Structural and morphological changes in supramolecular-structured polymer electrolyte membrane fuel cell on addition of phosphoric acid

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Abstract. Phosphoric acid is one agent used in membrane fuel cell to modify expected ionic conductivity. Therefore, its distribution in membrane is a key parameter to gain expected conductivity. Efforts have been made to distribute phosphoric acid in a supramolecular-structured membrane prepared with a matrix. To achieve even distribution across bulk of the membrane, the inclusion of the polyacid is carried out under pressurized chamber. Image of scanning electron microscopy (SEM) shows better phosphoric acid distribution for one prepared in pressurized state. It also leads to better performing in ionic conductivity. Moreover, data from differential scanning calorimetry (DSC) indicate that the addition of phosphoric acid is prominent in the change of membrane structure, while morphological changes are captured in SEM images.

1. Introduction
Polymer membrane is an essential part in Polymer Electrolyte Membrane Fuel Cell (PEMFC). The membrane only permits ions and exhibit electrone. Therefore, the higher ionic conductivity of the membrane would end in higher performance of fuel cell. Efforts have been made to improve ionic conductivity of the membrane including inclusion of small molecules including polyacids \cite{1} and phosphoric acid \cite{2}. The latter is chosen from its ability on self-dissociation that produces proton ion. The produced proton ion can assist proton conduction in the membrane. From this respect it is expected that the membrane prepared with inclusion of phosphoric acid will have characteristic of high conductivity in higher temperature and lower humidity \cite{2}.

However, it is well known that in PEMFC, sulfonate groups in the membrane are clustered \cite{3} in order to be able to facilitate ion movement from anode to cathode. The inclusion of small molecules in such clustered-structure could change the structure itself.

Membrane developed in LIPI is not constructed in such cluster-structured but rather aligned to form a rod-structured in order to arranged of sulfonate groups in sulfonated polystyrene. Sulfonate groups in sulfonated polystyrene are difficult to form cluster-like structure because the sulfonate groups are attached in benzene pendant group in polystyrene. A rod-like structure is likely to be one possibility and is constructed from hydrogen bond between succinic/anhydride group of polyethylene-graft-maleic anhydride (PE-g-MA) and sulfonate groups in sulfonated polystyrene. The stucture form thereafter called as supramolecular structure. SANS (Small Angle Neutron Scattering) analysis has been performed for the evident of the supramolecular structure \cite{4}.
As also occurs in cluster-like structured polymer electrolyte membrane fuel cell, the addition of phosphoric acid in the supramolecular-structured polymer electrolyte membrane fuel cell could also promote changes in structural arrangement and morphology. Therefore, this work will emphasize on the above mentioned problems. The inclusion of phosphoric acid will depend on the preparation method, in order to study the effect of the inclusion of phosphoric acid to the structural and morphological changes, the acid is added with and without pressure to the base of the membrane.

2. Experimental

2.1. Chemicals
Toluene and phosphoric acid are p.a. grade and they were supplied from E-Meck. The chemicals were used without any purification. Water used was demineralized water. Polyethylene-graft-maleic anhydride or PE-g-MA was from Aldrich (lot# MKBG0507V). Sulfonated polystyrene (SPS) was prepared by using method developed in our laboratorium.

2.2. Preparation of membrane
Solution of sulfonated polystyrene in toluene:methanol (9:1, v/v) and solution of PE-g-MA and benizimidazol in toluene were prepared separately before mixing at 40 °C. The solution thereafter called as supramolecular solution. Template for membrane was prepared by mixing SPS powder and PE-g-MA powder at 1:1 (w/w). Further, the mixed powder was hot-pressed at 105 °C at 10 kgf.cm\(^{-2}\) for 20 seconds. Phosphoric acid is added in two ways, i.e., for pressurized membrane samples, the template immersed in phosphoric acid in a closed vessel and heated at 50 °C for one hour, while non-pressurized membrane samples, the immersion is in open space and no heat is applied.

| Code | SPS | PE-g-MAH | H\(_3\)PO\(_4\) | Supramolecular Solution\(^\dagger\) |
|------|-----|---------|--------------|-------------------------------|
| (a)  | V   | V       | V            | -                             |
| (b)  | V   | V       | V            | -                             |
| (c)  | V   | V       | V            | -                             |
| (d)  | V   | V       | V            | V                             |
| (e)  | V   | V       | V            | V                             |
| (f)  | V   | V       | V            | V                             |

\(^\dagger\)Supramolecular solution is prepared by method described above and have to be in very dilute solution.

The supramolecular solution was added dropwise into the template according to the variation listed in table 1. The resulted products were hot-rolled at 150 °C using laminating machine prior to hot-pressed at 150 °C, 50 kgf cm\(^{-2}\) for 10 seconds, and immediately followed by compression at 150 °C, 100 kgf cm\(^{-2}\) for 20 seconds.

2.3. Scanning electron microscope
Samples were immersed in liquid nitrogen for couple minutes and suddenly broken into two parts. The cross-section area were gold-coated for SEM observation.

2.4. Fourier Transform Infra Red (FT-IR)
FTIR data were obtained using FTIR 4300 of Shimadzu. Samples were scanned at wavenumber of 400 to 5000 cm\(^{-1}\) at resolution of 2 cm\(^{-1}\). The data were collected after 25 scans for each samples.

2.5. Differential Scanning Calorimetry (DSC)
The samples were contained in closed chamber and applied into heat scan from 40 °C to 300 °C at 10 °C per minutes under nitrogen atmosphere. The presentations are taken from the second-run or second-heating of each sample.

3. Result and discussion
Figure 1 shows the thermal scan of differential scanning calorimetry of the membranes. It shows melting temperature which related to their crystalline region.

**Figure 1.** Differential scanning calorimetry (DSC) scan of membrane prepared with phosphoric acid, prepared with and without pressure: (a) comparison of melting profile of membranes with supramolecular structure at variation of preparation methods; (b) comparison of melting profile of membranes to observe the effect of pressure application in membrane preparation

Figure 1 shows that each treatment produces different melting temperature profile, indicating different crystallite structure. PE-g-MA shows two melting temperature peaks and the lower melting temperature peak is higher (or dominant) than the higher melting temperature peak. Each melting temperature peak represents a different crystallite size or domain of the sample [5].

An addition of phosphoric acid (sample dHdS) leads to profile changes where two peaks have similar high. When an addition of phosphoric acid is added in pressurized condition (sample dPdS) the higher melting peaks is dominant. As the peak is related to the crystallite structure [6], therefore the DSC scans in figure 1 above indicate changes of crystalline structure within membranes, e.g. the sample has more part which has a crystalline domain that melts at slightly higher temperature indicated by the melting peak temperature.

Table 2 shows melting points of the membrane. The onset temperature of all membranes are only have small differences or within experimental error as well as the first melting temperature peaks and the first melting temperature peaks.

Eventhough the peak temperatures are not significantly differ, the DSC scans shown in figure 1 exhibit an importance of phosphoric acid addition and method of the addition to the changes discussed above. The melting profile of membrane without addition of phosphoric acid (tHdS membrane, figure 1) is similar to melting profile of PE-g-MA. Addition of phosphoric acid changes the melting profile (dHdS membrane in figure 1a ), where the two melting peaks have similar height. The application of pressure during addition of phosphoric acid produces membrane with higher portion of higher melting peak temperature (dPdS membrane in figure 1a). This is the evidence that method of preparation of membranes could affect the structure of the membrane produced.


| Table 2. Melting point of the membranes. |
|------------------------------------------|-------------|-------------|-------------|
| Membrane | Melting Points (°C) | (a) | (b) | (c) | (d) |
| PE-g-MA | 85.2 | 96.6 | 102.4 |
| dHdS | 83.5 | 94.9 | 99.3 |
| dPdS | 83.5 | 94.0 | 99.8 |
| dHtS | 83.5 | 95.1 | 101.1 |
| dPtS | 83.2 | 95.9 | 101.7 |
| tHdS | 84.0 | 95.9 | 100.6 |

Moreover, membrane prepared without supramolecular solution (dPtS membrane in figure 1b) shows that the second melting peak temperature is much higher than membrane prepared with supramolecular solution and with pressure (dPdS membrane in figure 1a). This indicates that the phosphoric acid have more prominent effect in their crystalline-structural change.

To achieve goals of this works, morphology of the membranes were investigated using scanning electron microscope (SEM) as shown in figure 2 below.

![Figure 2](image)

**Figure 2.** SEM images of PEMFC membrane prepared in this work. Each sample is distinguished by sample code written below each picture.

Figure 2 shows the various morphologies with type of membrane preparation, especially on inclusion of phosphoric acid. According to the previous investigation a small dot represent a part of phosphoric acid [7]. Membrane prepared with pressurized (dPdS membrane) shows no small dots indicating even distribution of phosphoric acid. Meanwhile, membrane prepared without pressure (dHdS) shows some small dots indicating uneven distribution of phosphoric acid.

Moreover, membranes prepared without supramolecular structure (dHtS and dPtS membranes) always showing cracks. The cracks are not observed in dHdS membrane. The data imply the importance of supramolecular solution in the rigidity or robustness of the membrane. Those facts are evidence that application of pressure in the preparation of the membranes could affect into
morphological changes. In addition, the role of supramolecular structure can be seen by investigation of Fourier Transform Infra Red (FTIR) spectra, as shown in figure 3 below. Both membranes in the figure contain phosphoric acid but have no addition of supramolecular structure.

The figure shows that with addition of supramolecular structure (dHdS membrane) promotes intermolecular hydrogen bonding which can be seen in broader hydrogen bond absorption in wavenumber 3300 cm\(^{-1}\). Broader absorption can be seen by the shape of the spectra [8], e.g. shown as convex shape for dHdS membrane or concave shape for dHtS membrane (see the arrows in the figure). Therefore, the FTIR data emphasize the presence of supramolecular structured membrane introduced in this paper.

The supramolecular structure is built from hydrogen bonding between anhydride or succinic group with sulfonate group along every polymer molecule of PE-g-MA and SPS, respectively. One polymer molecule of SPS may build hydrogen bonding with more than one PE-g-MA molecules, and vice versa. As the interaction occurs in the very dilute solution, it can be understood that the the bonding could also occurs in the crystalline part of PE-g-MA, when it is in solid form. Consequently, when the solution is removed during the process of membrane preparation, the crystalline portions are affected.

4. Conclusion
The work has shown clearly that supramolecular structure contribute to the robustness of the membrane. Moreover the inclusion of phosphoric acid would lead to the change of its structure, especially in crystallite region. The important features of this work is that application of pressure in the sample preparation would lead to improved phosphoric acid distribution in the bulk of membrane, and the the addition of phosphoric acid would provide more prominent effect in their crystalline-structural changes.

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