Fabrication and Characterization of Sulfonated ABS-SiO\textsubscript{2} Composite Membrane for Solid Electrolyte Fuel Cell

Eniya Listiani Dewi\textsuperscript{1,*}, Sri Handayani\textsuperscript{2}

\textsuperscript{1}Agency of the Assessments and Application of Technology, Center for Materials Technology, MH. Thamrin 8, BPPT II/22, Jakarta
\textsuperscript{2}Department of Chemical Engineering, Institute Technology Indonesia, Serpong Tangerang
*e-mail: eniyalist@webmail.bppt.go.id

Abstract

PEMs in general have a functional group (usually sulfonic acid) attached to the polymer backbone. This group facilitates proton conduction. Upon hydration, the PEMs tend to show an increase in the proton conductivity. Current limitations in PEMs are poor proton conductivity at elevated temperatures (>100 \textdegree C) and low humidities; susceptibility to chemical degradation; and high cost. In addition to the above problems, most membranes also show high methanol crossover, which is detrimental to operation in direct methanol mode. Hence development of alternate membranes with desirable properties has been widely explored. Hydrocarbon membranes look promising in this scenario though durability remains a concern and low cost. Hence we studied properties of acrylonitrile-butadiene-styrene (ABS) membrane that have been sulfonated and modified with silica in a function of sulfonation time. Protons conducting additives like silica, have been added to PEMs then was sulfonated to produce composite membrane. By sulfonation process the s-ABS membrane becomes a conductive membrane which showed by proton conductivity of 0.011 S/cm at 10 hours sulfonation time. Furthermore, due to silica properties which they are usually hygroscopic and proton conducting by themselves or with help of attached acidic moieties, s-ABS-SiO\textsubscript{2} for 7 hours sulfonation time showed high proton conductivity of 0.042 and 0.02 S/cm in 3 and 5 wt% addition ratios. An important effect that results on addition of this additive is slightly lowering methanol permeability to 15% than blank s-ABS membrane. This is not only greatly augments the performance in PEM fuel cell mode, but also promising as a new candidate membrane from local polymer industries.

Keywords: Proton exchange membrane, composite, nanotechnology, fuel cell

Introduction

Fuel cells are efficient devices that generate electricity via chemical reaction of fuels and oxygen from air. Fuel cells technology using hydrogen or alcohol as fuel is a promising candidate system for portable electronic device and automotive applications. This is because of their attributes of high power density, low weight, simplicity of operation, high energy conversion efficiency and zero harmful emissions. Energy carrier of fuel cells is more than >50%, it is higher comparing to internal combustion engine (15%) [Larminie, 2002; Li, 2003].

Some of the most promising PEMs are develop at low temperatures below 80\textdegree C using hydrated perfluorosulfonic acid (PFSA) polymers, such as Nafion\textsuperscript{®} (Dupont), Flemion\textsuperscript{®} (Asahi Glass), Aciplex\textsuperscript{®} (Asahi Chemical Industry), Neosepta-F\textsuperscript{®} (Tokuyama) and Gore- Select\textsuperscript{®} (W.L. Gore and Associates). Although some of these membranes were originally developed for chlor-alkali electrolysis, they demonstrate good proton conductivities when used as electrolytes in a PEM fuel cell. Some of the requirements of PEMs, apart from high proton conductivity, include good chemical, morphological and thermal stability; excellent chemical durability; and low cost. However, PEM fuel cells operated at elevated temperatures (>100 \textdegree C, atmospheric pressure and therefore dry gases) have significant advantages over low-temperature PEM fuel cells as CO poisoning at the anode is effectively alleviated [Vengatesan, 2008; Tang, 2007]. Higher temperature operation also increases the energy efficiency, improves heat rejection, provides higher quality waste heat, and permits easier water management [Chu, 2008]. Nafion is still the most commonly used commercial membrane in PEM fuel cell to date. In order to realize elevated temperature performance, the Nafion membrane needs to be fully wet as the proton conduction in the membrane relies on the dissociation of protons from the constituent SO\textsubscript{3}H groups in the presence of water. Current research on solid electrolyte fuel cell (PEMFCs) is focused on the optimization of a device working at operational temperatures above 100\textdegree C and very low humidity levels [Vengatesan, 2008; Tang, 2007; Jung, 2007]. Thus the membrane in the PEMFC system requires
water to maintain its proton conductivity during operation.

In order to retain the optimum hydration level, water has to be supplied to the membrane by a humidifying system. On the other hand, a high humidity of the inlet reactant gases may lead to cathode flooding, which limits the access of oxygen to the active surface of the catalyst particles. Thus, proper hydration is critical to maintaining membrane conductivity and performance external humidification conditions. Other studies include self-humidifying membranes prepared by embedding catalyst particles into membrane [Watanabe, 1998]. The catalyst particles act as water-generation sites by recombination of permeated hydrogen and oxygen. This does, however, gives rise to the problem of short-circuits due to the electrical conductivity of the embedded particles.

Other researchers have prepared Nafion/SiO₂ composite membranes to improve cell performance at high temperatures [Arimura, 1998; Eniya, 2007; Chena, 2007]. Furthermore, several recent reviews well depict the state of the art on new polymers suitable as electrolytes for fuel cells. Protons conducting additives like silica, zirconium phosphate, heteropolyacids (HPAs) and various metal oxides have also been added to PEMs [Arimura, 1998, Eniya, 2007; Dormitrova, 2002; Arico, 2003]. They are usually hygroscopic and proton conducting by themselves or with help of attached acidic moieties, thus the ionic conductivity of Nafion® at elevated temperatures was increased. In the case of Nafion, whose proton conductivity is acceptable only at elevated hydration levels, this peculiar limit was partially solved by preparing composite membranes with active nanofillers [Jung, 2007]. In order to extend the temperature range, the attention was focused on membranes with thermal stability higher than Nafion itself. Many alternatives were proposed to this aim, ranging on a wide group of ionomers, like modified perfluoropolymers, ormolytes, blends of acid and base aromatic polymers. The optimization of high-temperature PEMFCs requires the development of new membranes in which the proton transport is not assisted by the water molecules. Some of the hydrocarbon polymers studied include poly(styrene sulfonic acid), sulfonated poly(ether ether ketone) [Li, 2003; Handayani, 2007; Ulbright, 2006], sulfonated poly(ether sulphone), sulfoarylated polybenzimidazole [Li, 2003; Handayani, 2007], sulfonated polyimides [Fang, 2006], sulfonated polysulfone [Deimede, 2000; Lufrano, 2000], sulfonated poly(phenylene sulfide) and sulfonated poly(phenoxoy benzoyl phenylene) [Son, 2001].

Up to now, a large number of sulfonated hydrocarbon polymers have been developed and also with inorganic addition modification. Among them, acrylonitrile-butadiene-styrene (ABS) was not yet have been investigated in this field to be the most promising membrane materials for PEMFC applications. This article describes the synthesis of sulfonated-ABS with various sulfonation time and the addition of inorganic particles such as silica. The relationship between structure, water stability and proton conductivity is also discussed.

**Materials and Methods**

**Synthesis of sulfonated-acrylonitrile-butadiene-styrene (s-ABS)**

Detail synthesis method as describe later, was adopt from simple sulfonation process with sulfuric acid. The ABS that use in these experiments was a gift from PT. ARBE Styriindo&ABSii (Cilegon Indonesia). An ABS pellet 7.5 g was dissolved on 50 mL methyl ethyl ketone (MEK) from Merck. ABS solution was stirred for 7 hours at ambient temperature and become a homogen solution. After stand for a night, solution was cast at a plate with 100 μm of thickness, and then dried at 50°C for 48 hours. Sulfonation process was done by soaked the membrane at concentration of sulfuric acid 10 M for 5, 7 and 10 hours at 60°C. Sulfonated membrane was then washes using distilled water for many times until pH neutral and dried at 50°C for 48 hours.

**Synthesis of silica modified s-ABS**

Silica modified sulfonated-ABS was done as describe above, with slightly modification as follows. A silica particle in 3 and 5 wt% was added on ABS solution and vigorously stirred for 7 hours to get a suspension. Casting and drying was done as describe above to get sulfonated-ABS-SiO₂.

**Determination of IEC**

The ion exchange capacity of all composite membrane was determined by the titration method. The cast film of s-ABS and s-ABS-SiO₂ were soaked in NaOH 0,01 N for 3 days at room temperature. Then it was titrated by adding sulfuric acid 0,01 M with PP indicator as sulfonate group/g polymer. Proton in the sulfonic acid group exchanged with the sodium ions in solution. Sulfonation degree and ion exchange capacity was calculated by Eq. 1 and 2, where $\text{meq s-ABS} - H$ is meq SO₃H in s-ABS, $\text{meq}$ miligram equivalent, $W$: dry membrane weight (g), $V$: volume (ml), $N$: normality (N), IEC: Ion exchange capacity (meq SO₃H/g s-ABS), $M_r$: relative molecule mass ABS (C₆H₅-C₆H₅-C₆H₅), 103: molecular mass SO₃Na.

\[
\text{IEC} = \left( \frac{\text{meq s-ABS} - H}{W} \right)
\] (1)
Measurements

Infrared (IR) spectra were recorded on a Shimadzu IR Prestige-21 spectrometer. Melting point and glass transition were recorded on a Matler Toledo DSC-821 and TGA/DTA-851. The morphology of the inorganic filler composite membrane was determined using a scanning electron microscope SEM Phillips XL-30.

Proton conductivity was measured using a four-point-probe electrochemical impedance spectroscopy technique over the frequency range from 1 Hz to 1 MHz by HIOKI 3522-50. A sheet of membrane (1 x 4 cm) was soaked in water for 4 days before clamped at cell and two pairs of gold electrodes were set in a Teflon cell [Handayani, 2007, Zawodski, 1991; Sancho, 2007]. The distance between two electrodes was 1 cm. The cell was contained a liquid chamber of bidistilated water for measurement at 100% RH in liquid water. The resistance value associated with the membrane conductance was determined from high frequency intercept of the impedance with the real axis. Proton conductivity (σ) was calculated from \( G \times (L/Wd) \) where \( G \) is conductivity value measured, \( d \) is thickness of membrane, \( W \) is width of membrane, \( L \) is distance between two electrodes [Zawodski, 1991; Sancho, 2007].

Water uptake was measured by immersing membranes into water at ambient temperature for 24 hours. Then the film was taken out, wiped with tissue paper and weight at microbalance. Water uptake (swelling) of the membrane was calculated from \( (W_{wet} - W_{dry})/ W_{dry} \times 100(\%) \) where \( W_{dry} \) and \( W_{wet} \) are weight of dry membrane and corresponding water swollen of membrane film, respectively. Water uptake of membrane was estimated from the average value of water uptake of each film.

Methanol permeability measurement was done using an H-cell [Won, 2003; Eniya, 2005]. The cell consisted of two reservoir made of glass of approximately 300 ml of volume separated by the stainless still clamp (φ23 mm). The membrane was equilibrated in pure water for 5 h before clamped vertical at the diffusion cell. Each chamber was provided with two orifices of communicating to the exterior used as solution inlet and outlet. The solutions circulated by means of a magnetic stirrer. Initially, one reservoir was contained a methanol-water mixture in 1, 3, and 10 M in cell A and the other reservoir contained only water in cell B. Increases over time in the concentration in the reservoir cell B were detected by picnometer. Methanol concentration in the receiving reservoir detected as a function of time has the following relationship [Won, 2003],

\[
C_B(t) = \left( \frac{A}{V_B} \right) \left( \frac{DK}{L} \right) C_A(t-t_0),
\]

where \( C_A \) and \( C_B \) are the concentration of methanol in cells, \( V \) are the volume of solution in cell A and B, \( A \) and \( L \) are the area and thickness of membrane, and \( D, K \) are the methanol diffusivity and partition coefficient, respectively. The assumptions are made here that \( D \) inside the membrane is constant and \( K \) does not depend on concentration. The \( DK \) is the membrane permeability. The permeability of Nafion 117 in the literature was \( 2.86 \times 10^{-6} \text{ cm}^2/\text{s} \) [Won, 2003].

Results and Discussion

There are several justifications for the development of composite membranes: (1) to prevent membrane (anode side) dry out by addition of hydrophilic materials, (2) to suppress the methanol crossover, (3) to better withstand mechanical stress during swelling—deswelling phenomena, and (4) to increase the pathways of proton conduction. In order to optimize the membrane capability of point (1)-(3), acrylonitrile-butadiene-styrene (ABS) product by PT. Arbe Styrindo was used as raw-material to develop polyelectrolyte membrane for fuel cell. ABS was sulfonated by sulfuric acid with simple method to got s-ABS \( 1 \) and then added with silica to produce composite membrane \( 2 \). The surface and cross-section morphology was determined by SEM analysis as shown in Fig.1. Membrane characteristics were summarized in Table 1.
Table 1 Spectrum and tensile characterization for sulfonated-ABS

<table>
<thead>
<tr>
<th>Membranes</th>
<th>FT-IR [cm⁻¹]</th>
<th>DSC [°C]</th>
<th>Tg [°C]</th>
<th>Tensile [kg/cm²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>s-ABS</td>
<td>νOH 3082, 3003; νO=S=O 1070; νS=O 1028; νS-O 763; νC=S 2237</td>
<td>102.57/133.71</td>
<td>102.57</td>
<td>261.92</td>
</tr>
<tr>
<td>s-ABS-SiO₂</td>
<td>νOH 3061, 3027; νO=S=O 1088; νS=O 1026; νS-O 965</td>
<td>103.54 / 129.2</td>
<td>103.54</td>
<td>283.82</td>
</tr>
<tr>
<td>Nafion 117</td>
<td></td>
<td>110</td>
<td></td>
<td>240.04</td>
</tr>
</tbody>
</table>

From Fig. 2, it is clear that ion exchange capacity would increased due to sulfonation time and also increased the degree of sulfonation. Although in higher sulfonation time the IEC showed constant value, thus sulfonation process optimal at 7 hours. The sulfonate (SO₃H) will bond at styrene with ion exchange capacity of 0.5028 meq/g. Furthermore, ion exchange capacity of Nafion was 0.9 meq/g [Handayani, 2007], with means that Nafion has more hydrophilic domain than that of s-ABS. The hydrophilic domain in s-ABS would become transport media of proton inside the membrane.

![Figure 2](image-url)  
**Figure 2** Sulfonation time and IEC relation of s-ABS.

IEC of composite membrane 2 were showed in Fig. 3. The relation showed constant IEC values which means that the addition of silica particles would not effect the sulfonation process.

![Figure 3](image-url)  
**Figure 3** Relation between sulfonation time and IEC of s-ABS-SiO₂.

According to the results of water-uptake (swelling) of membrane in Fig. 4, silica particle will increase the hydrophilic domain thus composite membrane 2 have more higher swelling than that of 1. Maximum water-uptake of 3.6% was showed at 7 hours of sulfonation time. This was confirmed by DS value. Increasing of silica particle addition in membrane will also increased methanol swelling of 3.5% at 7 hours sulfonation time due to the same polarity of water. Thus methanol was absorbed by silica which have average size of 50 nm, respectively.

As showed by Fig. 5, the relation between addition of silica particle and methanol permeability, silica could lowering the methanol crossover. This was due to the adsorption of methanol at silica surface thus methanol could not permeated through the composite membrane, respectively. The lowest methanol permeability was showed at 3 wt% silica addition that have permeability of composite membrane was 0.9728x10⁻⁶ cm²/s. Comparing to the Nafion which has permeability of 4.9x10⁻⁶ cm²/s, these all s-ABS composite membranes has lower values. Thus it is clearly that addition of nanoparticle silica could lowering methanol permeability.
Table 2 Characterization of sulfonated-ABS membrane for electrolyte fuel cell.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Sulfonation time (hour)</th>
<th>Parameters Analysis Polyelectrolyte Membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>IEC (meq/g)</td>
<td>Degree of Sulfonation DS(%)</td>
</tr>
<tr>
<td>s-ABS</td>
<td>5</td>
<td>0.418</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>0.583</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.543</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>0.538</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>0.536</td>
</tr>
<tr>
<td>s-ABS-SiO₂</td>
<td>5</td>
<td>0.527</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>0.581</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.552</td>
</tr>
<tr>
<td>s-ABS- SiO₂</td>
<td>5</td>
<td>0.503</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>0.571</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.531</td>
</tr>
</tbody>
</table>

Fig. 5 shows the relation between sulfonation time and methanol permeability.

Fig. 6 shows the relation between proton conductivity (proton) and silica content at room temperature and full humidity. By sulfonation process the s-ABS membrane becomes a conductive membrane which showed by proton conductivity of almost 0.011 S/cm at 10 hours sulfonation time. Furthermore, due to silica properties which they are usually hygroscopic and proton conducting by themselves or with help of attached acidic moieties, thus can increase water content in the composite as solid acid, so that proton conductivity may easily take in place. The composite display greatest conductivity at 3 wt% of silica content for 7 hours sulfonation time, while the maximum value can be seen in the s-ABS-SiO₂ composite membranes. The value was estimated to be 0.0453 S/cm and 0.0316 S/cm for 3 and 5 wt% addition filler at 7 hours sulfonation time, although it was approximately slightly lower than that of pure Nafion 117 in same condition was 0.082 S/cm. This maximum value consider with highest DS at 7 hours sulfonation time. Ionic conductivity increased as silica contains become higher due to hygroscopicity of composite make proton easier to transport as hydrate $\left[\text{H}^+ \ (\text{H}_2\text{O})_n\right]$. Although silica was added until 5 wt%, the ionic conductivity become lower, this also found in silica modified s-PEEK [Handayani, 2007].

According to a previous report, the typical Nafion/SiO₂ composite has a good cell performance and some useful properties, such as inhibition of methanol crossover [Eniya, 2007; Eniya, 2005]. But this s-ABS is firstly become a conductive membrane
and available as polyelectrolyte. And s-ABS was found to be competitive with another hydrocarbon composite polymer such as s-PEEK-SiO₂ and AAMPS-SiO₂ which have ionic conductivity of 0.02 and 0.0005 S/cm [Handayani, 2007; Eniya, 2005].

From Table 1, membranes 1 and 2 with 100 µm thickness which more thinner than Nafion H17 (180 µm) has higher tensile strength. And the addition of silica would not make membrane become rigid but give more strengthness 18%, respectively than that of Nafion. This is important to note for membrane electrode assembly manufacture, that electrolyte needed to be more mechanical strength with thinner film thus s-ABS is suitable candidate as PEM for fuel cells.

Conclusions

An important effect that results on addition of silica nano-particle is slightly lowering methanol permeability of 15% than blank s-ABS membrane, increasing ionic conductivity and mechanical strength. This is not only greatly augments the performance in PEM fuel cell mode, but also promising as a new candidate membrane from local polymer industries. And the application of electrolyte can be use for either direct methanol and hydrogen PEM fuel cell.

Acknowledgements

Authors acknowledge PT. Arbe Styrindo for supported raw materials of polymer. This recent work was supported by Indonesia Ministry of Research and Technology (RISTEK) for Incentives Research Grant.

References