PHOSPHORYLATED NATA DE PINA AS POLYMER ELECTROLYTE MEMBRANE IN FUEL CELLS

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ABSTRACT

The objective of this research is to prepare and determine the characteristics of nata de pina membrane and phosphorylated nata de pina membranes as polymer electrolyte membranes in fuel cells. In this work, pineapple fruit skin juice was fermented by *Acetobacter xylinum* then formed into a nata de pina membrane. Those membranes are phosphorylated through the addition of phosphoric acid solution with varying concentrations (1.5 M, 2 M, and 2.5 M). The membranes were characterized by several methods, such as functional group analysis by FTIR, ion exchange capacity, swelling degree, contact angle, mechanical properties, and morphological analysis. The characterization results showed optimum membrane conditions using 1.5 M of phosphoric acid, with an ion exchange capacity of 8.6400 mEq / g and a swelling index of 152.25%. The tensile strength of the produced membranes increases by the addition of phosphoric acid where the optimum result in tensile strength of 54.16 MPa and elongation of 5%, and the optimum results in the contact angle test of nata de pina membrane is 120.4°. These results prove that the phosphorylated nata de pina membrane can be used as a polymer electrolyte membrane in fuel cells.

Keywords: Fuel Cells, nata de pina, Phosphorylated, Polymer Electrolyte Membranes.

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INTRODUCTION

Energy is a basic need that cannot be separated from human life. Along with the development of science and technology and the rapid industrialization of the world driven by the rapid rate of population growth in demand for energy has also increased. However, the availability of energy supply doesn't meet the current energy demand, so the energy crisis cannot be avoided. Indonesia is a country with considerable energy consumption in the world at around 7% per year. Where the energy source which is quite high is almost 96.5% fulfilled from fossil fuels.¹ Of the total, 52.50% is the fuel oil that is not renewable.² One solution to overcome this problem is the fuel cell.

A fuel cell is a device that generates electricity directly through an electrochemical process.³ Fuel cells do not use fossil fuels as energy sources and are environmentally friendly.⁴ They are a special type of electrochemical cell in which chemical reactions will produce electricity continuously through hydrogen oxidation with oxygen as oxidizing agents.^{5,6,7,8} They have several advantages, which are environmentally friendly (free of CO₂ emissions) and have high efficiency (50-80%).⁹ The Fuel cells generally have the same components as batteries, consisting of two electrodes and are separated by electrolytes. Nevertheless, They are very different from batteries because these devices produce electrical energy through electrochemical reactions and are not devices for storing energy.^{10,11} Electrolytes used in fuel cells, especially PEMFC (Polymer Electrolyte Membranes Fuel Cells) are a type of proton exchange membrane that functions as an ion barrier negatively charged and is permeable to cations or protons.¹² The electrolyte polymer membrane commonly used today is Nafion®. Nafion® has a high ion exchange capacity, good chemical and physical stability. However, the Nafion® has several disadvantages, including restricted working temperatures that only hold up to 80 °C, not environmentally friendly because it's made of fluorinated carbon chains, and the price is also expensive.¹³ Therefore, a membrane design with good ion exchange quality, chemical and physical stability, lower cost, and environmentally friendly is required.

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One alternative membrane that potential to be used as polymer electrolyte membranes to replace Nafion® in fuel cell applications is the nata de pina membranes. Nata de pina or cellulose bacterial is a natural polymer that is generally produced from the fermentation of pineapple juice using *Acetobacter xylinum*.¹⁴ However, in this study pineapple fruit skin was used as the material for making nata de pina. This is due to the pineapple fruit skin is part of the pineapple that is less functional and is usually only disposed of as organic waste.¹⁵ The amount of pineapple waste reaches 60% of the total pineapple production. The proportion of pineapple canning waste consists of 56% skin, 17% crown, 15% shoots, 7% liver, and 5% pineapple pulp.¹⁶ Pineapple skin contains 81.72% water making it easy to rot if not utilized.¹⁷

The pineapple skin is chosen because the material is easily obtained. According to the data, pineapple production in Indonesia in 2016, 2017, and 2018 has increased. Pineapple production in 2016 was 1,396,153 tons / year, in 2017 which was 1,795,986 tons / year and in 2018 with the highest production of 1,805,506 tons / year.¹⁸ Nata is commonly used as low-calorie food, 2.5% fiber content, and has a water content of up to 98% formed by adding the bacteria *Acetobacter xylinum*.^{14,19} *Acetobacter xylinum* is a unique bacterium different from the other acetic acid bacteria because the pore cells can synthesize and produce cellulose fibrils.¹⁵ The high reducing sugar content in pineapple skin waste can be used as nata the pina.

The structure of nata de pina contains many free hydroxy groups so that it is hydrophilic.²⁰ The hydrophilic property can be utilized as an ion exchange in the membrane. Many studies have proven that membranes made from bacterial cellulose (nata) have the potential to be used instead of the Nafion® membrane. The membrane is then modified to improve proton conductivity.^{4,21} Modification of the membrane can be done through a phosphorylation reaction to the membrane. Phosphorylation is a chemical modification carried out to increase the ability to transfer protons of a polymer membrane by exchanging the hydroxyl groups with phosphoric groups on C-6 atoms.^{12,22}

Based on the background, this research carried out the preparation and the characterization of the nata de pina membranes and the phosphorylated nata de pina membranes were conducted to determine the effect of phosphoric acid concentration on the membranes. The preparation of nata de pina is from pineapple fruit skin waste by the addition of the bacterium *Acetobacter Xylinum*, then made into a thin membrane by pressure method. Nata de pina membranes are modified through phosphorylation reaction. It is hoped that with the presence of phosphorus groups, the nata de pina membrane's ability to transport protons will increase.

EXPERIMENTAL

Equipment and Materials

The equipment used in this research were analytical scale, fermentation containers, electric baths, chemical glass, filters paper, blenders, sterile paper, pH meters, WiseBath water baths, hydraulic press, oven, spatula, burette, stative and clamp, contact angle meter, ASTM D638-03 tensile strength test instrument, Fourier Transform Infrared (FTIR) spectrophotometer and SEM Jeol JSM 6360 LA. Materials used in this research were pineapple skin waste from the pineapple seller around Palu City, sugar from the local traditional market, *Acetobacter xylinum* starter from the local industry. Other chemicals such as urea ((NH₂)₂CO), acetic acid (CH₃COOH), sodium hydroxide (NaOH), hydrochloric acid (HCl), sulfuric acid (H₂SO₄), phosphoric acid (H₃PO₄) were obtained from E. Merck.

Preparation of Nata de Pina Membranes

Nata de pina was prepared according to the procedure carried out by Hamad et al.¹⁵ by adding water with a ratio of 1:2, adding nutrients in the form of 17.5 g of sugar and 3 g of urea, and the length of inoculation was 10 days. The resulted gels were then washed by adding boiling water for 15 minutes. Washing was continued by using 1% NaOH (w/v) solution and 1% CH₃COOH (v/v) for 24 hours to neutralize nata de pina.³¹ The final step of washing was done with running water until the pH was neutral. The nata de pina was finally pressed using a hydraulic press at room temperature under an applied pressure of 100 bar for 5 minutes then dried at room temperature to form a thin film of dry membranes.

Phosphorylation of Nata de Pina Membranes

Phosphorylation of nata de pina membranes was conducted using similar procedures by Eldin, et al.²³ Pieces of the nata de pina membranes were immersed in a solution of phosphoric acid at a concentration of 1.5 M then reacted in a water bath for 10 hours at 55°C. The resulting phosphorylated membranes were

washed with deionized water. The phosphorylation process was repeated by increasing the concentrations of phosphoric acid, namely 2 M and 2.5 M while other conditions were kept constant.

Characterization of Phosphorylated nata de pina Membranes

The ion exchange capacity determination was following the Radiman & Sarinastiti procedure.³¹ The procedure was using acid-base titration. Weighed samples soaked in 40 mL of 0.1 M HCl solution for 24 hours at room temperature. Then the membranes were neutralized and soaked again and were immersed in 40 mL of 0.01 M NaOH solution for 12 hours. 10 mL of the solution was titrated by 0.004 M sulfuric acid solution. The Ion Exchange Capacity (IEC) was calculated using eqn.-1.

$$IEC = \frac{(V_b - V_s)[Acid].f_p}{massa} \quad (1)$$

Where:

IEC = Ion Exchange Capacity (mEq/g)

V_b = Amount of H_2SO_4 solution to neutralize the blank solution (mL)

V_s = Amount of H_2SO_4 solution to neutralize membrane (mL)

[Acid] = Concentration of H_2SO_4 (M)

F_p = Dilution factor

m = Sample mass (g)

The Swelling index was following the Radiman & Rifathin procedure.⁴ Swelling index aims to determine the hydrophilicity of the membrane. For the Swelling index measurement, the sample was weighed to determine its mass, then soaked for 24 hours in deionized water. The membranes' surfaces were then dried using a tissue. Then the mass was weighed again. The procedure was repeated until the membranes reach a constant weight. The swelling index (SI) was calculated using eqn.-2.

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

Where: m = mass of dry membrane (g), m_o = mass of wet membrane (g)

Contact angle on the nata de pina membrane and the phosphorylated nata de pina membranes were performed used a contact-angle meter. The membranes were put on the plate of this equipment. Then, 15 μ L of water was dropped by using a syringe on the surface. The lamp was put on to get the projection of the droplet contour on a screen. The water contact angle is then measured.⁴

The mechanical properties consisted of two tests, namely the tensile strength and elongation. In tensile strength, the phosphorylated nata de pina membranes and nata de pina membranes were carried out using specimens from each sample and mounted between machine grips. Tensile strength is determined based on the maximum load when the membrane is broken.²⁴ For elongation, the elongation percentage is based on the elongation of the film when the film is broken.²⁵

Functional group analysis of the nata de pina membrane and the phosphorylated one were analyzed by ATR-FTIR (Fourier Transform Infra Red) using Tensor-27 Bruker spectrophotometer. One milligram of membrane powder was mixed with KBr and mechanically pressed to become KBr pellets. The sample was then put into the sample holder and scanned between 4000 and 500 cm^{-1} .³¹

Morphological analysis using Scanning Electron Microscope (SEM) was aimed to get information directly about topography (surface texture of the sample) and morphology (shape and size). Samples were analyzed using SEM Jeol JSM 6360 LA.

RESULTS AND DISCUSSION

Preparation of Nata de Pina Membranes

The basic ingredient of making nata de pina membrane is nata de pina gels made from pineapple fruit skin with the addition of bacteria *Acetobacter xylinum* and nutrients to support the bacteria growth. After 10 days of inoculation, the resulting nata de pina gels have a thickness of 0.1-0.2 cm and physical characteristics textured springy, slippery, and transparent (Fig.-1). The thin membrane is then produced from those nata de pina gels (Fig.-2).

Effect of Phosphorylation on Ion Exchange Capacity (IEC)

IEC shows the density of ionized hydrophilic groups in the polymer matrix which is responsible for the ionic conductivity of the membrane.²⁶ The IEC of the polymer electrolyte membrane is an important

characteristic of fuel cell applications because it shows how much ions can be transferred or delivered to the membrane. Data on the effect of phosphoric acid concentration on IEC is shown in Fig.-3.

Fig.-1: Nata de Pina Gels

Fig.-2: Nata de Pina Membrane

Figure-3 shows the IEC values of the nata de pina membrane have increased after the phosphorylation process. This shows how many phosphoric groups are attached to the membrane so that it binds more protons and facilitates ion transfer.²⁷ As more H^+ (proton) ions can be transferred, it is expected that the proton conductivity value of the membrane will also increase.^{19,28} This could also be due to triprotic phosphoric acid or the ability to self-ionize. The ability of phosphoric acid to self-ionize into $H_2PO_4^-$ and HPO_4^{2-} makes the ionic conductivity increase because $H_2PO_4^-$ and HPO_4^{2-} are effective proton carriers.^{29,22} However, the addition of phosphoric acid concentrations decreases IEC values. It caused by the addition of the amount of phosphoric acid causing cross-linking as shown in Fig.-4 where the oxygen atom in the phosphoric acid will crosslink so that it will reduce the place to bind the proton.³⁰ The $H^{\delta+}$ ions from $-O^{\delta-}$ in the phosphate group can also go easily and interact with water which produces protonated water. $O^{\delta-}$ will also interact with other protonated water so that it will reduce the place to bind to protons.⁴ Also, the formation of hydrophilic channels in cellulose phosphate is greater than cellulose, because the phosphate group is greater than hydroxyl. Interaction between molecules between polymer chains will decrease and interaction between phosphate and water will increase.³¹

Fig.-3: Effect of Phosphoric Acid Concentration on Ion Exchange Capacity (IEC)

Effect of Phosphorylation on Swelling Index

The swelling index shows how easily the water molecules enter the membrane matrix and also can be used to determine the permeability of the polymer electrolyte membrane ions or membrane hydrophilicity.^{31,32} The results of the swelling index are shown in Fig.-5.

The swelling index of a membrane expresses the membrane's ability to absorb water or its hydrophilicity. The higher swelling index means the membrane's ability to absorb water is greater. In this study, the highest swelling index was in the phosphorylated nata de pina membrane with a concentration of 1.5 M phosphoric acid that is equal to 152.25%. This correlates with the membrane IEC value which is caused by the number of phosphate groups attached to the membranes. A large number of phosphate groups causes bonds between

cellulose chains to become stretched and form a hydrophilic channel that facilitates proton flow.²⁷ Proton transfer mechanism on the membrane can be seen in Figure 6. The decrease in the degree of swelling that occurs in the addition of concentrations of 2 M and 2.5 M phosphoric acid caused by higher concentrations of phosphoric acid can be formed cross-linking where oxygen atoms in the phosphorus group will crosslink (Fig.-4) so that it will reduce the place to bind to protons.^{30,31}

Fig.-4: The Cross-linked Chain on phosphorylated nata de pina Membranes.⁴

Fig.-5: Effect of Phosphorylation on Swelling Index (%)

Effect of Phosphorylation on Contact Angle

The contact angle is one of the criteria that can be used to analyze the wetting or hydrophobic properties of membranes against liquids.³⁴ Contact angle test results are shown in Fig.-7.

Figure-7 shows that due to the concentration of phosphoric acid increases, the contact angle is greater. This is because phosphorylated membrane has replaced the hydroxyl group with a less hydrophilic phosphate group. This data also shows that the hydrophilicity of the phosphorylated nata de pina membrane and the nata de pina membrane is classified as low because the contact angle values are above 90°, making it difficult for liquid to wet their surfaces.³⁴

The Mechanical Property of Phosphorylated nata de pina Membranes

Tensile strength and elongation test methods on the membrane is a type of mechanical properties test. The mechanical properties test in this study was conducted on nata de pina membrane and phosphorylated nata de pina membranes with variations in concentration to see the effect of phosphorylation on membrane

strength and to compare the strength of nata de pina membrane with other polymer electrolyte membranes. Data on the results of the tensile and elongation tests are shown in Table-1.

Fig.-6: Proton Transfer Mechanism on Phosphorylated Cellulose Bacterial.³³

Fig.-7: Effect of Phosphorylation on Contact Angle (°)

Table-1: Mechanical Properties of Nata de Pina Membrane and Phosphorylated Nata de Pina Membrane

[H ₃ PO ₄], M	Tensile Strength, MPa	Elongation, %
-	24,98	3,3
1,5	37,81	5,0
2	48,75	3,3
2,5	54,16	5,0

Table-1 shows the results of the mechanical properties of the nata de pina membrane against the addition of phosphoric acid concentration. In general, the addition can improve the mechanical properties of the membrane except in the elongation of the addition of 2 M phosphoric acid there is no increase. The tensile strength results in Table-1 show that the strength of the membrane increases with the increase in the concentration of phosphoric acid. The nata de pina membrane with the addition of 2.5 M phosphoric acid has the highest tensile strength. The increase in the value of the tensile strength indicated indicates the occurrence of the force applied to the membrane until the membrane is broken. The increased tensile strength of the membrane after phosphorylation indicates a tighter membrane structure, meaning that the distance between the molecules in the membrane is getting tighter.³⁵ For elongation / elongation the resulting data results in a distorted trend. This can be caused by a very thin membrane thickness. However,

in general, phosphorylated does not reduce membrane elasticity. The elongation of % shows how long the membrane can be stretched by comparing the maximum length at the break with the initial length of the membrane.²⁵

Structural Analysis of Original Nata de Pina and Phosphorylated Nata de Pina Membranes

Analysis of functional groups using Fourier Transform Infrared (FTIR). FT-IR analysis aims to identify functional groups of the original nata de pina membrane and phosphorylated nata de pina membrane. The sample used in the functional group analysis consists of nata de pina membrane and nata de pina membrane phosphorylated so that the success of the phosphorylation reaction can be seen. The absorption value of the infrared membrane of the nata de pina membrane and the phosphorylated nata de pina membranes can be seen in Fig.-8.

Fig.-8: FTIR Spectrum of Nata de Pina Membrane (NDP) and Phosphorylated nata de pina Membrane (NDPF3)

Based on the results of the FTIR analysis shown in Fig.-8 it can be seen that the nata de pina membrane and the phosphorylated nata de pina membrane have functional group characteristics similar to cellulose, namely the vibration of the C-H group in the surrounding area 1427.32 cm^{-1} , the vibration of C-O stretching group in primary alcohol and C-O forming β -1,4-glycosidic bonds in the region $1112,93\text{--}1161,15\text{ cm}^{-1}$, vibration O-H group strain on the area 3352.28 cm^{-1} and group C=C in the absorption area 1645.28 cm^{-1} .^{36,37,38} The success of the modification in phosphorylated nata de pina membrane can be seen from the presence of new P-O-H uptake peaks in the area 2364.73 cm^{-1} , C-O-P group vibrations in the absorption band region $999,13\text{--}1058,92\text{ cm}^{-1}$ and O-P-O vibrations at 495.71 cm^{-1} .^{39,40} C-O-P, P=O and P-O groups are donated of phosphoric acid which is added during membrane modification. Phosphoric acid is bound to C-6 atoms in cellulose.⁴

Morphological Analysis of Phosphorylation Nata de Pina Membranes

Morphological analysis was performed on the sample nata de pina membrane and phosphorylated nata de pina membrane was 1.5 M and 2.5 M using a Scanning Electron Microscope (SEM) tool. The analysis is carried out on the image with the same magnification so that it can be compared to the structure of the fibers in the membrane.³¹

Figure-9 shows the surface of the bacterial cellulose membrane before and after phosphating. From the picture, it can be seen that bacterial cellulose fibers become smoother after phosphorylation. This correlates with the mechanical properties of the membrane where the smaller size of the cellulose fibers, the higher the tensile strength value produced.²⁵ The image shows the changes in which the cellulose fibers to be fading after phosphorylation. This is due to the presence of phosphate groups on the membrane surface.

CONCLUSION

From this work, it can be concluded that as a waste, pineapple peel has a potential resource to be used as polymer electrolyte membrane materials by phosphorylation modification. This result shows that

phosphorylation process can occur by simply way used a water bath. The synthesis of nata de pina and its phosphorylated products have also used cheap and environmentally-friendly materials and chemical techniques. The characterization results showed optimum membrane conditions using 1.5 M of phosphoric acid, it can be seen that the ion exchange capacity of 8.6400 mEq / g and swelling index of 152.25%. These results prove that the phosphorylated nata de pina membrane can be used as a polymer electrolyte membrane in fuel cells.

Fig.-9: SEM Photos: (A) Surface of nata de pina Membrane, (B-C) Surface of Phosphorylated nata de pina using Phosphoric Acid Concentration of (B) 1,5 M, (C) 2,5 M

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