SHORT COMMUNICATION

Synthesis and Characterization of Nanocomposite Sulfonated PVDF Membrane

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ABSTRACT

As a commercial fuel cell membrane, Nafion has disadvantages such as low stability at high temperature and low conductivity at low humidity. Sulfonated Polyvinylidene fluoride (PVDF) is known for good mechanical and thermal properties as a membrane. The purpose of this research is to synthesis a nanocomposite PVDF-TiSiO\textsubscript{4} membrane as a potential replacement of Nafion. PVDF sulfonation was performed using concentrated sulfuric acid. The nanocomposites TiSiO\textsubscript{4} were synthesized from TiCl\textsubscript{4} and TEOS. Ultrasonification was used to insert the nanomaterial to the sulfonated membrane. The infrared spectra analysis shows the peak for the Ti-O-Si ang. SEM-EDX analysis shows that the nanocomposite PVDF-TiSiO\textsubscript{4} membrane contents titanium oxide. The conductivity analysis shows the increasing of conductivity on addition of nanomaterials.

Keywords: nanocomposites, silicon oxide, titanium oxide, PVDF membrane

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1. INTRODUCTION

As fossil energy resources are rapidly decreased, the alternative energy resources are developing simultaneously. The researchers did their best to produce new alternative energy resources. They tried to produce an environmental friendly resource such as fuel cell. A fuel cell is a device that transforms chemical energy to electricity power through chemical reaction. Hydrogen gas is usually used as fuel as well as alcohol. Differ from battery, fuel cell continuously produces electricity as long as the fueled gas available.

Fuel cells can be categorized into five main groups including Polymer Electrolyte Membrane Fuel Cell (PEMFC). The main part of a PEMFC is proton membrane, which allows the proton transportation through the membrane and prohibits other compounds. The membrane is a specific polymer with special properties. The membrane usually has sulfonate branch that plays important role in proton transfer. The sulfonated polymers are usually used as basic membrane for the fuel cell [1,2]. The most familiar membrane used in PEMFC is Nafion. In order to improve the properties of Nafion, researchers have added some nanomaterial to the membrane [3-6]. There are many kinds of nanomaterial that can be used in this case. Nanoparticles TiO$_2$ and SiO$_2$ for examples have been used to increase the membrane conductivity and mechanical property. Polymer nanocomposite is defined as the combination of polymer with small portion of nanomaterial. The polymer was synthesized for special purpose including for the fire resistance, oxygen protection etc.

Since few years the organic-inorganic nanocomposite membrane has been attracted the PEM researcher attention. The membrane has a significant improvement in mechanical properties and conductivities. The gas cross over is also reduced on that membrane [1,7].

The PVDF polymer is predicted to have good thermal and chemical stability as a replacement of commercial Nafion. Unfortunately the polymer is hydrophobic that decrease the PEM performances. Heo et al. [8] have suggested inserting the sulfone group in order to increase the hydrophilic property of the polymer. Kim et al. [9] reported that sulfonate PVDF membrane using concentrated H$_2$SO$_4$ at 60 °C for 4 hours has effectively increased the membrane conductivity to reach the Nafion one. Nagarale et al. [7] also reported that composite of inorganic compound with polymer membrane increased the polymer ionic exchange property. The main role of the inorganic compound in the polymer is to increase the conductivity and ion exchange property. TiSiO$_4$ nanocomposite has been used successfully to increase the proton conductivity of membrane [10]. The addition of SiO$_2$ nanoparticle to polymer membrane has improved the mechanical and thermal properties of the fuel cell membrane [11]. Devrim et al. [12] also reported that the addition of 1:1 TiO$_2$:SiO$_2$ nanocomposite has increased the membrane conductivity.

In this research the synthesis and sulfonation procedure of PVDF is adapted from Kim et al. [9] and Kang et.al [11]. The sulfonation was performed with concentrated sulfuric acid at 60 °C for 4 hours. The SiO$_2$ nanoparticles were synthesized from TEOS [13-15].

2. MATERIALS AND METHODS

Deionized water, DMF, concentrated sulfuric acid, salt, sodium hydroxide, ammonia, PVDF, TiCl$_4$ and TEOS were used to perform the experiment. Ten mL of TiCl$_4$ was added drop by drop to deionized water in an ice bath. The mixture was neutralized by addition of
ammonia to reach pH of 7.5-8. The TiO$_2$ sol was centrifuged four times at 7000 rpm for 5 minutes. The gel TiO$_2$ was collected and dried at 110 °C prior to calcinations at 600 °C for 4 hours.

One gram of TiO$_2$ nanoparticle was added to the mixture of 5 mL ethanol, 5 mL of TEOS and 1 mL ammonia. The mixture was then put into ultrasonic bath for 1 hour. The gel was dried and calcined at 110 and 500 °C respectively to obtain nanocomposite TiSiO$_4$.

One gram PVDF was dissolved in 10 mL DMF solvent to form a solution with 10 wt% PVDF. Then nanocomposite TiSiO$_4$ was added to the solution with a variation of 1, 1.5 and 2% (TiO$_2$-SiO$_2$ 1:1). Then the mixture was stirred with a magnetic. The mixture was then put into ultrasonic bath for 1 hour. At the last the membrane was casted. Casting process was performed by leveling the surface of the mixture that has been stipulated by using the rod so that the thickness of the membrane produced uniform.

Sulfonation was conducted by inserting the nanocomposites membrane into concentrated sulfuric acid (95-97%), and heated at a temperature of 60 °C for 4 hours. The membrane was then washed with distilled water to remove residual acid.

3. RESULTS AND DISCUSSIONS

The nanoparticles TiO$_2$ was synthesized from precursor TiCl$_4$ based on sol gel method. TiCl$_4$ was added drop by drop to water in an ice bath. Due to exothermic reaction the ice bath is needed to reduce the reaction temperature. The mixture was then neutralized with ammonia. The white sol phase of TiO$_2$ was centrifuged several times prior to calcination.

![Figure 1. White TiSiO$_4$ sol](image)

In this research, PVDF (Polyvinilidene Fluoride) was composited with nanoparticles of TiSiO$_4$ at variation of 1, 1.5, and 2%. DMSO (Dimethyl Sulfoxide) was also used as solvent. The functional group of the membrane was analyzed using FTIR spectra. The spectra prove that the sulfonation process has inserted the sulfone function to the membrane. The data are shown in Figure 2 and Table 1.
Figure 2. FTIR spectra of nanocomposite PVDF-TiSiO$_4$ membrane
Table 1. FTIR stretching wave number (cm\(^{-1}\)) of nanocomposite PVDF-TiSiO\(_4\) membrane

<table>
<thead>
<tr>
<th>Sulfonated PVDF-TiSiO(_4) membrane (cm(^{-1}))</th>
<th>PVDF-TiSiO(_4) membrane (cm(^{-1}))</th>
<th>Literature [16-17] (cm(^{-1}))</th>
<th>Functional group</th>
</tr>
</thead>
<tbody>
<tr>
<td>481</td>
<td>483</td>
<td>488</td>
<td>Ti-O-Si scissoring</td>
</tr>
<tr>
<td>600</td>
<td></td>
<td>570-710</td>
<td>Asymmetric S=O stretching</td>
</tr>
<tr>
<td>838</td>
<td>837</td>
<td>837</td>
<td>Si-O-Si twisting</td>
</tr>
<tr>
<td>1163</td>
<td>1030-1275</td>
<td></td>
<td>symmetric S=O stretching</td>
</tr>
</tbody>
</table>

Table 1 shows the interpretation of the sample before and after sulfonation process and comparison with the reference. Sulfone group that is bound to the membrane of PVDF-TiSiO\(_4\) can be interpreted by absorption at wave numbers of 1163 and 600 cm\(^{-1}\) which are for the stretching of asymmetric and symmetric S=O respectively. The nanocomposite existence in the membrane was indicated by the absorption at 481 and 838 cm\(^{-1}\). These prove that the membrane contain TiSiO\(_4\) nanocomposite and sulfone functional group.

The degree of sulfonation was calculated to estimate the sulfone content in the membrane. The determination was performed by acid-base titration. The sulfonated membrane was soaked with NaCl to release the H\(^+\) from the membrane. The amount of H\(^+\) released from the sulfonated sample indicates the sulfonation degree.

Table 2. Sulfonation Degree (DS) of nanocomposite PVDF-TiSiO\(_4\) membranes

<table>
<thead>
<tr>
<th>Samples</th>
<th>Sulfonation Degree (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>sPVDF</td>
<td>8.1</td>
</tr>
<tr>
<td>sPVDF - 1.0% TiSiO(_4)</td>
<td>10.0</td>
</tr>
<tr>
<td>sPVDF - 1.5% TiSiO(_4)</td>
<td>11.1</td>
</tr>
<tr>
<td>sPVDF - 2.0% TiSiO(_4)</td>
<td>13.0</td>
</tr>
</tbody>
</table>

The measurement of the membrane conductivity was performed following the procedure shown by Devrim et al. [12]. The results are shown in Table 3. The highest conductivity was gained by the sulfonated membrane combined with 2% TiSiO\(_4\) nanocomposite. Devrim et al reported that the nanocomposites help the ion exchange and proton transport inside the membrane. Our result (0.0005291 S/cm) is lower than Nafion’s conductivity (0.00608 S/cm) [9].
Table 3. Nanocomposite PVDF-TiSiO$_4$ membrane conductivity

<table>
<thead>
<tr>
<th>Samples</th>
<th>Conductivity $\times$ $10^{-4}$ (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>sPVDF</td>
<td>1.783</td>
</tr>
<tr>
<td>sPVDF - 1.0% TiSiO$_4$</td>
<td>2.564</td>
</tr>
<tr>
<td>sPVDF - 1.5% TiSiO$_4$</td>
<td>2.840</td>
</tr>
<tr>
<td>sPVDF - 2.0% TiSiO$_4$</td>
<td>5.291</td>
</tr>
</tbody>
</table>

3. CONCLUSIONS

Nanocomposite PVDF membrane has been synthesized using TiCl$_4$, TEOS and copolymer PVDF. Infrared spectra of the membrane show the S-O bond to prove that sulfonation process. The increasing of nanocomposite content in the membrane has increased the conductivity. In the case of 2% addition of nanocomposite increases the membrane conductivity to 0.53 mS/cm.

References


