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Jakarta, October 28 – 29, 2009
Assalamualaikum Warahmatullahi Wabarakatuh

International Conference on Fuel Cell and Hydrogen Technology is organized by Center for Material Technology, Agency for the Assessment and Application of Technology, Indonesia in Ruang Komisi Utama, Building II BPPT, 3rd Floor, Jakarta on October 28 – 29, 2009.

International Conference on Fuel Cell and Hydrogen Technology provides an international forum for sharing of the knowledge, information, experience and review the latest scientific breakthroughs, materials R&D, commercial opportunities and infrastructure development from the world’s prominent hydrogen and fuel cell expert.

This conference also has aim to get the latest information of hydrogen technology production and hydrogen storage manufacture in advanced countries, to seek for hydrogen potential production and infrastructure strategic in advanced countries. And the output of the conference expected to motivate scientist and stakeholder in Indonesia, especially, to create the newest invention.

We would like to express our heartiest to thank to all speakers and participants for the active participation in International Conference on Fuel Cell and Hydrogen Technology and to all the paper reviewers, member of steering committee and member of the organizing committee for their support to the success of this conference. And we thank our sponsor, PT. PLN (Persero), PT. Honda Prospect Motor, GasHub — Singapore, PT. Sharp Electronics Indonesia, PT. Infratech Indonesia, and Teh Hitam Mind Tea, for their support to this event.

We hope this conference will accommodate scientific efforts that have been performed by scientists, practical applications in the industry, as well as the commercializations efforts.

Wassalamualaikum warahmatullahi wabarakatuh.

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KEYNOTE SPEAKER

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Proton Conductivity of Sulfonated Acrylonitrile Butadiene Styrene Membrane

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Abstract

Acrylonitrile Butadiene Styrene membranes were prepared for proton exchange membrane fuel cell (PEMFC) as solid electrolyte. In the preparation of membrane, the ABS membranes were sulfonated with Sulfuric acid for 5, 7 and 10 hours. In this work the measurement of membrane conductivity were done using electrochemical impedance spectroscopy (EIS) within 0.5, 1, 2, 3, 4 and 5 volt. It was observed that the increasing of voltage in measurement did not increase the result of proton conductivity significantly. Also, the highest proton conductivity of $8.33 \times 10^{-5}$ S/cm was reached by sulfonation for 7 hours.

Keywords: Sulfonated ABS membrane, Fuel Cell, Proton Exchange Membrane, Proton Conductivity

1. Introduction

There are several types of fuel cells but proton exchange membrane (PEM) fuel cells are the most suitable idea for transportation and portable applications because of their higher efficiency, and environmental friendly operation, they have a wide range of applications. The main component PEMFC is polymer Electrolyte Membranes which act as proton conductors. The most widely used class of membrane materials today for the PEMFC are of the perfluorinated sulfonic acid (PFSA) type, e.g., Nafion® (DuPont, USA), Flemion® (Asahi Glass, Japan), Aquivion® (Asahi Kasei, Japan), and derivatives thereof, such as the Gore-SELECT® membranes (W.L. Gore, USA). However, they have the disadvantage of being characteristically expensive due to the complex fluorine chemistry involved in their fabrication and too expensive to extend their application [1, 2]. Conventional PEMFCs typically operated with Nafion® as electrolyte, which offers quite good performance below 50°C. Unfortunately, the proton conductivity of Nafion® suffers greatly at temperature above 50°C due to the loss of water. However, to decrease the complexity and increase the efficiency and robustness of PEMFC system, there is a need for PEMFC capable of sustained operation above 100°C [3-4]. The main focus has been directed towards polymer based on aromatic polymer, and especially directly Sulfonated ones i.e. aromatic polymers with the sulfonic acid groups directly attached to the polymer chain via reaction with dichlorosulfonic acid or sulfuric acid [5].

Acrylonitrile butadiene styrene (ABS) membrane has been developed to replace Nafion® as electrolyte of PEM fuel cell. ABS copolymer was made from styrene and acrylonitrile polymerization with addition of polybutadiene which is long chain of polybutadiene. ABS has shiny and waterproof surface was given by styrene group. Butadiene is an elastic material which gives ABS constrain even at low temperature. In the other hand, acrylonitrile gives thermal and chemical resistant. Thus make ABS stronger than pure polybutadiene. Since ABS membrane is hydrophobic it needs to be sulfonated use sulfuric acid to make it hydrophilic so that it can be use as proton transfer media.
The most common approach for the synthesis is sulfonation of a preformed, often commercially available, polymer. Sulfonation groups are introduced to provide acidic sites and they were selected as the source of protons for three simple reasons: they are easy to introduce into aromatic rings; they dissociate more readily than typical carboxylic acids, resulting in a larger number of charge carriers; and, unlike phosphonic acid, they do not easily form anhydrides on dehydronation, resulting in easy and quick rehydration of sulfonated polymers in contrast to phosphonated ones. As a proton conductor, the polymer is substituted with acidic groups, and – with very few exceptions – proton transport requires considerable sulfonated aromatic polymers for fuel cell membranes 3 amounts of water to be present within the membrane. The acidic groups ensure swelling of the polymer membrane in water, and at the same time they provide a high number of charge carriers (protons) within the membrane by dissociation [6].

![Chemical Structures](image)

**Fig. 1** ABS grafts Polymerization.

Impedance can be used to measure the ionic resistance of an electrolyte membrane in a four-probe configuration. In the four-probe configuration, the current is generated through the outer two wires and the voltage is measured between the inner two wires. The advantage of the four-probe configuration is the minimization of the impact of contact resistance on the voltage measurement because the measuring device has high input impedance. If the distance between the voltage measuring wires is l, the thickness of the membrane is d, and the width of the membrane is w, then the in-plane bulk resistance of the membrane is

\[ R = \rho l / (w d) \]

And thus

\[ \rho = R w d / l \]

(1)

Warburg impedance is generally used to represent the resistance due to the mass transport. Mass transport resistance is not limited only to the reactants or the products. Transport of other species such as electrons and protons can also pose mass transport resistance. Proton conductivity, \( \sigma \), was calculated from equation:

\[ \sigma = d / (L a W h R) \]

(2)

where \( d \) is the distance between 2 electrodes, \( L a \) and \( W h \) the thickness and width of the membrane at standard condition of 70% RH, and \( R \) the resistance value measured [7].

For PEMFC application, a PEM should be impermeable to gases but it conducts protons. This paper was investigating proton conduction properties of sulfonated ABS membrane in comparison with those of Nafion® to evaluate the potential for PEMFC application.

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2. Experimental

ABS pellet was obtained from P.T. ARBE, Styrindo & ABSI (Ciagen Indonesia). Other chemicals were purchased from Merck and used as delivered. ABS membrane was sulfonated according to the method previously reported [9].

The ABS membrane were soaked in 10 M of sulfuric acid at 60 °C for 3, 7, 10 hours with stirring. The resulting precipitate was collected by filtration, washed with water until reach neutral pH, and dried in the oven at 50 °C for 48 hours.

Proton conductivity in plane direction membrane was determined using an electrochemical impedance spectroscopy technique over the frequency range from 4 Hz – 1000 KHz (Hoki 3532-80). A single cell with 2 gold electrodes at 1 cm distance was employed in the measurement. Proton conductivity for each membrane were examined on various voltage; 1, 2, 3, 4, and 5 Volt.

3. Result and Discussion

Fourier transform infra red (FTIR) was used to detect the presence of sulfonic group. Based on previous research FTIR spectra of ABS membrane before and after sulfonated for 5 hours are presented in Fig. 2. The spectrum of C-H aliphatic (CH and CH2) show strong bands at 3000 – 2850 cm⁻¹. The intensity of C=O stretching shows strong peak at 3300-2900 cm⁻¹. Characteristic for styrene aromatic vibration, which are showed by C-H aromatic stretching and C=C aromatic stretching aromatic results in strong peak at 1700-1600 cm⁻¹. Therefore, 5 hours sulfonated ABS membrane shows broad bands at 3440, 1252, 1080, and 709 cm⁻¹. The C-H stretching of sulfonate group results in strong peak at 3450-3430 cm⁻¹. It proves that sulfonation was done successfully. Additionally, the intensity of C-H stretching peak at 3450-3430 cm⁻¹ is relatively increased because of protonation cause by sulfonic molecules. Hydrogen bonds seem to play an important role in the proton conductivity system [9].

![Image: Infrared Spectra of 5 hours Sulfonated ABS and non-sulfonated ABS.](image)

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Nuclear magnetic resonance (NMR) was used to detect sulfoic group position. During the sulfonation reaction only one of the four proton in the ring is being substituted by the sulfonic acid, even though there are four ortho positions for sulfonation [10]. It was found there sulfonic groups substitute the sulfoic group after sulfonation process.

Proton conductivity of membranes was determined with Hioki - Impedance meter (3532-80). The membranes were sulfonated for 5, 7, and 10 hours each of them was investigated over the frequency range from 4 Hz to 1000 Hz. These ranges were chosen since they show Warburg impedance which is most the membrane in electronic.

![Graph](image)

**Fig. 1** Nyquist plots of 5 hours ABS membrane sulfonation

**Fig. 2** Nyquist plots of 7 hours ABS membrane sulfonation

**Fig. 3** Nyquist plots of 10 hours ABS membrane sulfonation

In this study, the proton conductivity was measured in plane direction of membrane, because the measurement of proton conductivity in thickness direction (normal to the plane) is very difficult for thin membranes [11].
Fig. 3, Fig. 4 and Fig. 5 give some nyquist plots of 5, 7 and 10 hours ABS membrane sulfonation at different voltage, respectively. Based on Fig. 4 it was found that 5 hours sulfonation was not stable at higher frequency measurement. Proton conductivity was calculated from cole-cole plot (Ra Vs Xc) and can be seen in Table 1. Proton conductivity for 5 hour sulfonated ABS membrane which is 20 μm thick reached 0.008 S/cm. As shown in Table 1 the proton conductivity decreases with increasing voltage. In the other hand, the proton conductivity of 7 and 10 hours sulfonation increase with increasing voltage.

Table 1. Proton Conductivity of ABS membrane at various duration of sulfonation

<table>
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<th>5 Hours</th>
<th>7 Hours</th>
<th>10 Hours</th>
</tr>
</thead>
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<tr>
<td>0.5</td>
<td>0.00809</td>
<td>0.00794</td>
<td>0.00769</td>
</tr>
<tr>
<td>1</td>
<td>0.00794</td>
<td>0.00812</td>
<td>0.00804</td>
</tr>
<tr>
<td>2</td>
<td>0.00775</td>
<td>0.00812</td>
<td>0.00811</td>
</tr>
<tr>
<td>3</td>
<td>0.00758</td>
<td>0.00823</td>
<td>0.00814</td>
</tr>
<tr>
<td>4</td>
<td>0.00746</td>
<td>0.00875</td>
<td>0.00818</td>
</tr>
<tr>
<td>5</td>
<td>0.00758</td>
<td>0.00893</td>
<td>0.00818</td>
</tr>
</tbody>
</table>

Effect of the duration of sulfonation on proton conductivity of ABS membrane was shown in Fig. 6. It is easy seen from Fig. 6 that sulfonation over 7 hours, which is 56 μm thick, result higher proton conductivity than 5 and 10 hours due to the reaction time. Reaction time allows controlling the degree of sulfonation. But 10 hours sulfonated ABS membrane, which is 42 μm thick, did not show better result than 7 hours. This seems because under acidic conditions, especially at higher temperatures, sulfonic acid groups are lost from activated sites.

![Graph showing proton conductivity vs voltage](image)

**Fig. 6** Proton Conductivity of ABS membrane.

Sulfonation for 5 and 7 hours did not show difference significantly. Those membranes had different thickness, whereas 5 hours sulfonated ABS membrane 30 μm thicker than 7 hours sulfonated ABS membrane. This is because higher conductance resulting from the lower thickness of composite membrane [12] the thinner the membrane the better the performance it was. In this case, because the resistances to mass transfer of the proton decrease, the flux increases [13].
Measurement on Nafion® 117 membrane, using the same procedure, showed higher conductivity for this membrane than for all ABS membrane. It reached 0.00132 S/cm. This, and the fact that the materials are commercially available, and have relatively low prices, may give these new materials an economic edge over the Nafion® membrane.

4. Conclusion

ABS membrane was sulfonated using sulfonic acid for over 5, 7, and 10 hours show different behavior in accordance with the duration they had sulfonated and the thickness of membranes. The experiment has indicated that duration of sulfonation and the thickness of the membrane are significant parameter to provide a good proton conductivity of membrane.

In the experiments, it was observed that 7 hours gave better proton conductivity than 5 and 10 hours. It was also found that the increasing of measurement voltage did not increase the proton conductivity of each membrane significantly. Thus, the sulfonation of ABS membrane is still very interesting for development and further study.

5. Reference

PF-09
Characterization of Zeolite/Sulfonated Polyether-ether ketone for Solid Polymer Electrolyte Fuel Cell

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Abstract

Various sulfonated polyether-ether ketone composite membranes containing H-zeolite has been synthesized. Solid polymer electrolyte fuel cell (SPEFC) at temperature operation more than 100°C is very interesting because at this range temperature, anode catalyst poisoned by CO so the kinetics of fuel oxidation will be improved and the efficiency of the cell will significantly enhanced. Current limitations in electrolyte membranes are high methanol crossover permeability at elevated temperature. To solve this problem, we studied properties composite based on zeolite dispersed in sulfonated polyether-ether ketone (sPEEK). The proton conductivity was investigated by standard bridge impedance spectroscopy at various temperatures (25-140°C). At temperature 140°C, the addition of sPEEK composite membrane contains zeolite has conductivities (0.07 S/cm) higher than blank membrane (0.05 S/cm). The addition of zeolite onto sPEEK could lower methanol permeability and showed high mechanical stability at high temperature rather than Nafton 117 membrane. Thus sPEEK composite membranes can be used as promising candidates for high temperature SPEFC.

Keywords: zeolite, sulfonated polyether-ether ketone, solid polymer electrolyte fuel cell.

Introduction

Proton exchange membrane fuel cell (PEMFC) and Direct methanol fuel cells (DMFC) using polymer electrolyte membranes are promising for application in portable device and transportation [1, 2]. Recently, fuel cell at temperature operation more than 100°C is very interesting because at this range temperature, anode catalyst poisoned by CO so the kinetics of fuel oxidation will be improved and the efficiency of the cell will significantly enhanced. At high temperature, cell operation will contribute in reducing the complexity of the hydrocarbon fuel cell systems [2].

Nowadays, perfluorinated membranes such as Nafton®, Asahi, Flemion, and Dow are widely accepted for commercial application. However, there is a major problem related to the application at both ambient and high temperature of DMFC, i.e. high methanol cross over, lower conductivity due to hydration and it is very costly [3]. Therefore, the performance of membrane will decrease fuel cell efficiency. To solve this problem, many researchers have been done developing alternative ways in finding more economical and efficient non-perfluorinated polymer proton exchange membranes. Many promising polymer are based on aromatic thermoplastic such as polyether sulfone, polybenzimidazole, polyetherimide, and polyether-ether ketone (PEEK) [3-7].

The polyether-ether ketone (PEEK) is an aromatic polymer in which 1,4-di-substituted phenyl group are separated by ether (-O-) and carbonyl (-CO-) linkage. It was selected as polymer based membrane due to chemical resistance, good thermal stability, mechanical strength and adequate conductivity [4, 5, 7]. In order to hydrophilicity polymer, polyether-ether ketone must be sulfonated using concentrated sulfuric acid to form sulfonated polyether-ether ketone (sPEEK). The process of sulfonation is being controlled by reaction time and temperature [7-11]. At high temperature, operation of DMFC, membrane will decrease many performance like lower conductivity, higher methanol crossover and higher swelling. Indeed, sPEEk membrane has significant drawbacks compared to Nafton®.

117 i.e. low proton conductivity [12]. In order to increase performance of fuel cell membrane
nace ionic conductivity, mechanical strength, thermal stability and to decrease methanol permeability, some researchers conducted experiment by adding filler inorganic such as SiO₂, Al₂O₃, ZrO₂ in Nafton membrane [13] and zeolite in FTPE [14]. From this approach, has been employed various filler to sPEEK [8-9, 15]. Research done by Mikhailenko et al. [9] synthesized composite membrane of boronphosphate into polymeric matrix of sulfonated PEKK producing ionic conductivity of these membranes higher than that of basic sPEEK membrane. But the composite membrane has pores, which is not suitable for application of DMFC due to high methanol mass over values. Tadoksowski synthesized composite electrolyte based on zeolite-polyesterfluorosiloxane which produces ionic conductivity 10⁻² S/cm for addition zeolite 90 mass%. The zeolite is functioned as ionic electrolyte transfer.

Based on these result above, this experiment was done to study the effect of additive H₂-Zeolite to sulfonated polyester-ether ketone. The aim of this experiment is to retain the absorbed water inside the cell, to prevent quick drying performance and to retaining methanol permeability fixed at higher temperature.

Experimental

Materials
Polyester-ether ketone grade 450-I in powder form is obtained from by Vistrex Inc., H-Zeolite purchased from Japan, sulfuric acid from Merck, 95-98 wt. %, n-methyl pyrrolidone from Alrich Chemical Corp.

Sulfonation of polyester-ether ketone
Polyester-ether ketone powder (5 g) were added concentrated sulfuric acid 100 ml under vigorous stirring for 3 h at desired temperature, ranging from 40°C to 70°C. To terminate sulfonation reaction, the polymer solution precipitated into a large excess of ice water. The polymer was washed repeatedly with deionized water until the rinse water is at pH 6-7. The recovered sPEEK were dried at an oven overnight [11].

Preparation of Composite Membranes
The pure sPEEK membrane, composite adding zeolite (sPEEK+z); membrane was prepared by solution casting. The sPEEK polymer was first dissolved in n-methyl pyrrolidone (12.5 wt. %) to prepare a solution and then 3, 5 and 10 wt. %, weight of zeolite was added to the solution. The resulting mixture was stirred for 7 h. Solutions were cast onto glass plates then dried at 60°C for 72 h to remove the solvents. The thickness of resulting membranes was in the range of 50-120 μm.

Characterization of Membranes

• TFM
  The morphology of membranes is analyzed by transmission electron microscopy TEM-1010.

• XRD
  The crystal structure of particles and membranes were investigated using X-ray Diffraction (XRD) Shimadzu XD-610.

• Proton Conductivity
  Ionic conductivity was measured using LCR (Impedance Capacitance Resistance), impedance spectroscopy (SHUOU1565, 1kHz-10 6Hz) with various frequencies from 3 kHz to 1 MHz and 26 mV oscillating voltage. A conductivity cell was made up of two gold foils carrying the current and two gold wires sensing the potential drop, which was apart 1 cm. The fully hydrated sPEEK membrane with deionized water during 24 h was cut in 1 cm wide, 4 cm long prior to measuring on the cell. After mounting sample onto two gold foils on the lower compartment upper compartment was covered, and then the upper and lower compartment were clamped as described by literature [16, 17].

Figure 1. Conductivity cell

The conductivity of each membrane was measured at 25, 50, 90 and 140°C under fully hydrated condition. A conductivity cell was made up of two gold foils carrying the current and two gold wires sensing the potential drop, which was apart 1 cm as shown in Figure 1. The fully hydrated sPEEK membrane with deionized water during 24 h was cut in 1 cm wide, 4 cm long prior to mounting on the cell. After mounting sample onto two gold foils on the lower compartment upper compartment was
covered, and then the upper and lower compartments were clamped as described by authors [18]. The proton conductivity ($\sigma$) of the membrane can be calculated using Eq. (1):

$$\sigma = G \times \frac{L}{w \cdot d}$$  

(1)

where $G$, $L$, $w$, and $d$ are conductance (S), the length between the electrodes (cm), width (cm) and thickness of the membrane (cm), respectively.

Membrane permselectivity was determined using a test cell. The membrane was equilibrated in pure water for 5 hours before clamped vertical at the diffusion cell. Magnetic stirrer were used to maintain the membrane in water uniformly. A solution containing 2 M methanol in water was placed in cell 1 (C1) and water was placed on cell 2 (C2) [13]. The duration of the initial and final solutions were measured by a means of a pycnometer. The duration of measurement was 4 hours. The membrane permselectivity (DK) was calculated as:

$$DK = \frac{C_2(t) \times V_2 \times t_1}{V_1 \times C_1(t - t_0)}$$

(2)

where $C_1$ and $C_2$ are the concentration of methanol in cells 1 and 2, $V_2$ are the volume of well 2, $t_1$ is the surface area and thickness of membrane, and $D$ and $K$ are the methanol diffusion and partition coefficients, respectively. The methanol permselectivity of such membrane was determined at 25, 50, 70, and 100°C.

Water uptake was measured base on water weight absorbing per dry weight membrane. Weighed films were immersed in deionized water at room temperature for 24 h. The membranes were saturated with water until no further weight gain was observed. The water on the surface of immersed membranes was removed using tissue paper before weighing.

Results and discussion

The XRD pattern of membranes has shown in Figure 2. The unmodified membrane sPEEK (Figure 2(a)) shows an amorphous structure, that it is according to Carbonaro's report [18]. In Figure 2(b) shows that the zeolite modified membrane structure, shows amorphous structure, whereas zeolite particles which have crystalline structure (Figure 2(c)) apparently on zeolite modified membrane of sPEEK shows amorphous structure although crystalline peak of zeolite was broadens determined although nearly disappeared at 2θ = 21.6° (Figure 2(c)). That it is naturally as zeolite addition only 5 wt % of sPEEK polymer weight.

The morphological observation of the blank membrane and modified membrane were determined by TEM (magnification x 25,000) as shown in Figure 3. In this figure light regions in hydrophobic domain (backbone polymer matrix) and dark region in hydrophilic domain (silicate acid group and particle). In Figure 3(a), it is indicated that unmodified membrane sPEEK has no pores. The addition of zeolite at membrane Figure 3(b) showed distribution and little separated phase between hydrophobic domain and hydrophilic.
Figure 3. Transmission electron micrographs of:
(a) unmodified PEEK,
(b) zeolite modified membrane of sPEEK.

Figure 4 shows that the proton conductivities of
the fully hydrated membranes sPEEK and
composite membranes (adding zeolite) which
was measured at 25°C in water. The addition zeolite
modified sPEEK membrane increase these
conductivity about 1.5-2.5 times higher than the
blank membrane. The conductivity of sPEEK
membrane with addition zeolite 0, 3, 5 and 10
wt. % results is 0.018, 0.042, 0.035 and 0.028
S/cm, respectively. Increasing proton
conductivity in composite membrane may be
caused by the acidity of the filler.

Figure 4. Influence of zeolite concentration in proton
conductivity.

The pH of slurry zeolite is 5.5. The acidity of
filler will increase absorbing of water in
membrane (water uptake), so that it raise proton
transport (Figure 5). This phenomenon is almost
similar to filler proportion added in Nafion®, that
increasing of proton conductivity in membrane
was influenced by pH of slurry [15]. The
decreasing of proton conductivity in sPEEK+Z
membrane after addition zeolite 3 wt.% caused
by proton conductivity of zeolite in dry state 10^-8
S/cm [15].

Figure 5. Influence of zeolite concentration in water
uptake.

As the resistance of membranes to the
permeation of methanol was measured as
methanol permeability. Figure 6 shows the methanol
permeability of pure sPEEK and composite
membrane at various concentration zeolite at
room temperature. It can be seen that the
methanol permeability of membrane tendency
constant with increment of addition zeolite.

Figure 6. Influence of zeolite concentration in
methanol permeability.

The modification of composite membranes with
additional of hydrophilic H-zeolite are aimed to
improve the overall hydrophilicity of composite
membrane because regions of resistance to
methanol transport may be generated in the
interface between hydrophobic polymer and
additive. Figure 7 is proton conductivity as a function
of temperature at 100% relative humidity (RH) of
unmodified, modified sPEEK and Nafion®-117
membrane. At room temperature, proton
conductivity (C) of modified membrane sPEEK
higher than unmodified sPEEK (0.018 S/cm) but

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still lower than Nafion®-117 membrane. For all membranes, proton conductivities were increased at higher temperature.

![Graph showing influence of temperature on proton conductivity](image)

**Figure 8** Influence of temperature on proton conductivity.

(*) Nafion®-117, (△) sPEEK, and (●) sPEEK+Z.

The addition of zeolite on sPEEK membrane caused the increasing of water uptake at room temperature and high temperature as shown in Table 1. It is indicated that addition of the acidic aluminate of zeolite, the adsorption is caused by water bonding (Demuth et al., 2001).

<table>
<thead>
<tr>
<th>Type</th>
<th>25°C (wt%)</th>
<th>90°C (wt%)</th>
<th>water uptake, 25°C (wt%)</th>
<th>water uptake, 90°C (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>sPEEK</td>
<td>0.018</td>
<td>0.052</td>
<td>1</td>
<td>15</td>
</tr>
<tr>
<td>sPEEK+Z</td>
<td>0.042</td>
<td>0.07</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>Nafion®-117</td>
<td>0.082</td>
<td>0.111</td>
<td>19</td>
<td>20</td>
</tr>
</tbody>
</table>

![Graph showing influence of temperature on methanol permeability](image)

**Figure 9** Influence of temperature on methanol permeability.

(*) Nafion®-117, (△) sPEEK, and (●) sPEEK+Z.

However, the addition of zeolite make the membrane capable to absorb more water as a consequence of higher proton conductivity.

The methanol resistance of membranes at high temperature, is conducted by measuring methanol permeability at temperature 25–140°C. Figure 9 shows the methanol permeability of membranes as a function of temperature. As shown at Figure 9, the slope of Nafion®-117 is larger than sPEEK based membranes. In order to know methanol permeability in the same condition of sPEEK, Nafion®-117 membrane was analyzed at 25°C and 90°C. It showed that Nafion®-117 had reached 3 times and this membrane was broken after applying temperature 140°C. Furthermore, the methanol permeability of unmodified sPEEK membrane was reached 4 times when analyzed from 25°C until 140°C. Whereas the sPEEK+Z membrane was reached about 3 times for the same condition. The addition zeolite in sPEEK will retain increasing methanol permeability at high temperature.

The membranes that have high absorbance of water would facilitate proton transport, thus proton conductivity could reach up. According to Nafion®-117 showed proton conductivity higher than unmodified and modified sPEEK membrane, in the range of temperature up to 90°C and could not determine a more than 90°C. On the other hand unmodified and modified sPEEK membranes were more stable at high temperature, up to 140°C. Proton conductivity in sPEEK and sPEEK+Z increases with temperature mainly due to higher proton mobility and bigger quantity of adsorbed water.
accompanied by proportionate improvement of the fuel cell efficiency and its power density.

![Graph](image)

**Figure 10** Selectivity of membranes as a function of temperature

**Conclusions**

Proton conductivity and methanol permeability was investigated at 25, 50, 90, and 140 °C. The morphology of cross-section and crystal structure membranes was studied by TEM and XRD analysis. The H-zeolite modified membrane showed high proton conductivity about 2 times of blank membrane. It caused by the acidity of inorganic filler. The proton conductivity of modified membranes can reach above 0.07 S/cm above 140°C at RH 100%. At high temperature of aPEEK and modified aPEEK membranes retaining better performance of methanol permeability, proton conductivity and selectivity value to Nafion®. Thus electrolyte membrane based aPEEK with addition zeolite 3 wt.% can be used to apply at high temperature (>100°C) direct ethanol fuel cell with better electrical performance than with Nafion® membranes, respectively.

**References**


