Performance of polymer electrolyte membrane for polymer electrolyte fuel cell membrane made with supramolecular structure

S Hendrana1,*, N Indayaningsih1 and Sudirman2

1Research Centre for Physics-Indonesian Institute of Sciences, Kawasan Puspiptek, Gedung 440-442, Tangerang Selatan, Banten - 15314, Indonesia
2Centre for Science and Technology of Advanced Materials- National Nuclear Energy Agency, Kawasan Puspiptek, Gedung 440-442, Tangerang Selatan, Banten - 15314, Indonesia

*E-mail: sunit.hendrana@lipi.go.id

Abstract. Most of membranes for Polymer Electrolyte Membrane Fuel Cell (PEMFC) are made by clustering sulfonate groups which part of hydrophobic portion. The portion then acts as proton conduction path by assistance of water absorbed in the membrane. In this work, the membrane is prepared based on constructing supramolecular structure by aligning sulfonate groups in sulfonated polystyrene (SPS) through formation of hydrogen bond of anhydride pendant group of polyethylene-graft-maleic anhydride (PE-g-MA). The performance was evaluated with many factors, i.e. addition of addition of benzimidazole, and effect of morphology. The addition of benzimidazole have tendency to modify hydrogen interaction within the membrane. In addition, water, which facilitates proton conduction, would also give a small microstructural change in membrane. However, the membrane could maintain its performance which is indicated by its ionic conductivity.

1. Introduction

An increasing demand to clean and non-pollutant energy resources lead to application of fuel cell as a new type of energy provider [1, 2]. Amongst types of fuel cell, polymer electrolyte membrane fuel cell (PEMFC) is the most widely demonstrated [3, 4]. In this membrane with good proton conductivity, also called proton exchange membrane, is used to facilitate the movement of proton, produced in anode, from anode to cathode. The membrane consists of sulfonate groups that can bind water to which proton is carried.

Most of the membranes are available for such purposes based on perfluorocarbon polymer [5, 6]. In this type of membrane, sulfonate groups in the membrane are forming clusters [7]. The clusters are swollen and connected on humidification, which enabling the membrane to conduct proton. However, while it is enjoying the performance of the membrane, there are still some drawbacks such as on its price and its application at medium temperature. Accordingly, efforts have been made to overcome the latter limitation by preparing sulfonated hydrocarbon membrane [8], including sulfonated polystyrene-based membranes [9, 10].

It is predicted that, in the sulfonated polystyrene-based membrane, there are difficulties for sulfonate groups to form clusters such as in Nafion®, due to steric hindrance of benzenic pendant
groups in sulfonated polystyrene. Thus, in our work, instead of preparing sulfonate groups forming clusters, the sulfonate groups in one single molecule of SPS is aligned by making hydrogen bond with anhydride group of polyethylene-graft-maleic anhydride (PE-g-MA). One single molecule SPS will interact with more than one PE-g-MA to form expected sulfonate group alignment. That is what it called supramolecular structure.

Accordingly, it is necessary to understand the characteristics of membrane prepared with the polymers. In this work, small molecule, i.e. benzimidazole, is added to observe the effect into its supramolecular structure. Moreover, the effect of addition of water, which is usually occurred during primary preparation prior to utilization into morphology, will also be analyzed.

In other words, this work is designed to evaluated performance of membrane prepared with supramolecular structure based on sulfonated polystyrene under different circumstances, i.e. whether there are some morphology changes on water and proton absorption and this effect to its ionic conductivity.

2. Experimental Methods
The experiment will involve evaluation of membrane and fuel cell stack prepared with our membrane. The detail of the experiments is as follow.

2.1. Chemical
Toluene, methanol, benzimidazole and sulfuric acid are supplied from E. Merck. All chemical used in this experiments are p.a. grade and no specific treatment prior to use.

2.2. Membrane Preparation
SPS is dissolve in toluene/methanol = 9:1 and PE-g-MA is dissolved in toluene. Both dissolutions are carried out at 40 °C. The solution is mixed gently by adding PE-g-MA solution to SPS solution drop-wisely at the temperature of dissolution. The resulted solution is casted into Teflon cloth sheet at 40 °C to remove the solvents.

2.2.1. Addition of benzimidazole. In the experiment involving benzimidazole, the chemicals were added to the solution of PE-g-MA and SPS prior to casting.

2.3. Instrumentation measurement
In this work the following measurements are involved.

2.3.1. Fourier transforms infrared. The Fourier Transform Infrared measurement was scanned from wavelength of 400 to 5000 cm⁻¹ at resolution of 2 cm⁻¹.

2.3.2. X-ray diffraction. The X-ray diffraction of the sample taken from 2θ = 10° to 80° at a scan rate 0.02° per second.

3. Results and Discussion
The concept of preparation of membrane for PEMFC with supramolecular structure have been introduced somewhere [11]. The formation of the supramolecular-structured membrane also has been proved. Therefore, it is important to understand the performance under different circumstances. In this work the variations not only from fuel cell stacking and operation point of view, but also from the membrane preparation point of view.

3.1. Role of addition of benzimidazole
In this works, benzimidazole is added to the formula of membrane preparation. Benzimidazole has a positive effect to oxidative stability [12]. The objective of the addition is to support of ion conduction while the membrane is poorly wetted. It is known that the dimension stability of the membrane is not good in higher water absorption. Therefore, in application, our membrane is much better used under lower water absorption which in many cases is an advantage especially in water management of fuel cell itself.

Figure 1 shows FTIR spectra of membrane with various concentration of benzimidazole, i.e 0.1% and 0.2%. There seem small hydrogen bond absorption at around 3500 cm⁻¹, but it seems that the hydrogen bond broadening and flattening. It could occur for solid samples [13]. This also indicates the
quite complex interaction in hydrogen bond which is a key in this membrane. More addition of benzimidazole results in more broadening hydrogen bonding absorption.

In addition, from the above spectra in figure 1, it is clearly shown that the hydrogen bonding absorption of sample (a) is thinner and concave in shape, while the hydrogen bonding absorption of sample (b) is wider and convex in shape. The latter indicating the prominently interhydrogen bonding. This figure, therefore, showing that the addition of benzimidazole could promote change in microstructure of the membrane, especially in the hydrogen bonding interaction.

3.2. Water content, morphology and ionic conductivity
In this works we also investigate the effect of water addition to the supramolecular-structured membrane. This work is carried out by addition of sulfuric acid solution. In this case, the membrane is wetted and added with hydronium ion (H\textsuperscript{+}).

The result can be shown in figure 2 which shown the differences of X-ray diffraction pattern of membrane before and after immersion in sulfuric acid solutions. The addition of sulfuric acid solution was either for adding proton ion in the membranes, and for wetting the membrane itself.
Table 1. Variation of ionic conductivity of membrane after addition of sulfuric acid solution in various concentrations.

| Membrane code | Sulfuric acid immersion (Molar) | Ionic conductivity $\times 10^{-2}$ (S·cm$^{-1}$) | Mass of sulfuric acid absorption (gr) | No. of proton in membrane $\times 10^{20}$ |
|---------------|---------------------------------|-----------------------------------------------|-------------------------------------|------------------------------------------|
| A             | 0                               | 0.02                                          | 0                                   | 0                                        |
| B             | 0.01                            | 1.34                                          | 0.07                                | 0.087                                    |
| C             | 0.1                             | 1.12                                          | 0.08                                | 0.099                                    |
| D             | 0.5                             | 1.12                                          | 0.06                                | 0.331                                    |

Diffraction of $2\theta$ at 20° is not change for both membranes. However, the dry membrane shows a sharp diffraction peak at $2\theta$ at 41° (figure 2 (a)). The peak disappear cannot be observed for wetted sample (figure 1 (b)). But, new crystalline peaks area was observed at $2\theta$ of 38° and 45.5°. The figure clearly shows that the morphology of the membrane changes in the addition of 0.5 M sulfuric acid. Therefore, this XRD data are evidence the change of morphology of membrane during the addition of water and/or ion. Even though, the changes only occur in small portion of the membrane microstructure.

Table 1 shows variation of ionic conductivity over water and proton content. The dry membrane has very low ionic conduction due to unavailability of proton in the membrane. Proton available in membrane will facilitate conduction of proton produced in anode either by Grotthus mechanism or by vehicle mechanism. The calculated proton added to the membrane is shown in Table 1 above. The immersion of membrane to sulfuric acid will alter entering proton of sulfuric acid solution to the membrane. The Table shows that small addition of proton (see sample B) will strongly affect to the proton conductivity. However, higher proton addition to the membrane C and membrane D) have no significance effect to ionic conduction. In fact, that small addition of water (see membrane A and membrane B) will strongly enhance ionic conductivity. This means that water assist proton conduction [7] as occur in Nafion®.

4. Conclusions
The work have shown clearly that performance PEMFC prepared by supramolecular is prone to small change in morphology and microstructure over addition of small molecules, such as benzimidazole, on preparation of membrane and water over operation of membrane. However, the membranes still can maintain its ionic conductivity performance.

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