Polymer Electrolyte Membrane Fuel Cell based on Sulfonated Polystyrene and Phosphoric Acid with Biocellulose as a Matrix

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Abstract

Membrane is one of the key performance for polymer electrolyte membrane fuel cell (PEMFC) and direct methanol fuel cell (DMFC). Commercial membrane often used in PEMFC and DMFC Nafion® has some drawbacks such as high cost, limited operating temperature and high fuel permeability. A new polymer electrolyte membrane based on sulfonated polystyrene (sPS) has been developed. Sulfonated polystyrene-based membrane with addition of biocellulose matrix and phosphoric acid additives was made in this research. The membrane was prepared by using hot rolling and press method through a matrix.

Sulfonate group on the membrane is characterized by FTIR. Morphology and atomic composition are characterized by SEM-EDS. Stability and heat resistance are tested by DSC, ionic conductivity tested by EIS and along with the water uptake capability. Result of this study showed the membrane contains sulfonate group as confirmed by FTIR spectrum with the peak stretching vibration of S=O at a wavelength of 1371 cm^{-1}. Morphology membrane changed due to the modified interaction between polystyrene with biocellulose. Water uptake of the membrane increased to the increase of phosphoric acid concentration. From the experimental data, it can be indicated that the addition of phosphoric acid modified morphology and structure of membrane.

Keywords: Bio-cellulose, phosphoric acid, sulfonated polystyrene (sPS).

Introduction

Proton exchange membrane is the important component in PEMFC due to its use as transportation protons and prevention for fuel crossover[1]. Therefore, the membrane acquires some characteristics such as high ionic conductivity at operating temperature, high mechanical properties, low permeability of fuels and low cost[2]. Up to now, Nafion membrane becomes one of the candidates for commercial membrane due to high proton conductivity and chemical and physical stability. However, Nafion still has some drawbacks such as high cost, limited operation temperature and high fuel permeability[3]. To improve the performance of proton exchange membrane, the new alternatives polymer and some of modification have been developed such as sulfonated aromatic-based membranes, composite membranes, inorganic or solid acid membranes[4,6].

One of the new alternatives polymer membrane is sulfonated polystyrene. Sulfonated polystyrene (sPS) has low cost and is widely available[5]. Nonetheless, sPS have lower mechanical properties than Nafion making sPS difficult to be formed[6].

Bacterial cellulose (BC) is a natural and low-cost biopolymer biosynthesized by *Acetobacter xylinum*[4]. It has many excellent properties such as high water holding capacity and high tensile strength[3]. Recent studies have investigated PEM based on blending bacterial nanocellulose pulp and Nafion[7].

The modification of PEM is required such that it allows transfer of proton at the elevated temperature[8]. Inorganic or solid acid membranes is another promising class of membranes for higher temperature fuel cells. Phosphoric acid (H_3PO_4) could be as a medium for proton carrier to increased conductivity. The mechanism that takes place depends upon which proton conducting medium is present[9]. In this work, PEM has been prepared by modifying sulfonated polystyrene-based membranes with addition of biocelullose and phosphoric acid. Since the phosphoric acid has significant effects on conducting proton, the differences of addition phosphoric acid were studied and characterized by FTIR, DSC, SEM-EDS, EIS and water uptake capability.

Material and Methods

Materials: Sulfonated polystyrene (sPS) and biocelullose were supplied by Research Centre for Physics (PPF) – LIPI. Aquadest and phosphoric acid 85% p.a. were obtained from Merck.

Membranes fabrication with addition of biocellulose and phosphoric acid: Sulfonated polystyrene powder was dissolved in aquadest and stirred at 60°C for 90 minutes. The sPS solution was immersed with biocellulose and variation concentration of phosphoric acid (PA) (table 1), then stirred at 60°C for 90 minutes. Membrane solution was dried in the gear oven at 40°C for 3 days. Membrane sheet was stored on Teflon sheet then rolled at 120°C and pressed at 180°C, 50 kgf/cm^2 for 10 seconds.

Table 1
Composition of membranes

Membran Code	Biocellulose : sPS (ratio)	H_3PO_4(w/t)
MSP-1	6.5	0%
MSP-2	6.5	0.04%
MSP-3	6.5	0.2%

Characterization of membranes: The functional groups of the obtained membranes were analyzed by using fourier transform infrared spectroscopy (FTIR, Spectrum 100, Perkin Elmer) and scanned from 4000 to 450 cm^{-1} at resolution of 2 cm^{-1}. The morphology and composition were analyzed by using scanning electron microscopy and energy dispersive spectroscopy (SEM-EDS, JEOLJSM-6510LA). Thermogravimetric analysis (TG) and differential thermal analysis (DTA) were carried out by using differential scanning calorimetry (DSC, type 8000, Perkin Elmer) and scanned from room temperature to 250°C at the rate of 10°C/minutes. Proton conductivity of membranes was calculated by electrochemical impedance spectroscopy (EIS, HIOKI353D-HO). Water uptake capability was measured by using ASTM method.

Results and Discussion

FTIR analysis of membranes: The comparative FTIR spectra of membranes MSP-1, MSP-2 and MSP-3 with different concentration of H_3PO_4 are presented in figure 1. The peak at 1371 cm^{-1} was assigned as –S=O stretching vibration of sulfonate groups. Meanwhile, the bands at 2921 and 3025 cm^{-1} were assigned as CH_2 and aromatic C–H stretching vibration of polymer backbone. The characteristics bands of cellulose at 3346, 2921, 1161 cm^{-1} were assigned as stretching vibrations of –OH, C–H and C–O–C (β glycosidic linkage) were observed in the spectra of all membranes.

A new peak in the spectra of membranes MSP-2 and MSP-3 appeared at 1279 cm^{-1} which is attributed to the stretching vibration of P=O groups. The broad peak at 3349-3350 cm^{-1} proves the presence of –OH groups. However, the peak of –OH groups became wider from MSP-1 membrane to MSP-3 membrane due to a bigger proportion of phosphoric acid that affected the quantities of intermolecular interaction of hydrogen bonds.

Thermal analysis of membranes: Figure 2 shows the DSC second run of membranes. The inflection point of the slope change of the heat capacity plot (onset) was taken as the transition glass (Tg)[10] and it was 98.5, 97.5 and 95.5°C for MSP-1, MSP-2 and MSP-3 membrane respectively. The decrease of Tg MSP-3 membrane could be attributed to the differential interaction caused by the presence of phosphoric acid. In other words, the addition of phosphoric acid would affect to polymer chain mobility as hydrogen bonding has been modified.

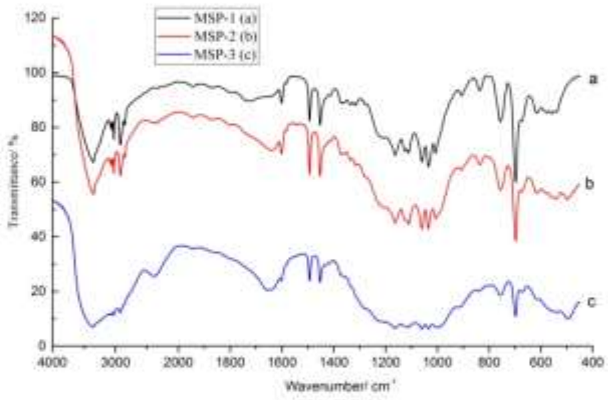


Figure 1: FT-IR spectrum of membranes

The cooling thermogram can be seen in figure 3. It is clear in the figure that MSP-3 membrane shows unique characteristic. It has crystallization peak at 140°C. The crystallization occurs in MSP-3 membrane because of the melting point at 204°C (figure 2).

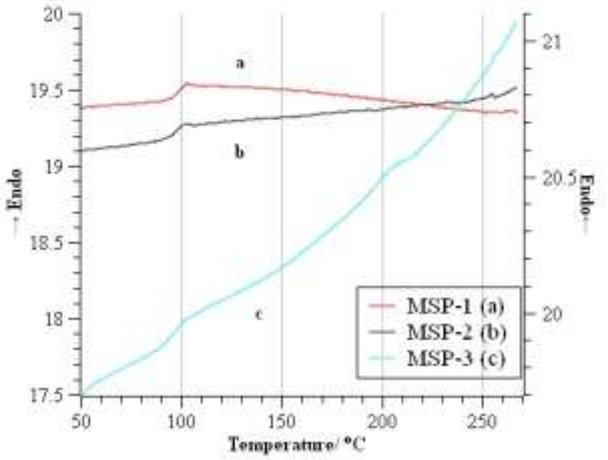


Figure 2: DSC thermogram second run of membranes

The strong interaction of MSP-3 membrane can also be seen in TGA thermogram (figure 4). The MSP-2 and MSP-3 membrane have a starting temperature of weight loss at 120°C. However, MSP-1 membrane shows a considerably lower temperature at 80°C. This is possibly due to the different content of water present in the phosphoric acid. The MSP-1 membrane weight loss is mainly associated to the loss of free boundary water. However, the MSP-2 and MSP-3 weight loss are related to the loss of boundary water.

Morphology and composition analysis of membranes: Figure 5 shows the morphology of membranes observed by SEM. It can be seen in figure 5(a) that MSP-1 membrane was rigid (no pores). However, MSP-1 membrane shows a distinct part of sPS and a distinct part of bio-cellulose. In figure 5(b), MSP-2 membrane, distinction was less prominent. Meanwhile, in figure 5(c), MSP-3 membrane the distinction can almost be seen. These observations may explain the thermal phenomena as observed in figure 3.

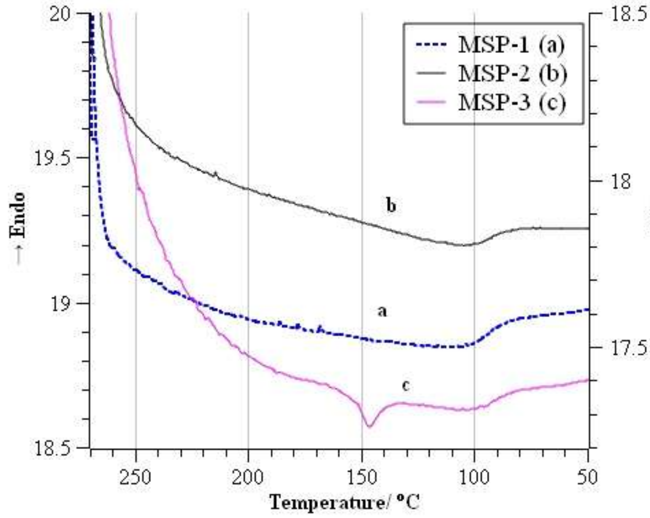


Figure 3: DSC thermogram cooling of membranes

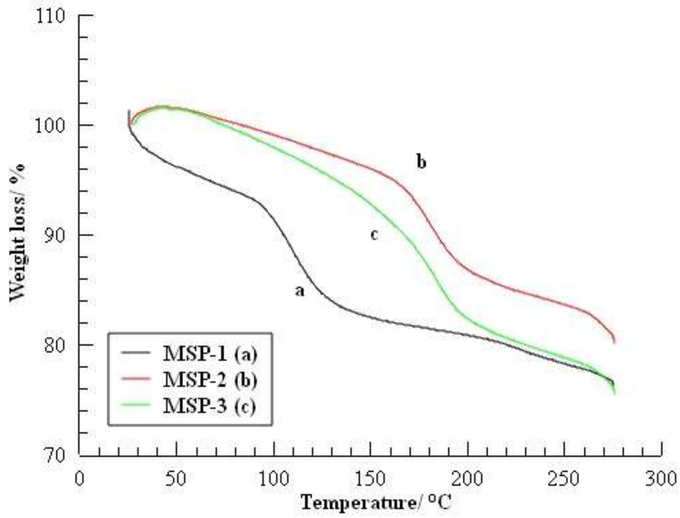


Figure 4: TGA thermogram of membranes

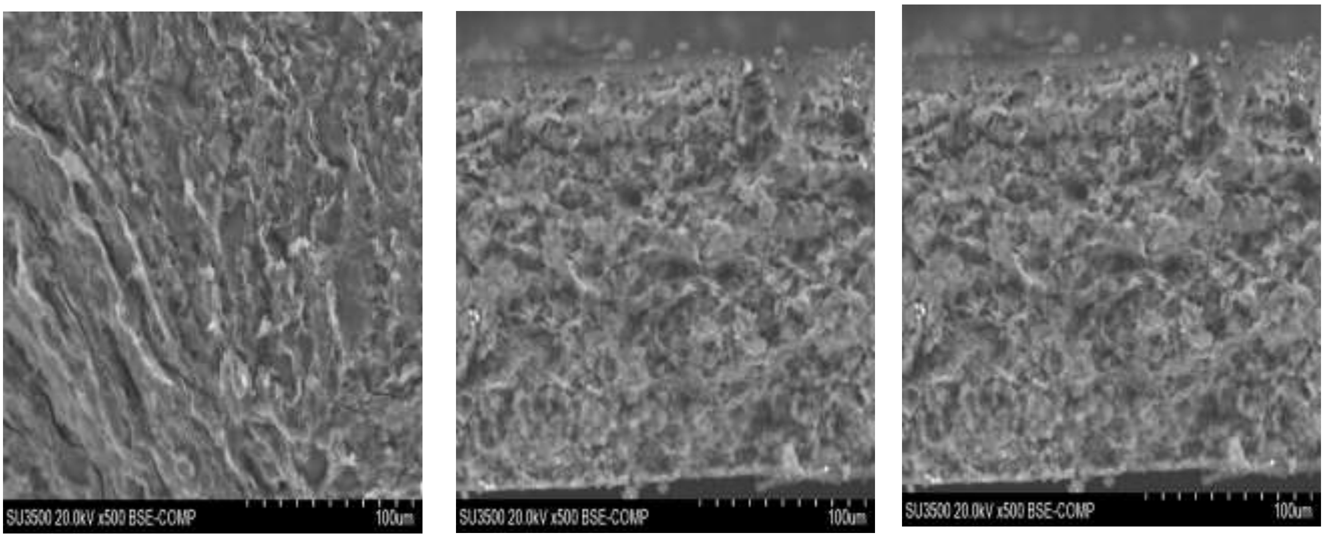
The membranes were analyzed by SEM-EDS to determine the content of sulfur on the surface of membranes. The sulphonate group of all membranes in figure 6 was distributed randomly.

Proton conductivity of membranes: As shown in table 2, all the membranes have ionic conductivity at similar level. The ionic conductivity for membrane MSP-1, MSP-2, MSP-3 and Nafion is 7.17 × 10^{-3}; 2.02 × 10^{-3}; 3.12 × 10^{-3}; 19.04 × 10^{-3} S/cm respectively. It was expected that the presence of phosphoric acid could improve proton conductivity of membranes from its ability to provide proton due to their self ionization[11]. However, it can be seen from the plot in the figure 8 that the similar of semicircle form indicates the characteristic of ionic transportation of membranes. MSP-2 and MSP-3 membrane showed a better Nyquist plot.

Table 2
Ionic conductivity of membranes

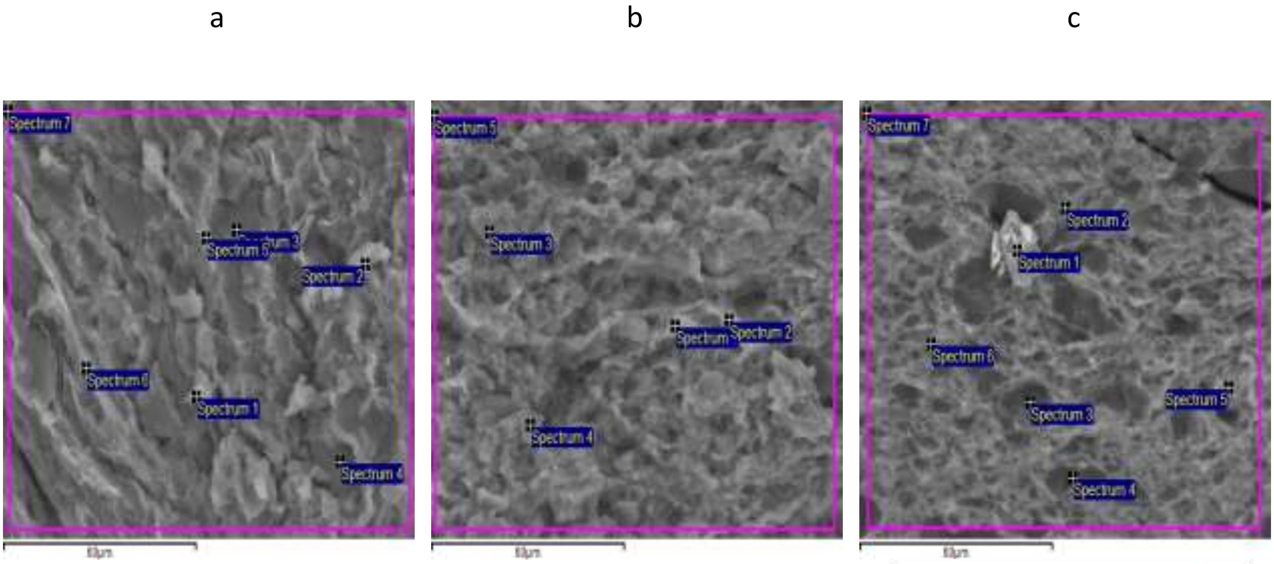
Membrane	Ionic conductivity/ (S/cm)
MSP-1	7,17 x 10^{-3}
MSP-2	2,02 x 10^{-3}
MSP-3	3,12 x 10^{-3}
Nafion	19,4 x 10^{-3}

Water uptake capability of membranes: Figure 7 shows the equilibrium water contents of membranes increased by many times. This increasing water uptake corresponded with higher phosphoric acid concentration. The increase of phosphoric acid could lead to hydration and loss of mechanical stability due to excessive water contents of membrane. Therefore, MSP-3 was increased to the highest value of water uptake.



a b c

Figure 5: SEM image of membranes MSP-1 (a); MSP-2 (b); MSP-3 (c)



Membrane	Spectra	% Element Sulfur
MSP-1	Spectrum 1	3.98
	Spectrum 2	5.45
	Spectrum 3	1.30
	Spectrum 4	0.62
	Spectrum 5	3.47
	Spectrum 6	5.42
	Spectrum 7	2.89
	Average	3.30

Membrane	Spectra	% Element Sulfur
MSP-2	Spectrum 1	9.62
	Spectrum 2	11.58
	Spectrum 3	1.57
	Spectrum 4	1.54
	Spectrum 5	3.65
	Average	5.60

Membrane	Spectra	% Element Sulfur
MSP-3	Spectrum 1	8.04
	Spectrum 2	9.96
	Spectrum 3	0.21
	Spectrum 4	1.01
	Spectrum 5	3.23
	Spectrum 6	11.39
	Spectrum 7	3.84
	Average	5.38

Figure 6: EDX data of membrane MSP-1 (a); MSP-2 (b); MSP-3 (c)

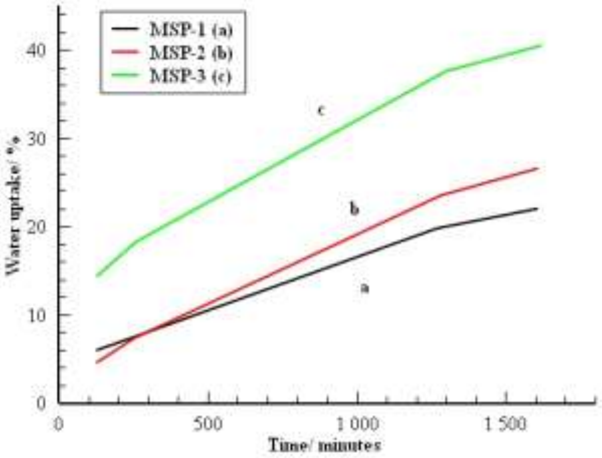


Figure 7: Water uptake of membranes

Conclusion

Based on the research that has been done, it has demonstrated preparation of membrane from sulfonated polystyrene and bio-cellulose with the addition of phosphoric acid. The addition of phosphoric acid modified morphology and structure of membrane prepared by sulfonated polystyrene and bio-cellulose. However, morphology has more important role in determining final ionic conductivity of membranes.

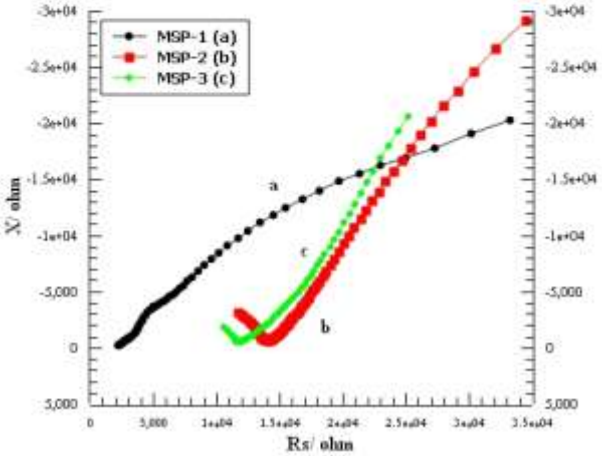


Figure 8: Nyquist plot of membranes

Acknowledgement

We acknowledge the Research Center for Physics – LIPI, for facilitating and funding this research. Great appreciation is also attributed to Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Padjadjaran for giving opportunity to conduct experimental works.

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