Diphenylsilicate-incorporated Nafion® membranes for reduction of methanol crossover in direct methanol fuel cells

Z.X. Liang, T.S. Zhao ∗, J. Prabhuram

Department of Mechanical Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong SAR, China

Received 20 April 2006; received in revised form 16 June 2006; accepted 19 June 2006

Available online 23 June 2006

Abstract

We synthesized organically modified silicate microparticles, known as diphenylsilicate (DPS), and showed that the synthesized DPS has a nano-layered microstructure. We utilized this material as a filler for fabricating Nafion®|DPS composite membranes for mitigating the problem of methanol crossover in direct methanol fuel cells (DMFC). The SEM and XRD analyses indicated that the incorporated DPS microparticles were uniformly distributed in the native membrane. The DMFC performance tests demonstrated that the use of the Nafion®|DPS composite membranes resulted in a lower rate of methanol crossover, higher open-circuit voltage (OCV) and better cell performance than did the pure Nafion® membrane, especially with a higher methanol concentration such as 10 M.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Direct methanol fuel cells (DMFC); Nafion; Diphenylsilicate; Composite membrane; Methanol crossover

1. Introduction

The direct methanol fuel cell (DMFC) has recently attracted much interest as it has been identified as a promising candidate to compete with conventional batteries for powering portable electronic devices [1,2]. However, one of the most challenging issues in the DMFC technology is crossover of methanol fuel through typical Nafion® membranes from the anode to cathode, seriously degrading cell performance [3]. Recently, tremendous efforts have been made either to develop new types of polymer electrolyte membranes or to modify existing Nafion® type of membrane to mitigate the methanol crossover problem. In the perspective of developing new types of electrolyte membranes, Yang and Manthiram [4] showed that the sulfonated polyetheretherketone (sPEEK)-based membrane exhibited a lower rate of methanol crossover, while the proton conductivity of this membrane was found to be more or less similar to the Nafion® type of membrane. However, the degree of swelling of the sPEEK membrane in methanol appears to be increased with increasing the level of sulfonation, which can cause delamination of the membrane from the membrane electrode assembly (MEA). It should be mentioned that when new types of polymer electrolyte membrane are used for fabricating MEAs, the interfacial contact between the new polymer membrane and Nafion®-based electrodes is unlikely to be good due to the difference in the properties of these polymeric materials. On the other hand, a substantial amount of work has been conducted with regard to modifying the existing Nafion® type membranes to reduce the rate of methanol crossover. For example, methanol impermeable proton conducting (MIPC) materials, such as Pd and its alloys, were deposited on the anode side of the Nafion® membranes either by the sputtering or by the electrochemical method; and these modified membranes were found to be effective in suppressing methanol crossover [5–9]. Interestingly, Uchida et al. [10] dispersed Pt nanoparticles into a Nafion® membrane, in which the permeated methanol and oxygen molecules, respectively, from the anode and cathode sides were being catalyzed on the Pt nanoparticles, thereby suppressing the rate of methanol crossover. Recently, Miyake et al. [11] have shown that the Nafion®/silica hybrid membrane prepared with 20 wt% of silica exhibited a lower rate of methanol crossover than did the unmodified membrane. Mauritz [12] prepared Nafion®/Ormosil composite membrane by sol–gel method with the Nafion® membrane as the template. Recently, Kim et al.

∗ Corresponding author. Tel.: +86 852 2358 8647.
E-mail address: metzhao@ust.hk (T.S. Zhao).

0376-7388/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.memsci.2006.06.031
[13] prepared Nafion®|Ormosil composite membrane with various organic silanes and found that serious ball-shaped segregate and the heterogeneous morphology was observed for the case of Nafion®|DPS(diphenylsilicate) composite membrane, which hindered its application in DMFC. Li et al. [14] found that the Nafion®|DPS (5%) membrane exhibited five times lower proton conductivity than the unmodified membrane. The composite membrane seemed to be unsuitable for the DMFC before other measures were taken to solve the proton conductivity problem.

In this work we synthesized diphenylsilicate (DPS) with a nano-layered microstructure, and utilized this novel material as a filler for forming Nafion®|DPS composite membranes by cast method for DMFC. Unlike the previous studies, we found that the composite membrane by this method showed a satisfactory proton conductivity even when the DPS content reached 20%. Then we demonstrated that the Nafion®|DPS composite membranes exhibited lower rates of methanol crossover, higher open-circuit voltage (OCV) and better cell performance at higher methanol concentrations than did the cast Nafion® membrane.

2. Experimental

2.1. Synthesis of DPS

An appropriate amount of diethoxydiphenylsilane (DEDPS) (Sigma–Aldrich) was added into the methanol (MERCH) and D.I. water mixture (9:1 ratio) and stirred for 10 min. After that, an appropriate quantity of EtNH₂ (70 wt%) solution (Sigma–Aldrich) was added, drop-by-drop, to the above mixture with stirring; and mixture was stirred continuously for 18 h at 22 °C until the Nafion®|DPS composite membranes were formed. In a similar manner, the Nafion®|DPS composite membranes with DPS content of 10 and 20 wt% were prepared by using the above method. Briefly, the DPS was dissolved in DMSO and the solution was mixed with the Nafion®-DMSO mixture. Then, the DMSO was evaporated until it became a concentrated solution (around 5 wt%). Finally, the solid mass was filtered and the resultant solid mass was washed with ethanol and then soaked in DI water or methanol at room temperature for 6 h, respectively. The membranes were blotted dry with Kimwipes to remove excess solvent absorbed on the surface and quickly weighed. The water absorption and the methanol absorption were calculated as follows:

\[ A = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \]  

(1)

2.2. Preparation of cast Nafion® and Nafion®/DPS composite membranes

Initially, the commercial Nafion® solution (5 wt%) was dried at 40 °C. The dried resin was refluxed in a solvent dimethylsulfoxide (DMSO). Afterwards, the solvent DMSO was evaporated until the concentration of the solution became 5 wt%. Then, the solution was transferred into a Petri dish (placed on a flat heater) and heated at 120 °C until the cast Nafion® membrane was formed. In a similar manner, the Nafion®|DPS composite membranes with DPS content of 10 and 20 wt% were prepared by using the above method. Briefly, the DPS was dissolved in DMSO and the solution was mixed with the Nafion®-DMSO mixture. Then, the DMSO was evaporated until it became a concentrated solution (around 5 wt%). Finally, the solution was transferred into a Petri dish and heated at 120 °C until the Nafion®|DPS composite membranes were formed. All the membranes (both the cast Nafion® and Nafion®|DPS composite membranes) were found to have a thickness of about 50 µm.

2.3. Characterization of membranes

Scanning electron microscope (SEM) was used to examine the morphology of the DPS particles (JEOL 6700F) and cross-section of the Nafion®|DPS composite membrane (JEOL 6300F). The infrared spectrum (IR) was collected on a FTS6000 (Bio-Rad), and recorded from 4000 to 650 cm⁻¹ for DPS (KBr pellets) in the transmission mode. For Nafion® membrane and Nafion®|DPS composite membranes, the IR spectra were collected in the attenuated total reflection mode (with ZnSe) due to the saturated absorption of C–F groups in the Nafion® membrane in the transmission mode. The X-ray diffraction (XRD) measurements for the DPS particles, bare Nafion® and the Nafion®|DPS composite membranes were carried out by using a Phillips PW 1830 diffractometer using Cu Kα radiation source operated at 40 keV and at a scan rate of 0.05° s⁻¹.

2.4. Water absorption and methanol absorption measurement

The membranes were dried in the vacuum oven at 60 °C for 24 h, weighed and then soaked in DI water or methanol at room temperature for 6 h, respectively. The membranes were blotted dry with Kimwipes to remove excess solvent absorbed on the surface and quickly weighed. The water absorption and the methanol absorption were calculated as follows:

\[ A = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \]  

(1)

2.5. DMFC performance test

Commercial E-TEK electrodes were employed both at the anode (PtRu black with 4 mg cm⁻²) and cathode (40 wt% Pt/C with 2 mg cm⁻²). The MEAs were fabricated by sandwiching the Nafion® and the Nafion®|DPS composite membranes between the anode and cathode and by hot pressing at 135 °C under a pressure of 4 MPa for 3 min. The MEAs were tested in a single-cell fixture (with an active area of 1 cm²) having three-pass serpentine flow channels with both width and depth of 0.7 mm.

The DMFC performance of these membranes was tested at 75 °C by feeding 1.0, 4.0 and 10.0 M methanol at a flow rate of 1 ml min⁻¹ using a high-pressure piston pump (Model Series III, Scientific Systems Inc.) and by purging dry oxygen gas into the cathode at a flow rate of 100 ml min⁻¹ at ambient pressure by fixing the load current, which was controlled with an electric load system (BT2000, Arbin Instrument Inc.). The cell resistance was measured by dc-pulse method after collecting the performance data.

2.6. Measurement of the rate of methanol crossover

Methanol crossover was evaluated by the voltammetric method using the DMFC configuration under the open-circuit condition as reported elsewhere [15]. The experiments were performed by connecting, respectively, the cathode of the cell to the
working electrode and the anode to the reference and counter electrodes of the potentiostat. During the course of the experiment, the anode of the cell was fed with 1.0 M of the methanol at a flow rate of 1 ml min$^{-1}$ and cathode of the cell was fed with humidified nitrogen at a flow rate of 100 ml min$^{-1}$.

3. Results and discussion

Fig. 1 presents the SEM images of the synthesized DPS particles and the cross-sectional morphology of the composite membrane with 10 and 20 wt% of DPS. It is interesting to notice from Fig. 1a that the synthesized DPS shows a layered microstructure, with each layer ranging from 100 to 300 nm in thickness. The formation of the crystalline microstructure of the DPS compound is supposed to be the first of its kind in the synthesis of DPS. Fig. 1b and c shows the composite membranes with the DPS content of 10 and 20 wt%, respectively. It can be seen from these figures that the DPS particles are uniformly distributed in the both the composite membranes and no gaps are found at the interface between particles and polymer, indicating a good compatibility between the DPS and Nafion® resin. We infer that the good compatibility of the DPS particles with the native Nafion® membrane might be due to the presence of organic phenyl groups on either side of the silica framework in the DPS. Additionally, the tiny holes can be observed from the SEM image of the composite membrane, which are well-understood to be raised by the evaporation of solvent during the membrane fabrication process.

Fig. 2 shows the infrared spectra of the synthesized DPS particles, cast Nafion® membrane and the Nafion®|DPS composite membranes with the DPS content of 10 and 20 wt%. The main peaks in the infrared spectra are listed in Table 1, where the assignment of the peaks was conducted based on previous studies [11,16]. The C–H stretching vibration absorption peaks (3000 cm$^{-1}$) and the aromatic stretching peaks (1500 cm$^{-1}$) can be observed in the spectra of the composite membranes (with the DPS content of 10 and 20 wt%). And the peak at 1126 cm$^{-1}$, which is attributed to the absorption of Si–O stretching, is present in the spectrum of the Nafion®|DPS (20 wt%) composite membrane. The presence of the C–H and Si–O groups in the composite membrane indicates that the DPS has been incorporated into the Nafion® membrane, because Nafion® (one kind of perfluorinated sulfonic acids) does not contain any C–H or Si–O groups in chemical composition. Additionally, there is no strong absorption peaks above 3000 cm$^{-1}$ (due to the O–H stretching vibration) in the spectrum of DPS, which implies that DPS is a highly hydrophobic material. And it can be inferred that the addition of DPS will lead to a loss in the hydrophilic property of the Nafion® membrane, which will be discussed later.

Fig. 3 shows the XRD patterns of the synthesized DPS particles, bare Nafion® 112 and the Nafion®|DPS composite membranes with DPS content of 10 and 20 wt%, respectively. In the XRD pattern of the DPS, very sharp peaks are observed at the 2θ values of 7–9° and 20°, demonstrating that the DPS particles existed in the highly crystalline form. The XRD pattern of our synthesized DPS is found to be similar to the crystalline polysilylenes reported in the literature. For example, Imae and Kawakami [17] showed that the glassy polysilylenes with two alkyl groups displayed a strong peak at 7–9° indexed as superposition of $d_{110}$ and $d_{020}$ of an orthorhombic lattice with hexagonally packed chains, and a broad peak centered around 20° was indexed as $d_{013}$. Thus, it is deduced that the DPS particles are formed in a two-dimensional order with hexagonally packed structure. In the case of the composite membrane with the DPS content of 10 wt%, the XRD pattern showed peaks similar to the bare Nafion® membrane, that is, a broad peak
Table 1: The peaks and their assignments of the infrared spectra of the Nafion® membrane, DPS and the Nafion®|DPS composite membranes

| Nafion® membrane | DPS | Nafion®|DPS (10 wt%) membrane | Nafion®|DPS (20 wt%) membrane |
|------------------|-----|---------------------|---------------------|---------------------|
| Wavenumber (cm⁻¹) | Assignment | Wavenumber (cm⁻¹) | Assignment | Wavenumber (cm⁻¹) | Assignment |
| 3800–3000 (str, b) | O–H stretch | 3000 (w) | C–H stretch | 3800–3000 (str, b) | O–H stretch |
| 1300–1100 (str, b) | C–F stretch | 1429 (w, sh) | Aromatic stretch | 3000–2900 (w, sh) | C–H stretch |
| 1055 (m, sh) | –SO₃ sym. stretch | 1118, 1110 (str, sh) | Si–O–Si, asym. Stretch | 1300–1100 (str, b) | C–F stretch |
| 980 (m, sh) | –CFRCF₃ stretch | 1055 (m, shoulder) | –SO₃ stretch | 980 (m, sh) | –CFRCF₃ stretch |
| 969 (m, sh) | C–O–C stretch | 969 (m, sh) | C–O–C stretch | 969 (m, sh) | C–O–C stretch |
| Note: The words in the blankets indicate the intensity and shape of the absorption peaks. str: strong, m: mild, w: weak, b: broad, sh: sharp. |

Fig. 2. Infrared spectra of the DPS, the cast Nafion® membrane and the Nafion®|DPS (10 and 20 wt%) composite membranes.

followed by a sharp peak appeared at 2θ values around 18° and 40°, respectively. These peaks are assigned to be the crystalline scattering of the polyfluorocarbon chains and the scattering of amorphous ionic clusters of the Nafion® membrane [16]. This composite membrane does not show any peaks responsible for the microstructure of DPS, implying that the DPS particles are completely blended with Nafion® resin. On the other hand, when the DPS content was increased to 20 wt% in the composite membrane, some peaks appeared at 2θ = 8–10° in the pattern. Apparently, the formation of these peaks are due to the presence of DPS particles in the composite membrane, indicating that the phase separation is likely to take place when the DPS content reaches a threshold value. However, the mechanical strength of this composite membrane remained to be good unlike those of the Nafion®–SiO₂ composite membranes, which are easily susceptible to brittleness when the silica content is increased to more than 15% [18].

Fig. 4 shows the change of the methanol absorption and water absorption in the different composite membranes. The water absorption decreased with the DPS content, while an adverse behaviour was observed for the methanol absorption. The addition of DPS into Nafion membrane enhanced the hydrophobic properties, and hence resulted in a decrease in the water absorption. Methanol is easier to be absorbed by DPS due to the presence of methyl group in the molecular structure, which led to an absorption increase with the increase of DPS content.

The rates of methanol crossover through the cast Nafion® and Nafion®|DPS membranes with 10 and 20 wt% of DPS were determined by the voltammetric method. The measured rate of methanol crossover through each membrane, represented by the equivalent limiting current density (j), is shown in Table 2. Clearly, the Nafion®|DPS composite membranes show a much lower rate of methanol crossover than does the cast Nafion® membrane. It is interesting to notice that the methanol per-

Fig. 3. XRD patterns of DPS, the Nafion® 112 membrane, the Nafion®|DPS composite membrane with 10 wt% of DPS and the Nafion®|DPS composite membrane with 20 wt% of DPS.
membrane with 0, 10, 20, 30 wt% of DPS. The methanol permeability ($P$) is the product of the solubility ($S$) and the diffusion coefficient ($D$). As we are aware, the diffusion coefficient is a kinetic parameter, while the solubility is a thermodynamic parameter which can be roughly expressed by the absorption.

Fig. 4 shows that the methanol solubility in the composite membranes increased with the DPS content. It can be inferred that the reduced rate of methanol crossover is mainly caused by the decrease in the diffusion coefficient due to the fact that the incorporation of the DPS particles increases the membrane tortuosity.

Table 2 also compares the proton conductivity of the cast Nafion® and composite membranes, which was calculated from the in-cell resistance by using equation:

$$\sigma = \frac{1}{R} \cdot \frac{l}{A} \quad (2)$$

where $R$ is the cell resistance, $l$ the membrane thickness and $A$ is the area of the electrode. The proton conductivity of the composite membranes is found to be decreased by 17 and 25% when the DPS content was maintained at 10 and 20 wt%, respectively. This is because the phenyl groups present on either side of the silica matrix of the DPS can impart the hydrophobic characteristics, which in turn, reduce the water absorption properties of the composite membrane. For instance, the water absorption of the composite membrane with 10 wt% of the DPS is found to be decreased by 30% when compared with the cast Nafion® membrane (see in Fig. 4). Thus, the incorporation of DPS into the membrane increases resistivity of the membrane by means of reducing the absorption of water, leading to the decrease in the proton conductivity of the composite membranes. The enhanced hydrophobic property of the composite membranes induced by the incorporated DPS might be helpful in reducing the flooding normally occurs in the cathode of a DMFC [15].

Fig. 5 compares the performance of the cell with the cast Nafion® and Nafion®|DPS composite membranes using 1.0, 4.0 and 10.0 M methanol at 75 °C, while Table 2 gives the OCV values corresponding to the three membranes. When the cell was fed with 1.0 M methanol, the cast Nafion® membrane showed a better performance than did the composite membranes with 10 and 20 wt% of DPS. However, the composite membranes showed higher OCV and better performance in the very low current density region (<50 mA cm$^{-2}$). When the methanol concentration was increased to 4.0 M, the composite membranes showed higher OCV and better performance than did the pure Nafion® membrane in the current density region of less than 400 mA cm$^{-2}$. At a higher current density region, the DPS modified membranes exhibited more or less a similar performance with that of the cast Nafion® membrane. When methanol concentration was further increased to 10.0 M, the Nafion®|DPS composite membranes showed much better performance than did the pure Nafion® membrane over the entire range of current densities; and among the two composite membranes, the membrane with 20 wt% of DPS was found to give slightly higher performance than the membrane with 10 wt% of DPS. Typically, the cell performance is affected by the combination of the membrane resistance and the rate of methanol crossover. For a lower methanol concentration (1.0 M), the methanol crossover is predominant only in the very low current density region and it decreases as the discharging current density increases [19]. For 1.0 M methanol, therefore, the rate of methanol crossover is much less important and the resistance is the predominant factor in determining cell performance. On the other hand, for a higher methanol concentration (4.0 and 10.0 M), the effect of methanol crossover becomes more significant than the cell resistance. Methanol crossover leads to a so-called “mixed over-potential” on the cathode, degrading the cell performance [3,20]. The composite membranes, especially the membrane with 20 wt% of DPS can effectively mitigate the methanol crossover at 10.0 M methanol, thereby exhibiting much improved cell performance at this higher methanol concentration, at which the methanol crossover was more serious. In the case of the composite membrane with higher amount of DPS (30 wt%) the cell performance became worse (not shown), despite the rate of methanol crossover for this membrane was lower than that of the mem-

<table>
<thead>
<tr>
<th>Type of membrane</th>
<th>$j$ (mA cm$^{-2}$)</th>
<th>$\sigma$ ($\times 10^{-2}$ S cm$^{-1}$)</th>
<th>OCV (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.0 M</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cast Nafion®</td>
<td>329</td>
<td>2.89</td>
<td>0.60</td>
</tr>
<tr>
<td>Nafion®</td>
<td>DPS (10 wt%)</td>
<td>183</td>
<td>2.39</td>
</tr>
<tr>
<td>Nafion®</td>
<td>DPS (20 wt%)</td>
<td>160</td>
<td>2.16</td>
</tr>
<tr>
<td></td>
<td>4.0 M</td>
<td></td>
<td>0.51</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.59</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td>10.0 M</td>
<td></td>
<td>0.34</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.53</td>
</tr>
</tbody>
</table>
brane with 10 and 20 wt% of DPS. This is because the proton conductivity of the composite membrane with 30 wt% DPS was found to be much lower. Further work is underway to improve the proton conductivity of the DPS incorporated membranes. The above test results clearly showed that the Nafion®/DPS composite membranes with DPS content of 10–20 wt% can be more suitable for the DMFCs, in which higher methanol concentration operation is demanded.

4. Conclusion

In the present investigation, the DPS particles having a nanolayered microstructure were synthesized and incorporated into the Nafion® membrane with different amounts (10 and 20 wt%) to reduce the rate of methanol crossover in a DMFC. The SEM and XRD analyses indicated that the incorporated DPS microparticles were uniformly distributed in the native membrane, thereby achieving a good compatibility between the DPS and the Nafion® resin. The Nafion®/DPS composite membranes exhibited lower rates of methanol crossover than did the cast Nafion® membrane. The DMFC performance tests demonstrated that the use of the Nafion®/DPS composite membranes led to higher OCV and better cell performance than did the cast Nafion® membrane, especially with higher methanol concentration such as 10 M.

Acknowledgement

The work described in this paper was fully supported by a grant from the Research Grants Council of the Hong Kong Special Administrative Region, China (Project No. HKUST6101/04E).

References