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FUEL CELL MEMBRANE WITH SUPRAMOLECULAR STRUCTURE : A BRIEF INTRODUCTION AND REVIEW

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ABSTRAK

Gugus sulfonat dalam membran komersial terstruktur dalam kluster yang akan mengembang dan menyambung antar kluster pada saat terjadi hidrasi pada membran. Membran dengan konsep baru telah dikembangkan di Pusat Penelitian Fisika Lembaga Ilmu Pengetahuan Indonesia (LIPI) yaitu melalui penerapan ikatan supramolekular. Pendekatan ini akan mengakibatkan fenomena konduktifitas yang berbeda dengan membran komersial. Paper ini akan membahas aspek-aspek tersebut dan prospek aplikasinya.
Kata kunci: *sulfonat, membran, ikatan supramolekular*

ABSTRACT

Sulfonate group in the commercial membranes are structured in clusters that will expand on hydration of membrane and lead to connection of one cluster to its neighbours. Membranes with a new concept has been developed in the Research Center for Physics of Lembaga Ilmu Pengetahuan Indonesia (LIPI), namely, by building supramolecular structure between two polymers constituent. This approach will result in a difference conductivity phenomenon compare to commercial one. This paper will discuss those aspects and featuring its application.

INTRODUCTION

There are an increasing demand on renewable energy and new energy system [1] as environment and climate change mitigation are concerned [2]. Polymer Electrolyte Fuel Cell (PEMFC), one type of fuell cell, is desired choice as it has very high energy density and produces only water as side product.

Principally, PEMFC convert electrochemical reaction into energy by separating ion and electron in the opposite pathways. The separation is controlled by membrane which passes ion but not electron which are produced in anode. The electron will then transport to cathode through the circuit and is what it called electricity.

In order to fulfil the function, a commercially available membran, i.e. Nafion®, is designed to have a sulfonate clusters to facilitate ion conduction in humid condition. The pictoral cluster-network in the membrane can be seen in figure 1 [3]. On hydration the cluster will expands and connect one to each other [4].

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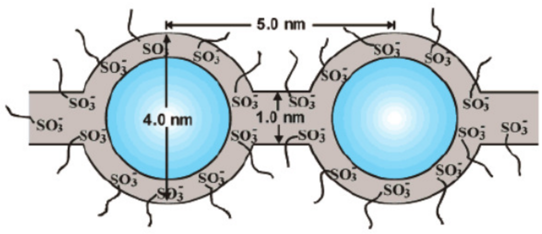
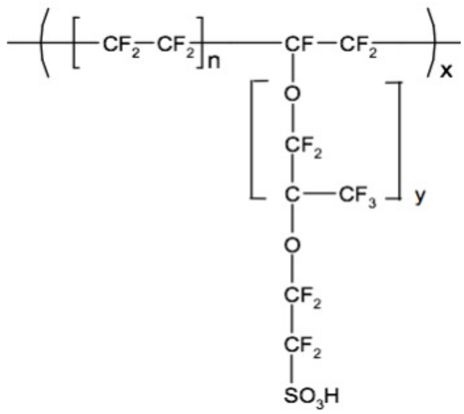


Figure 1. Sulfonate cluster in Nafion (R)[1].

The cluster can be formed because polymer structure of Nafion® has long pendant group, see figure 2 (*a*), where each sulfonate group is attached. The sulfonate is hydrophilic and the polymer backbone is hydrophobic creating an absorption of water in micro/nano level. The length of the pendant group will also assist the cluster to do swelling on hydration. The swelling behaviour occurs from the nature of long pendant group which has a degree of movement of its constituent atoms. The water molecules are key feature in order to be able to conduct ion which is produced during oxidation of hydrogen in anode. Therefore the chemical nature of pendant group affect a lot on the hydration behaviour of membran, an then consequently, on their ionic conductivity.



(*a*) (*b*)

Figure 2. Chemical structure of (*a*) Nafion® and (*b*) sulfonated polystyrene

In this work sulfonated polystyrene (s-PS) is used as main polymer for preparation of membrane for PEMFC application. The polymer only has very short pendant group. Consequently, the location of sulfonate group highly depend on backbone arrangement of s-PS molecule and it will result in difficulties to construct sulfonate clusters as takes place in Nafion®.

The Origin of Concept

On the examination of properties of membranes prepared, it is found that there is no linear correlation on higher sulfonated concentration to ionic conductivity [5], see figure 3. It is expected that increase of sulfonate concentration in polymer will increase ionic conductivity. However, figure 3 tells different stories, the increase of sulfonate group concentration does not push its ionic conductivity, even at very high concentrations of sulfonate groups and within wide range concentration, i.e. 10 % to 50 %.

Based on this finding, it is hypothesised that membran morphology play significant roles in its ionic conduction. There may be a lot sulfonate group in the polymer bulk, but the distances between neighbouring sulfonates group, might be too far for ion to move to or to push neighbouring ions.

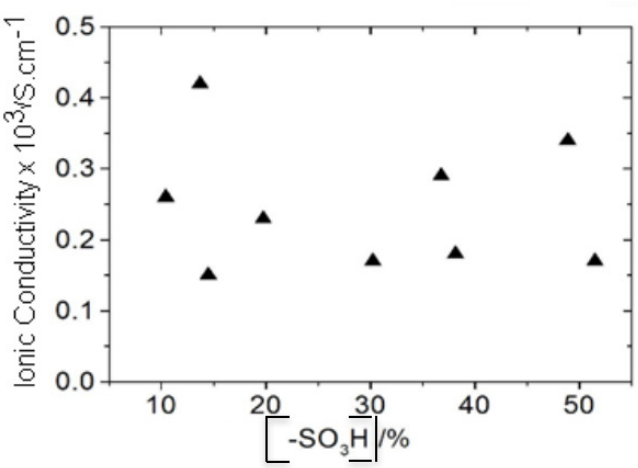


Figure 3. Variation of ionic conductivity to concentration of sulfonate group in s-PS based membrane [5].

In order to limit the effect morphology, sulfonate group need to be aligned. The aligned sulfonate groups would ease ion to conduct through. One possibility is constructing a hydrogen bond along, every single, s-PS polymer molecule. The pictorial description of this concept can be seen in Figure 4.

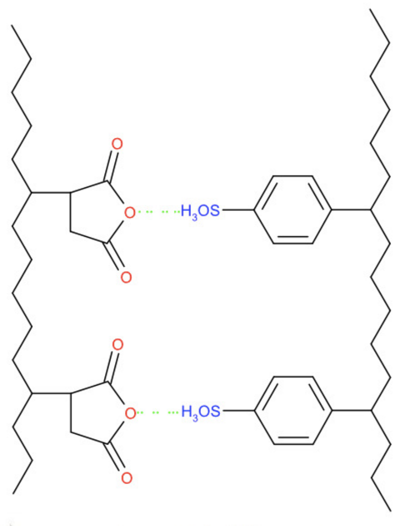


Figure 4. Pictorial description of supramolecular structured membran comprises sulfonated polystyrene and polyethylene-*graft*-maleic anhydride (PE-*g*-MAH). Hydrogen bonding mentioned in this discussion is represented by dash lines (- - - -).

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It is expected that sulfonated polystyrene molecules will be aligned by hydrogen bond between sulfonate group of s-PS and anhydride group in PE-*g*-MAH. One s-PS molecule would be aligned by more than two PE-*g*-MAH molecules. Therefore, the challenge is preparing a solution which has a non-entangled molecules prior to membrane preparation. In other word, polymer molecules, both for s-PS and PE-g-MAH, have to be in a free single form, not entangled with neighbouring molecules. During mixing of those two polymers' constituent solutions, the hydrogen bond, as decribed in Figure 4, is expected to occur. The more detail of this challenge can be seen in the experiment section.

Therefore, to make the supramolecular structure membrane having preferred properties need high precision of polymer structure such as grafting frequency for both polymers constituent. The preparation of precised structure of s-PS and PE-g-MAH is described elsewhere [6-8].

EXPERIMENT

It is mentioned earlier that the presence of single molecules is key concern in preparation of supramolecular structure in this fuel cell membrane. To fulfil of this requirement both polymers, i.e. s-PS and PE-g-MAH, are diluted in very dilute solution, the same procedure for preparation of solution for measurement of Gel Permeation Chromatography (GPC). The concentration of solution is very dilute, it can be range from 0,1 to 0,01 %. Further detail of this procedure can be seen in a patent document [9].

DISCUSSION

Figure 5 (*a*) show the results of Small Angle Neutrons Scattering (SANS) measurements. The results shows that the supramolecules has occurs and the shape of sulfonate clusters are spheroidal with the size of 28 Å [10].

TEM (Transmission Electrons Microscope) image, Figure 5 (*b*), indicates that sulfonate groups are homogeneously distributed. Therefore, the illustration of sulfonate group arrangement in membrane prepared with supramolecular-structured approach can be seen in Figure 6 below. In this feature, the hydrogen bond which form supramolecular structure are in random position (TEM data in Figure 5 (*b*)) and not in a parallel position.

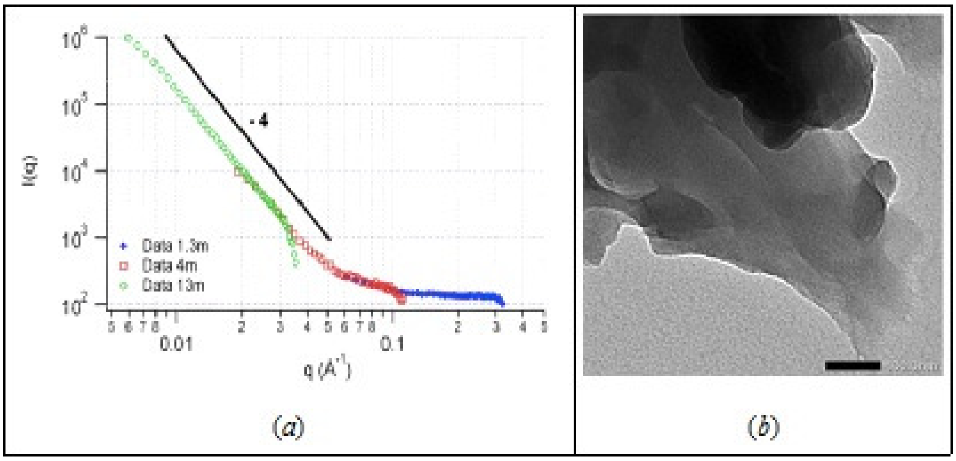


Figure 5. The evidence of supramolecular structure (*a*) SANS measurement at different detector distances and (*b*) TEM images.

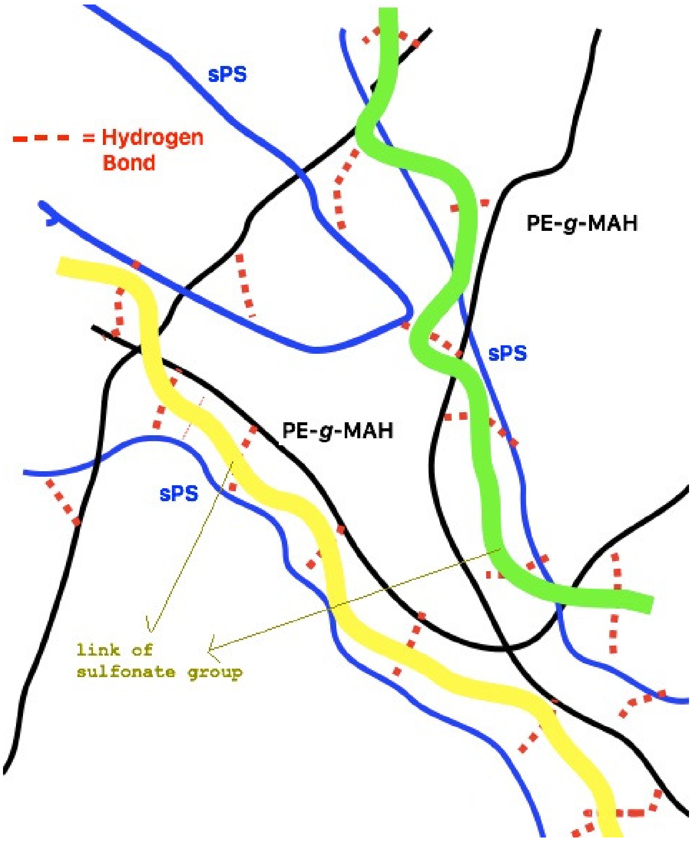
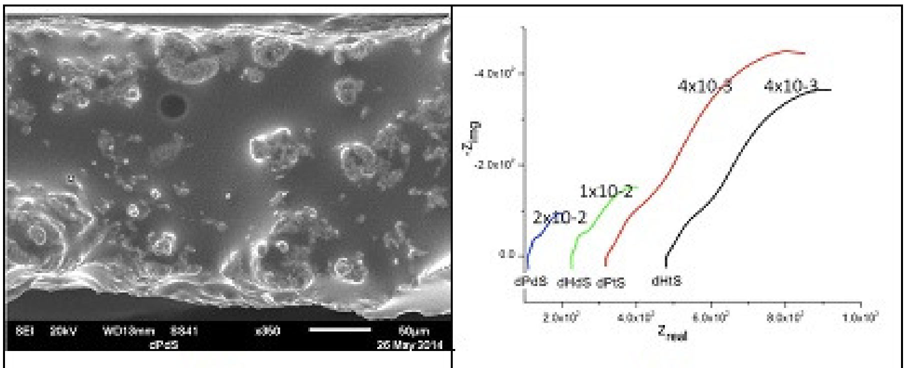


Figure 6. An Illustration of sulfonate group arrangement in membrane prepared with supramolecular-structured approach.

A trial for improvement of have been done by adding a polyacid into a membrane. The addition is carried out in many variations. The results can be seen in Figure 7.



(*a*) (*b*)

Figure 7. Addition of phosphoric acid (PA) to membrane, (*a*) SEM image and (*b*) ionic conduction behaviour at various conditions of PA.

The impendance spectroscopy measurements (Figure 7 (*b*)) shows that ionic conductivity can be adjusted by simply add PA and do some different preparation protocols. While SEM image of the membrane implies that there are need some improvement on homogeneity on distribution of PA within a membran. Other report says that, in the addition of small molecules such as phosphoric acid, morphology of membrane will affect end-value of its ionic conductivity [11].

CONCLUSION

It is described that the concept of supramolecular can be performed and show good ionic conductivity. The data also indicate the addition with small molecule such as phosphoric acid is can be done nicely in improving or modifying ionic conductivity.

However, there are still same challenge such as the ratio of polymer and solvent for preparation membrane is 1 to 10.000 at-most. This will create difficulties in reproducibility and on its continuous production. The SEM data also indicate that there need some improvement on distribution of small molecules added into the membrane. The other challenge is to clarify whether the ionic conductivity behaviours are differ or not from the commercial one, especially in low humidity.

Though there are still many issues to be discussed but this approach give a new route for preparation of membrane for PEMFC.

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