

MORPHOLOGY EFFECT ON BEHAVIOUR OF PHOSPHORIC ACID IN SUPRAMOLECULAR-STRUCTURED POLYMER MEMBRANE FUEL CELL

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ABSTRACT

MORPHOLOGY EFFECT ON BEHAVIOUR OF PHOSPHORIC ACID IN SUPRAMOLECULAR-STRUCTURED POLYMER MEMBRANE FUEL CELL. Study on the effect of morphology on the conductivity of small molecules added polymer membrane for fuel cell has been done. The polymer electrolyte membrane fuel cell was made by constructing of supramolecular interaction between sulfonated polystyrene and polyethylene-graft-maleic anhydride. The small molecules used was benzimidazole and phosphoric acid. The addition of benzimidazole and phosphoric acid, was expected to improve to ionic conductivity. However, in this work it was observed that morphology of the membrane play vital roles in the final properties of the membrane. In other words, beside concentration of phosphoric acid the morphology affects the conductivity of polymer membrane fuel cell.

Keywords: Supramolecular, Fuel cell membrane, Sulfonated polystyrene, Polyethylene-graft-maleic anhydride, Morphology, Phosphoric acid

ABSTRAK

EFEK MORFOLOGI PADA PERILAKU ASAM FOSFAT DALAM POLIMER BERSTRUKTUR SUPRAMOLEKULER. Telah dipelajari efek morfologi terhadap konduktivitas polimer membran untuk *fuel cell* yang ditambah molekul kecil. Membran elektrolit polimer untuk *fuel cell* tersebut dibuat dengan membangun ikatan supramolekular antara polistiren tersulfonasi dan polietilena-graft-anhidrida maleat. Molekul kecil yang digunakan adalah benzimidazol dan asam fosfat. Penambahan benzimidazol dan asam fosfat, diharapkan dapat meningkatkan konduktivitas ionik. Tetapi, dalam penelitian ini ditemukan bahwa morfologi membran memiliki peranan yang dominan dalam menentukan sifat akhir membran yang dibuat. Dengan kata lain, disamping konsentrasi asam fosfat, konduktivitas membran polimer untuk *fuel cell* dipengaruhi oleh morfologinya.

Kata kunci: Supramolekular, Membran *fuel cell*, Polistiren tersulfonasi, Polietilen-graft-anhidrida maleat, Morfologi, Asam fosfat

INTRODUCTION

Fuel cell is one of the key technology for the future to reduce air pollution [1]. For example, the fuel efficiency of fuel cell applied in vehicle can reach 70% while hybrid vehicle can only reach maximum 40% fuel-to-wheel conversion efficiency [2]. Polymer Electrolyte Fuel Cell (PEFC) is the most favorable type of fuel cell. PEFC can provide power from Miliwatt to Megawatt leading its application widely ranging from small devices into power plan.

Membrane is important and crucial part in constructing fuel cell stack. Membrane will conduct ion but not electron. Commercially available membrane is Nafion[®]. However, Nafion[®] is too expensive, it is easily damaged, and loss its proton conductivity at operation above 80 °C [2]. Therefore, many works and methods have been done to break the limit. The methods include [3]: (i) modification with inorganic acid, (ii) modification with conductive polymers, (iii) modification with proton conductive filler, and (iv) modification with

acid-base complexes. Adding heteropolyacid can maintain proton conductivity at high temperature and low humidity when the sulfonate groups loss this capacity due to lack of loss of water when operate at high temperature ($> 80\text{ }^{\circ}\text{C}$) [4]. The effort on application of nanocomposite also have been done [5, 6].

Inorganic particle improve conductivity of its polymer host without destroying polymer flexibility [7]. Polymer flexibility is very important parameter because polymer segmental movement affect the conductivity of proton within polymer [8].

Phosphoric acid also could be used as agent for proton-conducting liquid electrolyte [9] and can be used for high temperature PEFC [10]. In addition, embedded phosphoric acid improves the ionic conductivity from its original [11]. Having H_3PO_4 in polymer membrane could improve thermal and chemical stability, improve ionic conductivity at high temperature, performance at high temperature and mechanical properties [3]. Therefore, many work have been carried out on embedding or doping phosphoric acid into membrane for modifying proton conductivity [11-18]. There are also many other approaches to modify ion conductivity of fuel cell membrane [3, 5, 9-10, 19-23]. Some molecules, such as imidazole have also been used for such purpose [24, 25].

In this work, phosphoric acid was added to polymer membrane which has supramolecular structure [26] at the presence of imidazole. Imidazole has some possibilities to improve conductivity of the membrane [15], but it will also possible to disturb the supramolecular structure of the membrane itself. On the other hand, the presence of both phosphoric acid and imidazole could improve ionic conductivity. Both small molecules can form proton conduction path as describe in Figure 1 [17]. Moreover, salt formation between imidazole and phosphoric acid [15] (Figure 2) could improve ionic conductivity as well. Meanwhile, the imidazole can also take part on the self ionization of phosphoric acid and assist proton conduction of the

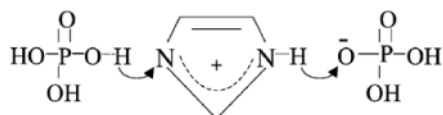


Figure 1. Possible path of proton conduction between imidazole and phosphoric acid proposed by Schechter [17]

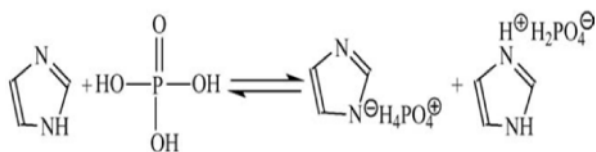


Figure 2. Proposed interaction and formation of salt between imidazole and phosphoric acid mentioned by Pu and Wang [15]

entire membrane [15]. However, distribution and interaction of both small molecules would affect the final ionic conductivity properties of the membrane. Therefore, ionic conductivity behavior of the membranes was studied based on their morphological observation.

EXPERIMENTAL METHOD

Materials and Chemicals

Methanol, toluene, chloroform used in this experiment were pro analysis from E-Merck and were used directly without pre-treatment prior to used. Sulfonated polystyrene (sPS) was prepared with method developed in our laboratorium [27]. Polyethylene-graft-maleic anhydride (PE-g-MAH) were prepared from microencapsulated polyethylene [28].

Membrane Preparation

Sulfonated polystyrene was dissolved in toluene at $40\text{ }^{\circ}\text{C}$ with gently stirring to prevent polymer molecules entanglement. PE-g-MAH was dissolved in toluene at $90\text{ }^{\circ}\text{C}$ with gently stirring. sPS solution was added dropwise into PE-g-MAH solution with gentle stirring. Benzimidazole was added to the solution drop by drop followed by addition of phosphoric acid. The solution produced was ready for casting to make a membrane. The membrane was prepared by casting the solution in the glossy plate at $80\text{ }^{\circ}\text{C}$ (unless noted).

Characterization

Fourier Transform Infrared (FT-IR) measurements were carried out using FT-IR spectrophotometer 4300 of Shimadzu and scanned from 5000 to 400 cm^{-1} at resolution of 2 cm^{-1} .

Thermal data were obtained using Differential Scanning Calorimetry (DSC) Perkin Elmer Type DSC 8000. The samples were scanned from room temperature to $250\text{ }^{\circ}\text{C}$ at the rate of $10\text{ }^{\circ}\text{C}/\text{minutes}$. The data presented in this paper are generate from the second run of each sample.

Morphology of the membranes were discussed based on Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM) images. The SEM images were obtained from SEM of JEOL type T30A and the TEM images were obtained from TEM of JEOL type JEM-1400. Electrolyte properties of the membrane was observed using Electro Impedance Spectroscopy (EIS) of HIOKI 353D-HO.

RESULTS AND DISCUSSION

In this work we prepare membrane with different procedure as described in Table 1. The first three samples in table one was observed with FT-IR spectrophotometer

Table 1. Samples preparation used in this works

No	Sample Code	Description
1.	THD	Sample preparation is as described, sample is casted directly at 40 °C
2.	THE40	Sample preparation is as described, solvent is evaporate at 90 °C for 4 hours prior to cast at 40 °C.
3.	THE80 (THF80)	Sample preparation is as described, solvent is evaporate at 90 °C for 4 hours prior to cast at 80 °C.
4.	HAA	Sample preparation is as described, solvent is evaporated at 90 °C for 4 hours prior to cast at 80 °C. Benzimidazole: Phosphoric acid = 1:1 (mole)
5.	HAB	Sample preparation is as described, solvent is evaporated at 90 °C for 4 hours prior to cast at 80 °C. Benzimidazole: Phosphoric acid = 1:2 (mole)
6.	HAC	Sample preparation is as described, solvent is evaporated at 85 °C for 3 hours prior to cast at 80 °C. Benzimidazole: Phosphoric acid = 1:3 (mole)

and DSC to investigate the nature of supramolecular formed in those three membranes.

Figure 3 is Fourier Transform Infrared (FT-IR) spectrum of THD, THE40 and THF80 samples. The chemical shift of the absorption of sulfonate and anhydride was observed. The chemical shift can be seen in Table 2. The different absorption only occur for sample THD for both group's absorption. It indicates that sample THD differ from the other two, *i.e.*, THE40 and THF80. It is not easy to determine which sample(s) pose supramolecular structure. It could be membrane THD or membrane THE40 and THF80. However, the DSC data that will be discussed later determine that membrane THE40 and THF80 posses supramolecular structure. Therefore, the shift of absorption of -CO- and -SO₃H could arise from the formation of hydrogen bond between those groups.

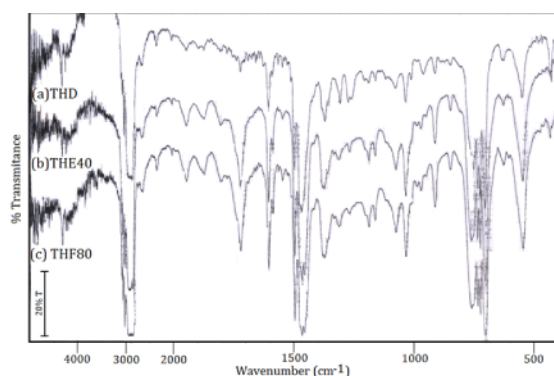


Figure 3. FT-IR spectrum of fuel cell membrane : (a). THD, (b). THE40 and (c). THF80

Table 2. Chemical shift of sulfonate and carbonyl absorption of membrane prepared with different method

Sample	Absorption (cm ⁻¹)	
	-CO-	-SO ₃ H
THD	1717.8	1029.4
THE40	1718.4	1028.0
THF80	1718.4	1028.0

Thermal measurement of those three membranes (Figure 4) show the differences between membrane THD and the other two membranes. The DSC thermogram of membrane THD show two endothermic peaks, while membrane THE40 and membrane THF80 show only one endothermic peak. Melting point of the membranes can be seen in Table 3.

The three membranes show differences in the first melting points. There is only little difference between membrane THE40 and THF80. The thermogram of the two samples in Figure 4 prove that they are identical.

Membrane THE40 and THF80 have a thermal transition showing the presence of glass transition temperature (T_g). It is sure that the T_g is not from PE-g-MAH, because the polymer is soft at room temperature. Therefore, the T_g arised from sPS.

Membrane THD shows no T_g in Figure 4. However thermogram of the membrane shows a little exothermic peak and it overlaps with the glass transition temperature of sPS. Melting point at 163,61 °C may presence from this crystal formation. The origin of the endothermic peak is not understand yet, but it can prevent the formation of supramolecular structure.

Supramolecular structure is built from the formation of hydrogen bonding sulfonate group between sulfonated polystyrene and anhydride group polyethylene-graft-maleic anhydride (Figure 5). The hydrogen bonding occurs along the backbone of the polymer and most likely constitute from sulfonate group and anhydride group belong to different polymer chains. For example on polymer chain of sulfonated polystyrene most likely interact with anhydride group from more than one polymer

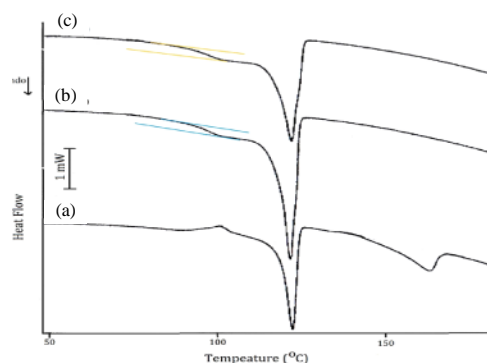


Figure 4. DSC thermogram of membrane (a) THD, (b) THE40 and (c) THF80

Table 3. The melting temperature of membrane samples

No	Membrane	Tm ₁ (°C)	Tm ₂ (°C)
1	THD	123.28	163.61
2	THE40	121.69	-
3	THF80	120.99	-
4	HAA	123.23	-
5	HAB	124.11	-
6	HAC	123.47	-

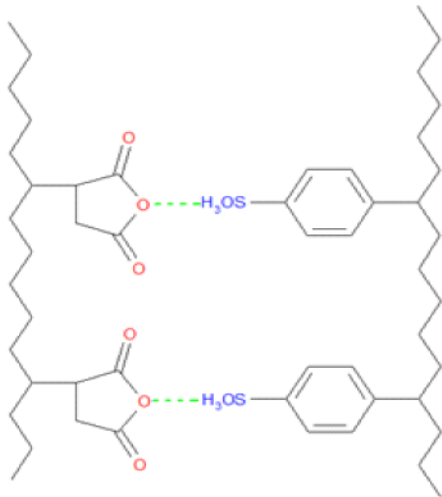


Figure 5. Artist concept of supramolecular structure between sulfonated polystyrene and polyethylene-graft-maleic anhydride

chain of polyethylene-graft-maleic anhydride and *vice versa*.

The hydrogen bonding occurs at the amorphous part of each polymer constituents. Thus, it was expected that the formation of supramolecular structure should not affect the crystal part of the membrane.

Figures 4(a) and 4(b) show that membrane made at different casting temperature, 40 °C and 80 °C, exhibit a little change on crystallite size. Membrane THF80 have broader endothermic peak than that of THE40. It means that membrane THF80 have more variation in crystallite size. This is the evidence that casting temperature could affect part of crystal structure.

Second melting peaks of membrane THD is 163.61 °C. The melting value is below melting point of polystyrene. This melting point could be belong to sulfonated polystyrene.

Behavior of Small Molecules

In this works two small molecules are used, i.e., benzimidazole and phosphoric acid. Both of them are added during the formulation of the membrane. The procedure differ from the other

works on embedding phosphoric acid into polymer membrane [9, 11, 29].

During the observation of samples using TEM, it appears figures where some part of the material 'melt'. This observation is recorded in Figure 6. The observation itself takes place less than 2 minutes.

In the first moment as appear in Figure 6(a) there is no spot in the sample. The sample is then shows a melt of materials and after several second recorded which can be seen in Figure 6(b). The further exposure in this sample, shows further 'melt' of some part (the dark part) resulting sample with many spot as can be seen in Figure 6(c) (see the arrows). The 'melted' parts are not from giant molecules such as polymers used in this membrane. Thus the melt was arising from the responds of small molecules under strong exposure of electron.

Phosphoric Acid in Fuel Cell Membrane

The FT-IR spectrum of membrane blend with phosphoric acid can be seen in Figure 7. Protonation of polyimide with phosphoric acid and self ionization of phosphoric acid can be found in the blend of polyimide/ phosphoric acid/imidazole [15]. The interaction can be observed by absorption of infrared in wavenumber of 1076 cm^{-1} and in the absorption between 890-975 cm^{-1} . In this work, the infrared absorption at wavelength of

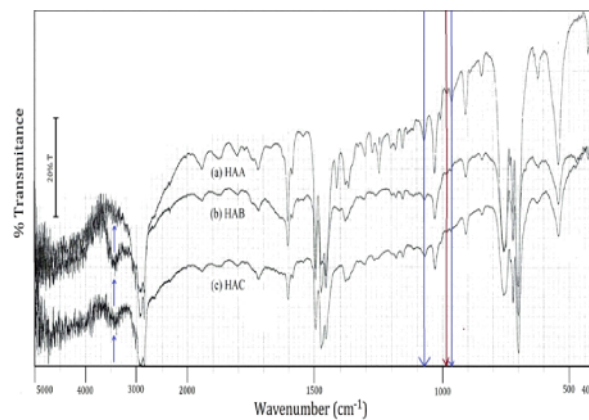


Figure 7. FT-IR spectrum of fuel cell membrane filled with phosphoric acid with variation of concentration of phosphoric acid. Detail information of each membranes in Table 1

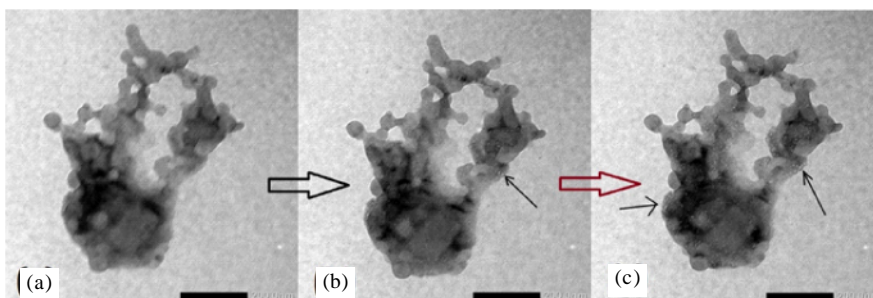


Figure 6. The 'melt' of small molecules under exposure of electron bombing during the measurement of TEM. The observation is less than 2 minutes

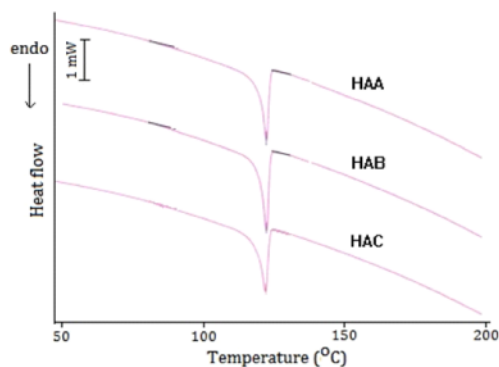


Figure 8. Thermal transition of membrane HAA, HAB and HAC observed by Differential Scanning Calorimetry (DSC)

1070, 985 and 965 cm^{-1} are observed. The mentioned infrared absorptions indicating possible interaction between imidazole and phosphoric acid and the self ionization phosphoric acid. Strong and broad absorption occurs at wavenumber of 3,450 cm^{-1} for membrane HAB and membrane HAC. The absorption could arise from interaction between imidazole and phosphoric acid. The infrared absorption at 3,450 cm^{-1} for membrane HAA is very weak, indicating other factor play role other than concentration of phosphoric acid itself solely. The phenomena will be discussed later in TEM observation.

Thermal behavior of membrane HAA, HAB and HAC do not show any sign of differences as shown in Figure 8. Their endothermic peaks are very similar. The melting point of three membranes as in Table 1 also do not significantly different as well. The gaps of melting point only in the range of 1 °C. Therefore, the thermal behavior of the membranes are quite similar. Small amount of phosphoric acid that added to the blend of membrane may the reason. The results of TEM micrograph can explain this behavior.

Membrane Morphology and its Effect

Figure 9 is the TEM image/micrograph of membrane HAA. Figure 9(a) shows main polymer membrane and cluster of small molecules (see arrow A). The formation of the cluster could be initiated by the properties of phosphoric acid which behave as strong and polarized hydrogen bond [30]. The cluster of small molecules (benzimidazole and phosphoric acid) forming disk-like shape with diameter around 300 nm (or 3,000 Å). This size is very large compare to sulfonate cluster forming in Nafion® which is only 40 Å in diameter [31]. The distance between disk (Figure 9(a)-B) is around 400 nm. There are two concurrent consequences. Once ion reach the cluster, it will be trapped within the cluster and consequently no ion flowing unless the ion can pass through the main polymer membrane. But, this requirement difficult to achieve as the ion are likely to move within small molecule

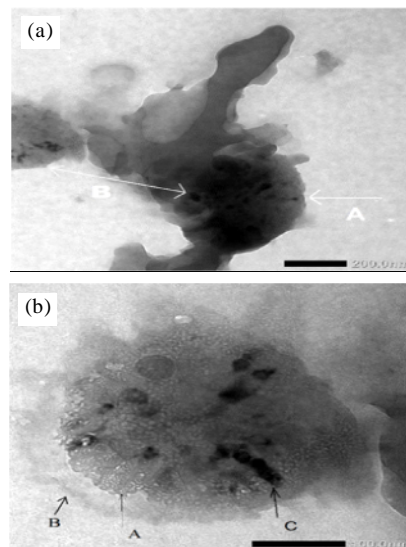


Figure 9. TEM micrograph from membrane HAA showing (a). part of cluster of small molecules and (b). detail of cluster of small molecules

and they are distributed equally within the cluster itself (Figure 9(b)). In addition, benzimidazole and phosphoric acid can form proton conduction path (Figure 1) [17]. In other world, ion could be trapped within the cluster. The path would keep ion moving within the cluster as the size is very big, i.e., around 400 nm. Figure 9(b) show the anatomy of cluster. Part A is the main polymer part where the small molecules reside, B is the 'melted' small molecules (see the discussion in *Behavior of small molecules*), and C is part of small molecules which is not 'melted' yet.

This observation agree with the figure of membrane HAA observed by Scanning Electron Microscope (SEM), see Figure 10(a) for details. In this SEM micrograph it can be seen the presence of small dot with different sizes. The dot might be arise from the part of small molecules. The dot also observed in membrane HAB in (Figure 10(b)) lesser content. The dot then, seems disappear for membrane HAC (Figure 10(c)). TEM observation confirm that the small molecule within membrane HAC presence in very small size less than 100 nm. See the dots in Figure 11(b) for more details information. This is differ from the other membrane which have cluster of small molecules in around 100 nm in size (Figure 11(a)-B).

Therefore, it is clear that the small molecules, i.e. benzimidazole and phosphoric acid, did not distribute even within main polymer membrane. It can be presence in cluster with 4,000 Å in size, or small dot less than 100 n, and dot around 100 nm in size. Most of them are separated far from one dot to another or from one cluster to another. The distance between dots or between clusters could give negative effect to the ionic conductivity. This phenomena explains the reason that three membranes has similar pattern in DSC measurements (Figure 8). In addition, the big size of the

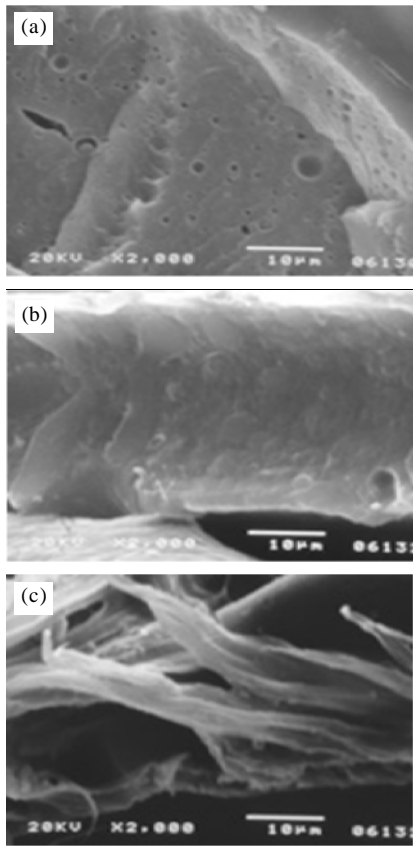


Figure 10. SEM micrograph of membrane (a). HAA, (b). HAB and (c). HAC

small molecules cluster, could lead the proton transfer occurs mostly within cluster [32].

The impedance spectroscopy measurements reflect the strong influence of the effect of morphology of the membrane, especially how small molecules are settle and distribute within main polymer membrane. The ionic conductivity for membrane is 3.77×10^{-5} , 1.1×10^{-5} , 1.63×10^{-5} and 9.86×10^{-7} S/cm for TH0i (no phosphoric acid), HAA, HAC and HAB, respectively. Within identical condition, the Nafion 117 have conductivity of 3.94×10^{-3} S/cm. The wide range of membrane in the plot reflect the explanation of TEM observation, *i.e.* when ions turn in into cluster, they tend to stay longer within the small molecules cluster. Longer movement of ion within membrane is not expected,

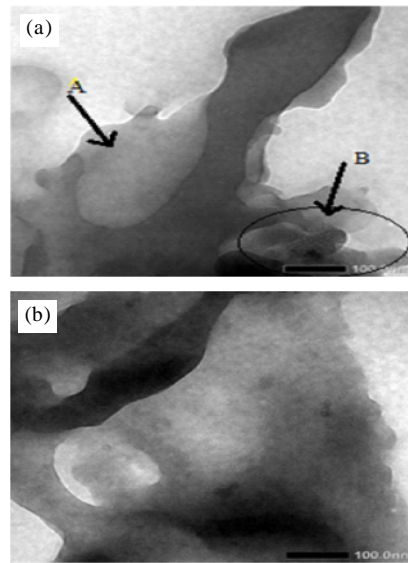


Figure 11. TEM micrograph observation of the part of the existing and distribution of small molecules in the membrane prepared with blend of imidazole and phosphoric acid (a). part showing polymer compatible portion, A and small molecules side which attached to polymer portion, B and (b). small molecules clustered themselves (membrane HAC) and distributed across the main polymer membrane

because it will trap ion cause less tendency to move to cathode. To be part for improving ion conductivity, the small molecules should be layered and oriented perpendicular to the membrane [33].

It was expected that the presence of phosphoric acid could improve conductivity of the membrane, from its ability to do self ionization [15] and its ability to make conduction path with benzimidazole [17]. However, morphology of the membrane made greatly affect to the final properties.

CONCLUSIONS

This work observed that beside concentration of phosphoric acid other factor play role in the conductivity of polymer electrolyte. The factor mentioned is morphology of the final product. In other words, the distribution and ways of interaction of small molecules, benzimidazole and phosphoric acid, play important role.

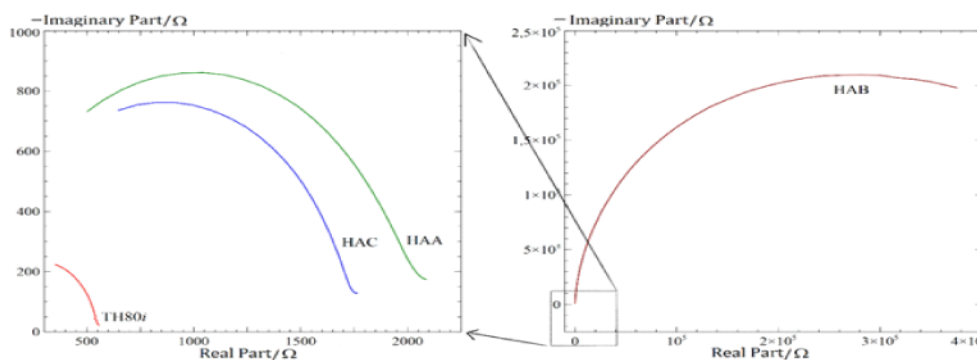


Figure 12. Nyquist plot of TH80i HAA, HAB and HAC membranes

The role of supramolecular structure is not clearly observed yet. however, the conductivity properties observed in this work represent the strong effect of morphology of the membrane made.

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