative humidity for Nafion 115 and Nafion/WO₃ composite membranes at 100°C.
We can observe that the proton conductivity of the Nafion/WO$_3$ composite membrane is higher than that of Nafion 115 membrane under low RH. This can be explained by the fact that tungsten trioxide 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.

The performance of the single cell with Nafion 115 and Nafion/WO$_3$ composite membranes operated above 100°C and lower humidifying temperature is represented in Figure 4. The fuel cell performance with Nafion 115 depends on the operating temperature and humidifying conditions. It is reported that the maximum current density of the cell with Nafion 115 was lower than 100 mA cm$^{-2}$ operating at 140°C and humidifying at 130°C (Costamagna et al., 2002). This result is consistent with our results. The cell with the composite membrane (100 μm, measured after fuel cell testing by SEM) has shown a better performance than that with the Nafion 115 membrane (100 μm). At a potential of 0.4 V, the Nafion/WO$_3$ composite membrane cell has delivered a current density of 240 mA cm$^{-2}$, which is 1.5 times higher than that of the cell with Nafion 115 membrane at 110°C. This lower performance of the cell with Nafion 115 membrane is owing to the presence of higher membrane resistance (1.3 Ω cm$^2$), which is in turn caused by lower water vapor pressure in the cell. When the reaction gas humidifying temperature is raised to 100°C at the working temperature of 110°C, the relative humidity is found to be only 70%. This lower relative humidity leads to loss of hydration water from the MEA, resulting in the proton conducting being reduced and the resistance being increased in the Nafion membrane.

The other advantage of incorporating WO$_3$ hydrate in the Nafion membrane is owing to its high hydrophilicity, which helps maintain the water retention property in the Nafion membrane nanoporous structure. Also, it is interesting to note that tungsten trioxide hydrate is capable of maintaining proton conductivity in the order of 10$^{-2}$ S cm$^{-1}$ under 65% relative humidity conditions (Li et al., 2000). Therefore, the properties offered by WO$_3$ can help maintain a lower membrane resistance.
(0.75 Ω cm² compared with 1.3 Ω cm² of Nafion 115) at the working temperature of 110°C and a lower relative humidity condition (humidifying temperature of 100°C) for the Nafion/WO₃ composite membrane. Alberti and coworkers (2001) have reported that the conductivity of Nafion remains practically constant in the temperature range from 80°C to 160°C and at constant relative humidity. Li et al. (2000) have reported that the proton conductivity of tungsten trioxide hydrate significantly increased in the same temperature range. From the above discussions, it is clear that the conductivity of the Nafion/WO₃ composite membrane improves with an increase of temperature.

Conclusions
Tungsten trioxide hydrate incorporated Nafion composite membrane is fabricated for high-temperature operated (above 100°C) PEMFCs. The thermal stability of the composite membrane has no appreciable change compared to that of the native Nafion membrane. The proton conductivity of the composite membrane is found to be better than that of the native Nafion membrane at high temperature and lower relative humidity. The single PEMFC built up with the composite membrane has been able to deliver a current density of 240 mA cm⁻² at 0.4 V, which is 1.5 times higher than that of native Nafion membrane under the operating conditions of above 100°C and low relative humidity. Hence the new composite membrane can be considered as a potential electrolyte candidate for the PEMFCs operated above 100°C.

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References


