Synthesis of proton-conducting membranes based on sulfonated polystyrene and bacterial cellulose

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Abstract. Synthesis of composite material based on sulfonated polystyrene and bacterial cellulose as a proton membrane has been carried out. In this study, the membrane was made with the variations mass ratio of sulfonated polystyrene : bacterial cellulose 1.5: 3.5, 2: 3, 2: 5, 3: 5: 1.5. The previous step was sulfonation of polystyrene, in which the polystyrene used is styrofoam from electronic goods packaging waste. Polystyrene in this case styrofoam is sulfonated using the sulfonating agent trimethylsilyl chlorosulfonate. The membranes have characterized by analyzing of functional groups, proton conductivity, cation exchange capacity, and degree of swelling. The FTIR spectrum showed that the sulfonated polystyrene-bacterial cellulose composite material was successfully synthesized which was shown at the peak at wave number 1124.767 cm\(^{-1}\) which was a SO\(_3\) stretching vibration. The peak at wave number 962-1150 cm\(^{-1}\) was assigned the stretching of CO vibrations for C-OC and C-OH which indicates cellulose glycosidic bonds. The highest Cation Exchange Capacity (CEC) value and proton conductivity were in the composite membrane: bacterial cellulose mass ratio 3: 5: 1.5, the CEC value 2.25 meq/g and the proton conductivity value 1.176 x 10\(^{-6}\) S/cm\(^{2}\). This result shows that the sulfonated polystyrene-cellulose bacterial composite membrane has the ability to deliver protons so that it has the potential to be developed as a fuel cell membrane.

1. Introduction
In the global era the demand for fossil energy was increasing while availability was declining so alternative energy was needed such as Proton Exchange Membrane Fuel Cell (PEMFC) [1]. Fuel cells were electrochemical cells that convert chemical energy into fuel and oxidants (oxygen) into air and produce electrical energy, by processes that use an electrode-electrolyte system. One very promising source of energy especially for vehicle engines was the proton exchange membrane fuel cell (PEMFC), where the proton exchange membrane fuel cell has a high power density, quickly undergoes a transfer of the required power requirements and was very fast at initiation process. The fuel of the cell was hydrogen oxidized by oxygen which produces air and energy [2].

Polystyrene was a chemical used to make styrofoam as a packaging material. The packaging based on polystyrene often causes problems in the environment because it was difficult to repair biological damage and was difficult to recycle. Styrofoam waste could be used as an alternative fuel if its sulfonated. The research on sulfonated polystyrene that was composites with zeolites for the application of electrolyte polymer membranes has conducted [3]. Polystyrene was sulfonated by adding sulfonate groups to its side chains so that the polystyrene has a charged group so that it could be used...
to increase conductivity. Therefore in this research, synthesis of polystyrene derived from styrofoam will be formed into sulfonated polystyrene.

Coconut water which was the basic ingredient of making bacterial cellulose (SB) was a natural material that could be modified so that its properties could be improved. Coconut water which was fermented by Acetobacter xylinum has been used as an alternative to electrolyte membranes in fuel cell applications through phosphorylation with 4 hours immersion process [4].

2. Experimental

2.1. Material Preparation

Styrofoam has used from electronic packaging waste, coconut water have taken from the modern traditional market of Bengkulu City, trimethylsilyl chlorosulfonate (TMSCS;Sigma-Aldrich), dimethylformamide (DMF;Merck), ammonium sulfate (Merck), acetic acid (Merck), bacteria *Acetobacter xylinum*.

Bacterial cellulose (BC) has been synthesis refers to [5], the coconut water is filtered, then one liter of filtered coconut water is brought to a boil. After boiling, 6.7 grams of sugar, 5 grams of ammonium sulfate and 1 mL of acetic acid are added. When it is hot then transferred to a plastic container measuring 15 x 20 cm and covered with paper. After chilling/room temperature, the next step was inoculated with the starter bacteria *Acetobacter xylinum* (10% of the volume of the fermentation medium) by opening the paper cover, then closed again and fermented / incubated at room temperature for 7 days. Polystyrene preparation and sulfonation refers to [6], the dried polystyrene was put into a reactor containing 200 mL of dichloroethane and then stirred until homogeneous. After being homogeneous, 15 mL of sulfonating agent was added and reacted for 7 hours, where the sulfonating agent used was trimethylsilyl chlorosulfonate (TMSCS). During the reaction, nitrogen gas flow must be maintained. Then the sulfonation reaction is stopped by pouring polystyrene into methanol and then stirring it until it forms white threads that form clumps. Then the sulfonated polystyrene (PST) is dried at 60 °C until the PST is completely dry. Then the PST was stored in a desiccator for further analysis.

Preparation proton conducting membranes have been done that bacterial cellulose was blended until smooth so that it becomes pulp then filtered, then bacterial cellulose was formed with a mass of 5 grams, while PST was dissolved in DMF solvent then PST membrane was printed with a mass of 1 gram, for the composite membrane after PST was dissolved then cellulose residue was added with a mass ratio of PST: cellulose bacteria was 1,5: 3,5, 2,5: 2,5, 3,5: 1, then stir for up to 8 hours. Then casting on the glass plates, the solvent was evaporated slowly at temperature of 35 °C for transferred to membrane.

2.2. Material Characterization

The degree of sulfonation of sulfonated polystyrene has been done by the titration method. To determine the exchange rate of cation capacity has used the titration method. The level of swelling has been determined by cutting the membrane with a size of 1 x 1 cm and then heated at 60 °C for 5 hours then weighed, dry weight was obtained. Then the membrane was immersed in distilled water for 24 hours at room temperature. The surface of the membrane was dried with a tissue and weighed then a wet weight was obtained. Functional group analysis by FT-IR spectra were recorded on a Bruker Alpha-P in attenuated total reflectance (ATR) in range of 4000-400 cm⁻¹. The proton conductivity of membrane was measured by IM 3590 Chemical Impedance Analyzer HIOKI in frequency 1 KHz, 0,05 Volt and temperature at 26 °C.

3. Results and Discussion

Polystyrene was prepared by cutting styrofoam into small pieces. The purpose of this action was to make it easier when soaked with acetone. Then styrofoam soaked using acetone for 3 days so that the impurities was appear. After being soaked with acetone, styrofoam has a denser form, this shows that the additives in styrofoam could dissolve with acetone.
Polystyrene does not have proton conductive groups so the sulfonation process was carried out so that polystyrene has proton conductive groups. The sulfonation reaction was a substitution reaction that aims to replace the H atom with the ~SO3H group. In this study the sulfonation agent used was trimethylsilyl chlorosulfonate (TMSCS). To carry out the polymer sulfonation process and the sulfonate agent must be in the same phase, the polystyrene was dissolved using dichloroethane solvent. In the sulfonation process also uses nitrogen gas. The sulfonation process was carried out for 7 hours. During the sulfonation process, nitrogen gas flow was guarded to prevent the formation of HCl and reduce water vapor [7], figure 1 showed the sulfonated polystyrene.

![Figure 1. The sulfonated polystyrene membrane.](image1)

To find out how many sulfonate groups were attached to polystyrene, the level of sulfonation was determined. Where the degree of sulfonation was the number of H atoms in benzene converted to sulfonate groups. In this study the degree of sulfonation obtained was equal to 73.61%. After 7 hours, the sulfonation process was stopped by adding methanol then stirred and evaporated until the methanol was used up and a yellowish dry solid was obtained. After drying the sulfonated polystyrene was molded into membrane with mass of 1 gram, thin PST membrane with thickness of 0.464 mm was obtained.

Synthesis of bacterial cellulose uses several ingredients namely ammonium sulfate coconut water, glacial acetic acid, granulated sugar and Acetobacter xylinum bacteria. Bacterial cellulose was made by mixing filtered coconut water, sugar, ammonium sulfate and then made to boil, for the addition of glacial acetic acid after the mixture was rather cold and then the mixture was placed in a container. After being cold the bacterium Acetobacter xylinum was inoculated into the mixture. This treatment was done because the bacterium Acetobacter xylinum will die if the mixture was still hot. Acetobacter xylinum was a bacterium that produces cellulose, the nutrients that play a role were nutrients that contain glucose [5].

In the process of making bacterial cellulose the thing that must also be considered was the pH, which according to [8] the bacterium Acetobacter xylinum could convert glucose into cellulose in the pH range of 3.5-7.5. In this study pH 4 was obtained after the addition of glacial acetic acid.

![Figure 2. Bacterial Cellulose.](image2)

After forming the gel as shown in Figure 2, bacterial cellulose gel was soaked with water for 24 hours, the water used was often replaced, because the purpose of soaking was to remove unwanted...
impurities such as ammonium sulfate which will dissolve in water and then be wasted when the water was replaced. Bacteria cellulose were washed using aquades in the temperature range of 80-90 °C. Bacterial cellulose was also washed with 2% NaOH. Then the bacterial cellulose gel was washed again with distilled water at a temperature range of 80-90 °C and the bacterial cellulose gel was obtained whiter when compared to before purification.

The purpose of composite membrane synthesis was to obtain better material properties than the properties of the constituent polymers. The constituent polymers used in this study were sulfonated polystyrene and bacterial cellulose. The steps to synthesize the composite membrane was to smooth the bacterial cellulose using a blender first, the purpose of this treatment was to facilitate the next work step and to increase the reactivity of the bacterial cellulose during the reaction.

Functional group analysis was performed to show the absorption band on the composite membrane, the absorption band could come from the constituent polymer material or from the interaction between PST and bacterial cellulose.

![Figure 3. FTIR spectrum of composite membranes PST : BC 1,5: 3,5, 2,5: 2,5, 3,5: 1,5.](image)

Figure 3 showed FTIR spectrum that there were 3 distinctive peaks of sulfonated polystyrene which was not owned by polystyrene, namely at wave number 3456.401 which was OH stretching vibration and at wave number 1124.767 cm⁻¹ which was SO₃ stretch vibration and at wave number 1026.247 cm⁻¹ was a stretch vibration S = O. in bacterial cellulose there was absorption at the wave number 962-1150 cm⁻¹ which was a stretching CO vibration for C-OC and C-OH which states the relationship of cellulose glycosides.

Cation Exchange Capacity (CEC) was a measure of the ability of a material to exchange cations in a functional group with cations added to replace cations in a material [9]. Cation exchange capacity of the PST membrane 2.1 meq/g, composite membrane 1,5: 3,5 that was 0.923 meq/g, composite 2,5: 2,5 which was 0.965 meq/g and composite: 3,5: 1,5 which was 2.25 meq/g.

The degree of swelling (DS) has been determined by weighing the membrane weight after being immersed in distilled water. The degree of swelling was one important thing because it could affect the flow of electrons in the membrane. In this study the degree of swelling obtained for PST composites: bacterial cellulose (SB), bacterial cellulose and PST was shown in figure 4.
Figure 4. Graph of degree of swelling membranes PST : BC 1.5: 3.5, 2.5: 2.5, 3.5: 1.5.

The proton conductivity was a very important parameter for proton transfer membranes because if the proton conductivity was small then the membrane could not be used as a proton transfer membrane. Proton conductivity could also have different results depending on the instrument used in the measurement\[10\]. The conductivity obtained in this study were presented in Table 1.

| Membranes                  | Proton conductivity 26 °C (S/cm) |
|---------------------------|----------------------------------|
| PST                       | 1.096 x 10^-6                   |
| Bacterial cellulose (SB)   | 0.521 x 10^-6                   |
| PST : Bacterial cellulose |                                  |
| 2.5 : 2.5                 | 0.4148 x 10^-6                  |
| 1.5 : 3.5                 | 0.606 x 10^-6                   |
| 3.5 : 1.5                 | 1.176 x 10^-6                   |

4. Conclusion
The optimum composition of the composite membrane was at a ratio of 3.5 grams of PST and 1.5 grams of bacterial cellulose. PST composite membrane - bacterial cellulose 3.5: 1.5 has better characteristics compared to PST membrane without composite.

Acknowledgment
This work was supported by the University of Bengkulu. Therefore, the authors thank the chemistry laboratory staff University of Bengkulu for supporting this research.

References
[1]     Wafiroh S, Suyanto S, and Yuliana Y 2016 *Journal Kimia Riset* 1(1) 14.
[2]     Gustian I, Asdim, Maryanti E 2016 *Pengantar Sintesis dan Karakterisasi Membran Sel Bahan Bakar Berbasiskan Polimer* (Bengkulu Badan Penerbitan Fakultas Pertanian UNIB) pp 2-7.
[3] Wicaksono A 2012 Sintesis dan karakterisasi membran komposit polistirena tersulfonasi dengan zeolit untuk aplikasi membran polimer elektrolit (Universitas Sebelas Maret Surakarta).

[4] Radiman C L, Sarinasititi A 2012 Jurnal Selulosa 2(2) 46.

[5] Gustian I, Sutanto T D, and Adfa M. 2006 Jurnal Gradien 12(1)127.

[6] Gustian I, Ghufira, Fajar W K, 2014 Prosiding semirata bidang MIPA BKS PTN Barat, Kampus IPB Baranang Siang (Bogor, Indonesia) 510-518.

[7] Naim R, Ismail A F, Saidi H, & Saion E 2004 Proceedings of the Regional Symposium on Membrane Science Technology, Puteri Pan Pacific Hotel (Johor Bharu, Malaysia) 21-25.

[8] Rizal H M, Pandiangan D M, & Saleh A 2013 Jurnal Teknik Kimia 19(1) 34.

[9] Gustian I, Ghufira, Oktiarni D 2017 Rasayan Journal Chemistry, 12(1), 284.

[10] Muljani S, Dahlan, Wulanawati A 2014 International Journal Of Materials, Mechanics And Manufacturing 2(1) 36-40.