Silicon modified ultrafiltration-based proton-conductive membranes with improved performance for H$_2$/Cl$_2$ fuel cell application

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A B S T R A C T

Ultrafiltration (UF)-based proton-conductive membranes, which comprised nanosize SiO$_2$, polyethersulfone and aqueous acid absorbed, as an alternative to traditional ion exchange membranes, were first proposed and successfully prepared for H$_2$/Cl$_2$ fuel cell. Various membranes were prepared with different weight fractions of SiO$_2$ nanoparticles. The effect of silicon content on the performance of membranes was characterized. The ionic conductivity of a membrane doped with 3 M hydrochloric acid increased with the silicon content and reached 0.150 S cm$^{-1}$ at 15 wt.% SiO$_2$. A non-optimized H$_2$/Cl$_2$ fuel cell assembled with the modified UF membrane (115 $\mu$m thick) exhibited better performance than that with Nafion 115 membrane. It demonstrated that 12.67% and 55.03% improved at 10 wt.% and 15 wt.% SiO$_2$, respectively. The study provides an effective way to fabricate high performance porous membranes for H$_2$/Cl$_2$ fuel cell application.

1. Introduction

H$_2$/Cl$_2$ fuel cell has been suggested as an alternative to H$_2$/O$_2$ fuel cell, because of the advantages of chlorine reduction in terms of relatively nonpolarizable and much faster electrode process compared with that of the corresponding oxygen reduction [1]. However, hydrogen chloride produced in the H$_2$/Cl$_2$ fuel cell removes most water from the membrane even with a high degree of humidification [2], due to its highly hygroscopic nature. In order to obtain a proper water management, the strategy is to dissolve the chlorine reactant in the aqueous solution of hydrochloric acid [3,4] or apply composite aqueous acid/membrane electrolyte in the fuel cell [1,2,5]. The proton-conducting membrane (PCM) in such H$_2$/Cl$_2$ fuel cell not only transfers protons, but also prevents the acid solution from crossing over the membrane, as well as in the direct methanol fuel cell (DMFC) and other direct-oxidation fuel cells. Any membranes with the basic function could possibly be used in the H$_2$/Cl$_2$ fuel cell. However, up to now, only Nafion membrane has been reported to be used in such H$_2$/Cl$_2$ fuel cell [2,3,5–8]. However, it is generally believed that the Nafion membrane has several critical disadvantages in terms of cost, fuel permeability and ion conductivity [9,10]. Thus, developing alternatives to Nafion membrane is one of the most important research topics now [11–13].

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One substituted membrane is nanoporous proton-conducting membrane (NP-PCM), which consists of nanosize ceramic power, polymer binder and aqueous acid absorbed [14,15]. Compared with Nafion membrane, the NP-PCM has several advantages, namely much lower cost, higher conductivity and avoiding the gas humidification. However, the polymer binder was PVDF or PTFE and their hydrophobic nature was a serious problem. In addition, the preparation of NP-PCM took a long time at high temperature. The ion conductivity of the reported NP-PCM [14,15] was lower due to the lower porosity of the membrane. So the strategy is to prepare a NP-PCM with high porosity and good selectivity with a simple method.

Considering the fact that ultrafiltration (UF) membrane consists of a porous support layer and a very thin selective layer [16], UF-based PCM can absorb much aqueous acid and decrease the fuel permeability. In this case, silicon modified polyethersulfone (PES) UF membranes were prepared. PES was selected due to its good chemical resistance, super thermal conductivity and avoiding the gas humidification. However, several advantages, namely much lower cost, higher conductivity and avoiding the gas humidification. Compared with Nafion membrane, the NP-PCM has much lower cost, higher conductivity and avoiding the gas humidification. The SiO2 content varied between 0 and 15 wt.% of the SiO2/PES. The resulting slurries were spread on a clean glass plate with a doctor blade. Phase inversion membranes were obtained by the prompt immersion of the glass plate into a water bath for 0.5 h and then stored in ethyl alcohol to prevent fiber shrinkage and pores collapse. The membranes are named as PESSiX, where X is the SiO2 content (wt.%) in the membrane. The thickness of the UF membranes was 115 μm.

2.2. Membrane characterizations

The morphology of membrane was observed by a scanning electron microscope (SEM) (JEOL JSM-6700F) with an acceleration voltage 20 kV. The membranes were firstly immersed into liquid nitrogen for a few minutes, then broken and deposited into a copper. All samples were coated with gold under vacuum before test.

The static contact angle of the membrane was measured by a contact angle system (Drop Shape Analyzer 100, Kruss, Germany). To minimize experimental error, an average contact angle was determined from 5 measurements.

Mechanical properties of the dry membranes were measured by WDW-10 tensile test machine (Changchun keXin Co., China) at a loading velocity of 5 mm/min.

The thermal stability of membranes was evaluated by thermal gravitational analysis (TGA, TA DSC-Q1000, USA). The TGA was measured in the range of temperature under nitrogen atmosphere at a heating rate of 10 °C min⁻¹ from 50 to 850 °C.

The porosity ε (%), average pore radius (r_m) and water uptake were calculated by the methods reported in the literatures [18,19].

The bubble point measurement was carried out under in situ conditions as reported in Ref. [20]. The membrane was incorporated into the fuel cell hardware as part of the MEA. Nitrogen was then passed through the cell from one side and water was circulated through the opposite side at 425 ml min⁻¹ (at room temperature). The nitrogen pressure was slowly increased, until bubbles were observed in the water stream.

The in-plane ion conductivities of UF-based proton-conducting membranes, pressed on two platinum-wired electrodes (the distance between the electrodes was 2 cm), were measured at room temperature (20 ± 1 °C) by 2-probe DC method with a Solartron SI 1260 analyzer over a frequency range from 10⁶ to 100 Hz at a voltage amplitude of 10 mV. The electrodes and membrane were pressed between two stainless-steel plates and clamped tightly by four bolts. Before these measurements, samples were immersed in 3 M HCl for 3 h at 80 °C. The residual acid on membrane surface was then removed by filter paper. For comparison, the conductivity of Nafion 115 membrane was measured in water.

2.3. Fabrication of membrane electrode assembly (MEA)

The cathode was prepared by spreading 70% Pt/C (Johnson Matthey) over Toray carbon paper with Pt loading of...
0.9 mg cm$^{-2}$. A commercial gas-diffusing electrode (Sunrise Power Co. Ltd., China) with Pt loading of 0.4 mg cm$^{-2}$ was used as the anode. The electrode active area was 5 cm$^2$. The top-layer of the membrane contacted with the anode when the membrane electrode assembly (MEA) was prepared by hot-press at 100 °C and 0.1 MPa for 60 s.

2.4. Single-cell test

During cell operation 3 M hydrochloric acid dissolved with chlorine was circulated over the cathode side at a flow rate of 850 ml min$^{-1}$, while dry hydrogen was fed to the anode side at a flow rate of 110 ml min$^{-1}$. Cell resistance was measured by 2-probe DC method with PARSTAT 2273 (Princeton, USA) at open circuit voltage. Output performances of the cells were tested with an electronic load PLZ-50F (Kikusui, Japan).

3. Results and discussion

3.1. Membrane morphology

The cross-section and surface morphology of the membranes were recorded with a SEM (Fig. 2). Asymmetric structure with dense top-layer supported by finger-like macrovoid substructure was observed from PESSi0 to PESSi15 membrane, although micron-order SiO$_2$ agglomerates were showed on the top-skin with addition of SiO$_2$. In the fuel cell, these voids were filled with aqueous acid and thus allowed proton conduction. And the pores of the skin layer were small enough to maintain a large gas-pressure gradient when filled with water, especially at higher SiO$_2$ concentration, as seen from the bubble point measurements (Table 1). The PESSi10 and PESSi15 UF membrane were able to retain a pressure of at least 0.2 and 0.3 MPa, respectively, without visible bubbles crossing the membrane. This showed that the membranes are suitable for fuel cell application.

As shown in Fig. 2, the membrane structure was obviously improved with addition of SiO$_2$, because SiO$_2$ with high specific areas and good hydrophilicity would affect the mass transfer during the phase inversion process. With the increase of silica content in the membrane matrix, the long finger-like structure under the top-layer became shorter and more compact. In addition, there was also a transition from the finger-like macrovoid substructure to the sponger-like structure from PESSi0 to PESSi15, which indicates higher water uptake due to the increase of porosity. These results were possibly attributed to the formation of higher crosslinking inorganic and organic networks because the formation of inorganic network had an important effect on the formation of the organic network [18].

3.2. Membrane characterizations

Surface wettability, effective porosity ($\epsilon$) and average pore size ($r_m$) are shown in Table 1. The surface hydrophilicity was

![Fig. 2 – The cross-section and surface morphology of (a) PESSi0, (b) PESSi5, (c) PESSi10, and (d) PESSi15 membrane.](image-url-

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<p>| Table 1 – Properties of fabricated PSF–SiO$_2$ UF membranes with different SiO$_2$ content. |
|---------------------------------|---------------------------------|------------------|------------------|------------------|</p>
<table>
<thead>
<tr>
<th>Membrane</th>
<th>Contact angle $\theta$ (°)</th>
<th>Porosity $\epsilon$ (%)</th>
<th>$r_m$ (nm)</th>
<th>Bubble point pressure (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PESSi0</td>
<td>75.66</td>
<td>71.01</td>
<td>13.91</td>
<td>0.075</td>
</tr>
<tr>
<td>PESSi5</td>
<td>66.41</td>
<td>71.57</td>
<td>12.30</td>
<td>0.10</td>
</tr>
<tr>
<td>PESSi10</td>
<td>64.27</td>
<td>73.41</td>
<td>10.85</td>
<td>0.21</td>
</tr>
<tr>
<td>PESSi15</td>
<td>67.61</td>
<td>74.26</td>
<td>9.46</td>
<td>0.31</td>
</tr>
</tbody>
</table>
increased with increasing SiO2 concentration to 10 wt.%, which could be attributed to the hydrophilic SiO2 particles containing large amount of –OH groups absorbed on the membrane surface. The increased hydrophilicity is beneficial to the adsorption of more water molecules in the membranes. However, the contact angle of composite UF membranes increased when SiO2 content was increased to 15 wt.%. This result indicates that the hydrophilic area and the effective hydroxyl groups decreased. The reason could be the strong condensation interaction between Si–OH to form large-scale inorganic network at high SiO2 content, which consumed hydroxyl groups.

The porosity of UF membranes increased with the increase in the SiO2 amount, while the mean pore size was smaller with higher SiO2 content. This was related with the formation of denser skin layer and sponger-like structure when the content of SiO2 increased, which could be observed in Fig. 2. When 5 wt.% SiO2 was added to the membrane, the mechanical strength of dry membranes was enhanced, and then declined with the further increase of silicon content (Table 2). At higher SiO2 content, the formed brittleness inorganic network (as stated above) increased the rigidity of membrane, which finally resulted in the decrease of the mechanical properties, such as elongation at break.

The thermal decomposition temperature $T_d$ (defined as the temperature at 3% weight loss) increased by the introduction of nanoparticles (Fig. 3), indicating a better thermal stability of the composite membranes, probably because of the interaction between PES chains and SiO2 surface groups (–OH).

### Table 2 – Mechanical properties of PES–SiO2 composite UF membrane.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Tensile stress at break (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PESSi0</td>
<td>3.62</td>
<td>24.21</td>
</tr>
<tr>
<td>PESSi5</td>
<td>3.84</td>
<td>29.58</td>
</tr>
<tr>
<td>PESSi10</td>
<td>3.55</td>
<td>13.98</td>
</tr>
<tr>
<td>PESSi15</td>
<td>2.75</td>
<td>13.72</td>
</tr>
</tbody>
</table>

3.3. Ion conductivity and water uptake

The water uptake of the composite membranes increased with the silica content, as well as the ionic conductivity, as shown in Fig. 4. The water uptake of PESSi15 membrane could reach to 213.41%, and the corresponding value of NP-PCM and Nafion 115 were only 40% [15] and 26.32%, respectively. The continuous hydrophilic network formed by SiO2 particles allowed the adsorption of more acid molecules to form more migration sites, which further improved the proton transport and increased the proton conductivity. The proton conductivity of PESSi10- and PESSi15-based PCMs reached 0.106 and 0.150 S cm$^{-1}$, respectively, while the maximum conductivity of Nafion 115 was 0.107 S cm$^{-1}$.

3.4. Cell performance

To minimize the chloride ions diffusing through the membrane to the anode side, it was necessary to flushing the anode with hydrogen gas before feeding the cathode with the hydrochloric acid. And the continuous hydrogen feed was not stopped throughout the entire test. The H2/Cl2 fuel cell performances were improved with the increased acid flow rates (Fig. 5). The reason was that chlorine can complex with chloride ions to form trichloride ions (Cl$_3^-$) [3], thus more Cl$_3^-$ would reach to the surface of cathode with the increase of the acid flow rate.

Fig. 6 shows the preliminary performance of non-optimized H2/Cl2 fuel cells with PESSi10- and PESSi15-based PCMs. For comparison, the output performance of an H2/Cl2 fuel cell with Nafion 115 as electrolyte is shown in the figure as well. First, open circuit voltage (OCV) about 1.25 V was achieved for three different membranes. This value is close to the theoretical OCV of H2/Cl2 fuel cell [21], indicating the crossover of chloride ions and trichloride ions has little influence on the cell performance. As shown in Fig. 6, the voltage–current relation was linear, indicating that cell performance was governed by the cell ohmic resistance. The maximum power density was improved by 12.67% and 55.03% by introducing PESSi10 and PESSi15 UF-based PCMs compared with that of Nafion 115.
To understand the reason of differences in cell performance, EIS analyses were performed on the cells at open circuit condition. Fig. 7 shows the impedance spectra of the cell when the cell was in the configurations corresponding to Fig. 6. There were two intersections with the real axis. The smaller one obtained at high frequencies was attributed to the ohmic resistance and the interval between two intersections represented the charge-transfer resistance by the electrochemical reaction at the electrode [22]. The charge-transfer resistance was similar regardless of the type of membrane, because the electrode reactivity was similar when using the same electrode. The ohmic resistances of the single cells using PESSi10, PESSi15 and Nafion 115 membranes as separators were 0.68, 0.57 and 0.96 Ω cm$^2$, respectively. Because all MEAs were assembled using the same components except for the membrane in this experiment, the difference of ohmic resistance was mainly caused by the difference in the membrane resistance. It is thus concluded that the reduced ohmic resistance of the UF-based PCM is the main reason for the better performance than that with Nafion membrane.

Although this work is only preliminary, the characterizations of the PESSi UF-based proton-conductive membranes still make it a promising candidate membrane for the H$_2$/Cl$_2$ fuel cell application. Further work is still in progress on the optimization of SiO$_2$-based UF membranes. The pore size will be decreased in order to further improve the performance of the H$_2$/Cl$_2$ fuel cell by preparing the nanofiltration (NF) membrane.

4. Conclusions

For the first time, silicon modified UF-based PCMs were proposed and designed for H$_2$/Cl$_2$ fuel cell. The composite membranes showed high hydrophilicity, high porosity and narrow pore size distribution, as a result, high bubble point pressure and high ion conductivity. H$_2$/Cl$_2$ fuel cells assembled with SiO$_2$ modified UF-based PCM exhibited maximum power density about 195.3 mW cm$^{-2}$, which was two times that with Nafion 115 membrane. This indicated that SiO$_2$ modified UF-based PCM with a much lower cost is promising candidate for H$_2$/Cl$_2$ fuel cell.

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