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UTILIZATION AND MODIFICATION OF PINEAPPLE SKIN WASTE FOR POLYMER ELECTROLYTE MEMBRANE APPLICATION

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ABSTRACT

The latest fuel cell development uses biodegradable polymer electrolyte membranes (PEM) to separate the cathode and anode components, making it an exciting research topic. This research develops a cheap and eco-friendly polymer electrolyte membrane (PEM) material. The membrane material is pineapple peel waste, which is easily biodegradable and naturally abundant. Sulfonate groups were added together with varied sulfuric acid concentrations to modify it. The membrane was then evaluated for its mechanical strength, proton conductivity, swelling index, and ion exchange capacity (IEC). In addition, this study performed morphological, sulfur content, and functional group analyses using FTIR, SEM, and EDS. In accordance with the findings, the best nata de pina membrane had a proton conductivity of 1.85 x 10^{-2} S/cm, an IEC of 3.85 mEq/g, a degree and swelling of 118.55%, and was sulfonated with 1.08 N sulfuric acids. Additionally, the resulting membrane's mechanical strength increased significantly. Therefore, pineapple peel is an environmentally friendly natural resource useful in manufacturing electrolyte membranes.

Keywords: Membrane, Nata de Pina, sulfonated Nata de Pina, Fuel cell.

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INTRODUCTION

Increased human activities raise the consumption of energy, whose main source is fossil fuels. Continuous use of fossil fuels could cause global warming, which results in the melting of polar ice caps, acid rain, and the destruction of agricultural land and forests. There is a global energy crisis due to the limited availability of non-renewable fossil fuels. Therefore, there is a need for new sources of renewable and environmentally friendly energy. One alternative energy source being developed is a fuel cell with a polymer electrolyte membrane (PEM) that uses hydrogen gas or methanol. Most fuel cells use perfluorocarbon polymer (Nafion) as the basic membrane material. However, the membrane material is expensive and uneconomical, and the methanol transport or cross-over is high, reducing the cell's efficiency. Moreover, the availability of methanol fuel is limited and causes environmental pollution as a waste. Therefore, electrolyte polymer membrane materials are a better and more economical alternative.[1-7] To overcome this problem, it is necessary to develop a new polymer material as a proton-conducting membrane with good properties, is cheaper, and is environmentally friendly. Because it is a natural and affordable polymer, bacterial cellulose from coconut water (nata de coco) is a superior option in this case. *Acetobacter xylinum* bacteria are used to ferment coconut water in order to make it. In addition, the cellulose could undergo sulfonation and phosphorylation modifications to create electrolyte polymers. Sulfonation has been carried out on nata de fina using 0.36 N H_2SO_4 resulting in an ion exchange capacity of 3.47 mEq/g.[8] Phosphorylation on nata de banana using variations of phosphoric acid has also been carried out with optimum conditions on the addition of 2 M phosphoric acid and ion exchange capacity 5.14 mEq/g.[9] It has also been modified by adding a phosphate group through a continuous reaction in a microwave oven, and the proton conductivity value is 1.17 x 10^{-1} S/cm.[10] Another research on bacterial cellulose (nata de coco) phosphatized (using 17.35 mMol phosphate ion) found that the proton conductivity was 1.20 x 10^{-2} S/cm.[11] Furthermore, modification of nata de coco can increase proton conductivity which is close to Nafion. Bacterial cellulose (nata) synthesis of the microorganism *Acetobacter xylinum* utilizes sugar (sucrose) as a food source which will then be broken down into glucose and fructose and further form nata. The sugar content in coconut water, the basic ingredient for making nata de coco (1.6%), is lower than in pineapple (7.5%).[12-15] The relatively

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high sugar content makes pineapple a basic ingredient for making nata with *Acetobacter xylinum*, known as nata de pina, abundantly available in Indonesia. Nata de pina, nata de coco, and nata de banana are bacterial cellulose synthesized from pineapple, coconut water, and bananas using *Acetobacter xylinum*. Modification of the membrane with sulfonate groups and phosphate groups can increase IEC and proton conduction ability.[8-10] Furthermore, modifying the nata de pina membrane through the phosphorylation reaction has also increased the IEC, swelling index, and proton conductivity.[15] Similar results are obtained when bacterial cellulose membranes from nata de pina are sulfonated. The reaction is expected to increase the electrolyte membrane's hydrogen ion conductivity (proton transfer), thereby increasing the proton conductivity. Sulfonated nata de pina has a sulfonate and hydroxyl (–OH) group interacting with hydrogen ions (H^+). Therefore, it has great potential for fuel cell electrolyte polymer membrane applications. Maximum proton transfer (proton transfer) from anode to cathode results in high proton conductivity and enhances the membrane performance. Therefore, the nata de pina membrane was modified through sulfonation to enhance the IEC and proton conductivity. The increase of IEC and proton conductivity in sulfonated nata de pina membranes is expected to be an alternative to the Nafion membrane as the main electrolyte polymer membrane currently used.[11] Based on the description, this research will make a polyelectrolyte membrane material for fuel cells in the form of a modified nata de pina membrane with a sulfonate group to increase conductivity, thermal stability, and mechanical strength because the chain is rich in sulfonate groups and crosslinks. A hydrophilic channel that promotes proton transfer through the membrane matrix is created as a result of the interaction between the sulfonate groups tied to the cellulose chain. The cellulose chain's ability to bind phosphate-sulphonate can have an impact on the membrane's proton conductivity qualities. Because more contacts will result in the formation of hydrophilic channels, the membrane's proton conductivity will increase as the number of bound sulfonate increases.

EXPERIMENTAL

Material

The sugar, pineapple skin, and *Acetobacter xylinum* were obtained from traditional markets and local industries. Furthermore, sodium hydroxide and acetic, hydrochloric, sulfuric acids, and food-grade urea were performed without purification.

Filmmaking for Nata de Pina

The nata de pina obtained utilizing the previous experiment[8,16,17] was fermented for ten days at room temperature to produce a gel. This gel was then placed in boiling water for 15 minutes before being immersed in 1% (w/w) sodium hydroxide and acetic acid solutions for 24 hours in turn. Furthermore, it was washed to a neutral pH value, then pressed under 100 bar pressure at room temperature for five minutes.

Nata de Pina Membrane Sulfonation

Utilizing the Wafiroh and Rahmawati-described reactants, the nata de pina membrane was sulfonated.[8,18] The difference in the variation of the concentration of the reagent. The film was then immersed in 100 mL H_2SO_4 0.72 N for 4 hours at room temperature, followed by a microwave reaction for 150 seconds. After the sulfonation process was completed, the membrane was washed using distilled water to remove excess H_2SO_4. The membrane was put in a plastic container, and air-dried[11,18] and the reaction was performed again with 1.08 N and 1.44 N sulfuric acid concentrations.

Characterization of Sulfonated Nata de pina

The characterization carried out included the IEC test, degree of the swelling test, contact angle test, mechanical test, functional group analysis, and morphological analysis. The IEC test follows the procedure.[8-9,16] The membrane is submerged in 40 mL of HCl 0.1 M for 24 hours at room temperature as part of the sample preparation for the IEC test. The membrane is additionally neutralized. The membrane was neutralized and then submerged for 12 hours in 40 mL of a 0.01 M NaOH solution. A standardized 0.004 M H_2SO_4 solution was used to titrate 10 mL of the solution initially. IEC is calculated using eqn.-1.

$$IEC = \frac{(Vb-Vs)[Acid].fp}{mass} \quad (1)$$

Information:
IEC = Ion Exchange Capacity
Vb = NaOH solution needed to neutralize the blank (mL)
Vs = the required volume of a NaOH solution to neutralize the membrane (mL)
[Acid] = acid chlorosulfonic concentration (M)
fp = diluting factor
m = size of the sample (gram)

The procedure for the Swelling index (SI) test adopted from[8-9,16] was performed to determine the membrane's hydrophilicity. During preparation, the membrane's mass was determined before immersing it in water for 24 hours. In addition, tissue paper was used to dry the membrane surface before weighing it to obtain a constant mass. The SI is determined as presented in equation (2).

$$\%SI = \frac{m-m_o}{m_o} x\ 100\% \quad (2)$$

where: m = membrane mass before immersion in water (gram)
m_o= membrane mass after immersion (gram)

For proton conductivity measurement, membrane samples were immersed in a 0.1 M solution of sulfuric acid for 24 hours to eliminate all groups of hydroxyls and sulfate. The next step involved repeatedly washing the membrane in deionized water to eliminate residual acid until the filtrate's pH was neutral. Impedance due to electrochemistry Ionic resistance was evaluated using spectroscopy (EIS) with platinum as the electrode wire at 80 °C and 61.5% relative humidity. Measurements were made using an LCR meter E4980 A with a frequency range of 30 Hz to 2 MHz at 10 mV.[11] Equation (3) shows the calculation of the proton conductivity:

$$\sigma = \frac{l}{RA} \quad (3)$$

Where, σ = proton conductivity (S/cm)
l = Thickness (cm)
R = Resistance at frequency am (Ohm)
A = Area (cm^2)

The mechanical test involves elongation and tensile tests with the procedure.[8-9,16] The tensile test for the membranes and sulfonated nata de pina was performed using each sample's specimens gripped with a machine. Furthermore, the tensile strength was determined according to the maximum load that breaks the membrane. In comparison, elongation percentage refers to the elongation at which the membrane breaks.[19,20] Determine the functional groups and changes in functional groups in the nata de pina membrane before and after sulfonation using functional group analysis. Functional group analysis using FTIR (Fourier Transform Infra-Red) spectroscopy. Membrane and sulfonated nata de pina were analyzed by means inserted in place snippets, then measuring the infrared spectrum to obtain the FTIR spectrum.[8-10,16] For the morphology test using SEM-EDX, sulfonated membranes nata de pina were tested in Malang central laboratory using SEM Jeol JSM 6360 LA. With the presence of EDX, it can be seen the mass percentage of sulfur contained in the membrane.[11]

RESULTS AND DISCUSSION

Effect of Sulfonation on the IEC and Proton Conductivity

We can determine the number of ionic groups in the polymer matrix by measuring the IEC. Figure-1 shows that adding sulfuric acid to 1.08 N may increase the IEC and proton transfer capacity. The formation of hydrophilic channels causes the increase in the proton conductivity value of sulfonated bacterial cellulose membranes due to sulfate groups, which are larger than the hydroxyl groups, which stretch the interactions between the cellulose chains. The sulfate ester formed facilitates the transfer process on the membrane matrix because from within the sulfate, the group can be separated easily and reacts with water, thereby forming protonated water. Moreover, it interacts with protonated water, causing the transfer of protons and increasing the sulfonated nata de pina membrane's proton conductivity. Figure-2 depicts the proton transport system in sulfonated nata de pina. IEC and proton conductivity values of the membrane both rise

with the number of H^+ ions (protons) that can be transmitted.[21-23] From the experimental results of Radiman and Rifathin[11], proton conductivity for Nafion 117 obtained at 80 was 3.9 x 10^{-2} S/cm. The proton conductivity data at the optimum condition (H_2SO_4 1.08 N) from this research was obtained at 1.85 x 10^{-2}/cm. These indicate that the proton conductivity for the sulfonated nata de pina membrane has a value close to that of Nafion 117.

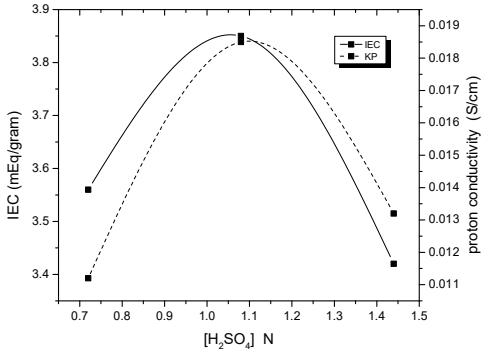

Fig.-1: Effect of Sulfuric Acid Concentration on Sulfonated Nata De Pina Membranes' IEC and Proton Conductivity

The decrease in the conductivity of sulfonated bacterial cellulose membranes at a 1.44 N sulfuric acid concentration was probably due to cross-linking. The crosslinks formed will prevent protons and water from passing through the membrane matrix (Fig.-3). High sulfuric acid concentrations raise the potential of polymer chain crosslinking and make it difficult for ions to flow through the polymer network.[8-10,16,24]

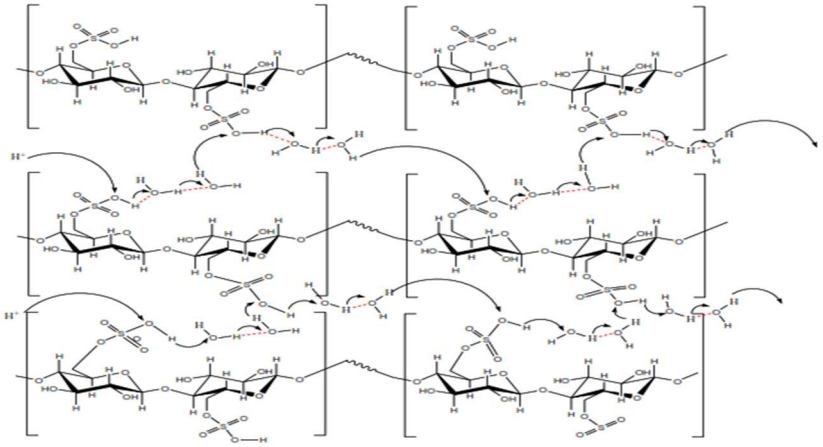

Fig.-2: Schematic of Proton Transfer on Sulfonated Bacterial Cellulose Membranes[8]

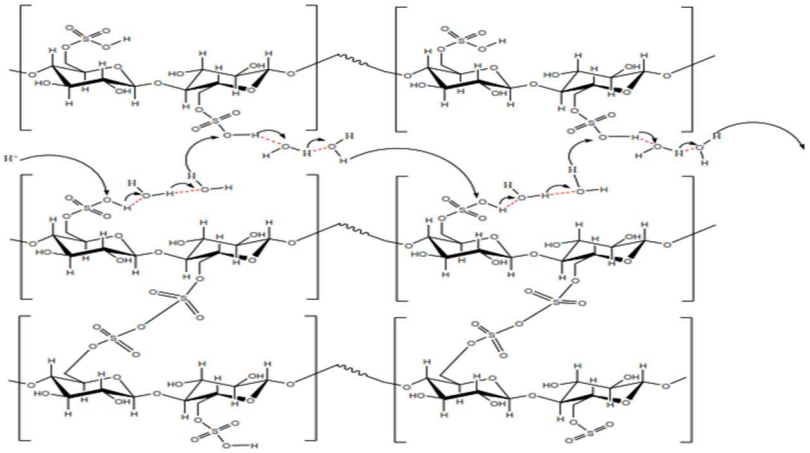

Fig.-3: Schematic of Proton Transfer on a Sulfonated Bacterial Cellulose Membrane with Crosslinks[8]

Effect of Sulfonation on the Swelling Membrane Index

Figure-4 shows that the swelling index of sulfonated nata de pina was reduced by the addition of sulfate groups to the membrane. In Table-1, the electrolyte membrane's water intake ability determines its proton conductivity. The fuel cell membrane should contain a moderate swelling degree for high ion mobility because nata de pina and other polymers benefit greatly from the use of sulfuric acid as a crosslinking agent. At high sulfuric acid concentrations, crosslinked chains can develop, which causes the membrane to become less inflated and lower proton conductivity.

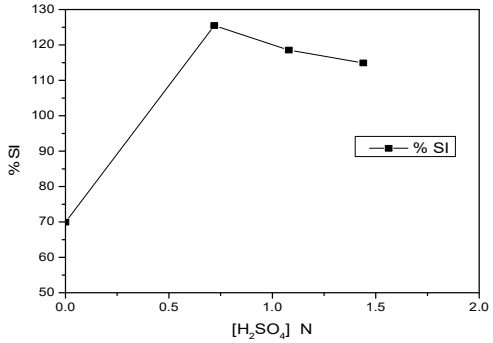

Fig.-4: Effect of Sulfuric Acid Concentration on Sulfonated Nata De Pina Membranes' Swelling Index

Mechanical and Morphological Properties

Table-1 displays the mechanical characteristics of sulfonated membranes using various sulfuric acid concentrations. The membrane's mechanical strength increases with acid concentration but decreases in elasticity as a result of the creation of a crosslinked structure (Fig.-3).

Figure-5 shows the Scanning electron microscopy (SEM) surface morphology of nata de pina. It is concluded that the surface morphology of the membrane still has a regular and good pattern of bacterial cellulose fibers (nata de pina), regardless of sulfonation conditions. Additionally, this morphology shows the resulting membrane's high mechanical properties.[11]

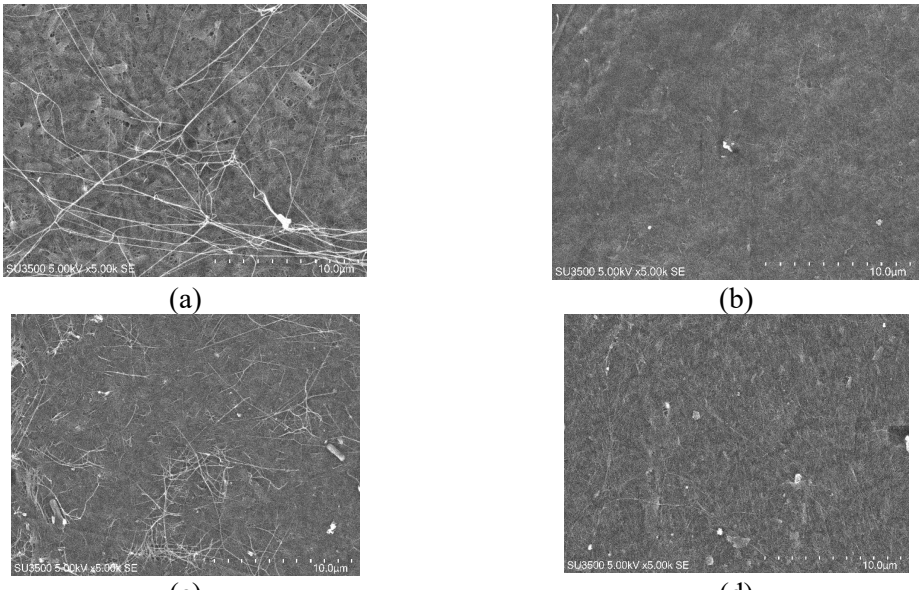

Fig.-5: Photo of Membrane Surface (a) Nata De Pina and (b-d): Utilizing a Quantity of Sulfuric Acid to Sulfonate Nata De Pina b). 0.72 N; c) 1.08 N; d) 1.44 N

Analysis of Nata De Pina Membrane Structure

Figure-6 shows the FTIR spectrum. Some groups experienced vibration at wave number in the T Table. A new peak appears after the sulfonation process at wavenumbers 1338.60, 1373.32, and 1429.25 cm^{-1} are respectively, the stretching vibration of S = O, S – O, and C – O – S. The presence of the C – O – S group

proves that cellulose sulfate has been formed.[25-27] Group of hydroxyls at position C-6 glucose units substituted by sulfate groups, resulting in a network C-O-S.[28]

Table-1: Sulfonated Nata de Pina Membrane Mechanical Characteristics

Sulfuric acid concentration, N	Voltage (MPa)	Strain (%)
0	24.98	3.3
0.72	37.14	2.8
1.08	45.55	2.5
1.44	67.18	1.3

Table-2 The ATR-FTIR Spectra of Nata de pina

Compound	Wavenumber (cm^{-1})	Group
Nata De Pina	3377.36	O-H
	1163.08	C–O–C
	1031.92	C-O (primary alcohol)
Sulfonated Nata de Pina	3390.86	O – H
	1172.72	C – O – C
	1429.25	C – O – S
	1373.32	S – O
	1338.60	S=O (sulfonate)
	1089.78	C-O (alcohol primer)

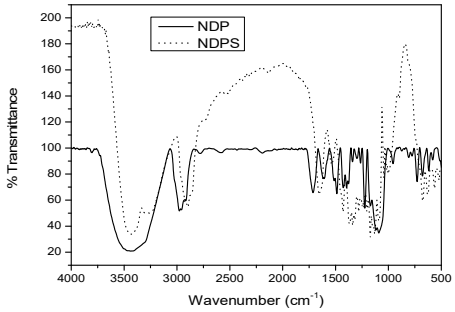

Fig.-6: FTIR Spectra of Sulfonated Nata De Pina (NDPS) and Nata De Pina (NDP)

In Fig.-7, the peak at 0.25 keV and 0.52 keV is generated from carbon and oxygen atoms in the NDP and NDPS, while the sulfur atom is detected in the NDPS at 2.25 keV.

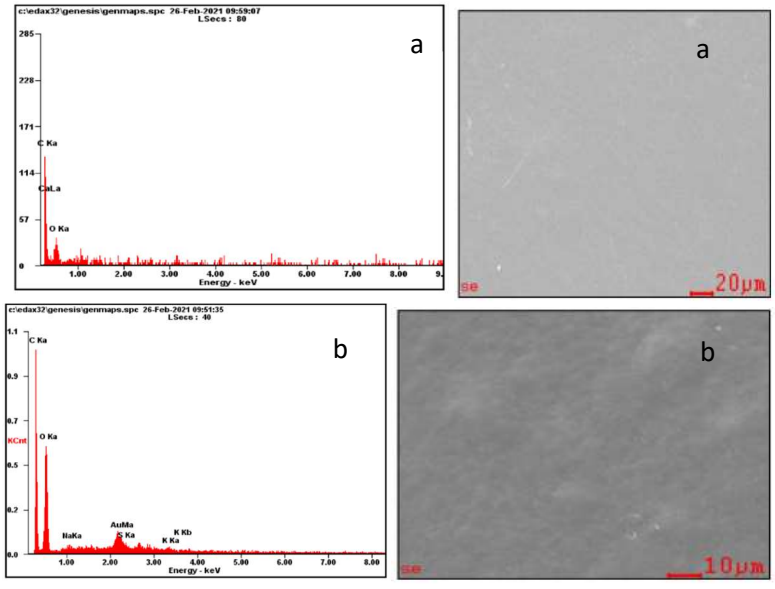

Fig.-7: SEM-EDX of Membranes Made of (a) Nata De Pina and (b) Sulfonated Nata De Pina

Also, C, O, and S have average mass percentages of 53.56%, 44.75%, and 0.54 %, respectively. This characterization proves that the sulfonation of nata de pina to form cellulose sulfate has been successfully formed.[11]

CONCLUSION

This research employed an electrolyte polymer membrane from pineapple peel waste as a renewable and environmentally friendly natural resource. Results of the research showed that sulfonation makes the polymer membrane from nata de pina. Additionally, synthesizing the nata de pina and the resulting sulfonated products involves using less expensive and eco-friendly techniques and materials. Therefore, the membrane's proton conductivity reaches $1.85x10^{-2}$ S/cm at optimum sulfonation.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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