Promising Potential of Eugenol (Clove) Based Organic Membrane for Polymer Electrolyte Membrane Fuel Cell

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Abstract. Fuel cell is one of alternative method to replace fossil fuel energy. The important component of fuel cell is a membrane that used for separating cathode and anode also as a proton conductor. The purpose of this research is to produce polymer electrolyte membrane from poly (eugenol sulfonate) (PES) as polymer matrix, characterize the resulting membrane analysis using ionic properties analysis by calculating ionic conductivity using impedance spectroscopy, ion exchange capacity (IEC), solvent absorption analysis by calculating water uptake and methanol permeability, and studying mechanism Proton transport that occurs on the membrane. This research was initiated by making polymer of PES, and then fabrication and characterization of electrolytic polymer membrane. The formed membrane has an optimal proton conductivity of 0.00095 S.cm⁻¹ with PES composition of 22% (wt).

1. Introduction

The continuous used fossil fuels as a non-renewable natural resource that will eventually run out. Another problem that is also caused is the occurrence of environmental pollution and global warming. Therefore, it is necessary to find alternative energy that is sustainable and economical with low emissions. One alternative energy that has received attention to be developed is the fuel cell, which have an electrochemical device that directly converts chemical energy from redox reactions into electrical energy [1].

Direct methanol fuel cell (DMFC) is a type of fuel cell that uses methanol as an energy source, DMFC can generate great power, have a simple design, easy operation, light weight, low pollution, and are easy to transport. Therefore, DMFC has been widely raised as a source of clean energy that is convenient to used [3,4,5]. The basic components of this fuel cell are two electrodes (cathode and anode) which are separated by a membrane [8]. The anode directly acts as a catalyst (electro-catalyst) which accelerates the methanol conversion reaction. The catalyst that is usually used is platinum [11,12]. The workings of DMFC can be seen in Figure 1. At the anode side, methanol and water are injected into the reaction batch at a constant speed. Collision with the catalyst helps the catalytic conversion of methanol into protons, CO2 and electrons. CO2 gas is removed from the system, protons move across the membrane to the cathode which then reacts with oxygen to produce water. The pile of electrons at the anode produces a potential difference that forces electrons to flow in a current circuit, then arrives at the cathode, thus completing the reaction for the formation of water molecules [13].
One of the important components of DMFC is a polymer electrolyte membrane (PEM) which functions as an electrolyte that separates the cathode and anode. The polymer membrane is an important component where there is proton conduction activity. PEM is a thin polymer sheet that can pass hydrogen ions but is able to hold electrons. The reaction that occurs at the anode produces protons which in the next step will react with oxygen atoms at the cathode. Protons will pass through the electrolyte membrane to the cathode, while electrons will pass through the external circuit and generate electricity [14,15].

Commercial polymer membranes that have been used so far are Nafion, the type is non-porous, isotropic cross-section, and the thickness is 50-500 μm. Nafion's ability to separate reactants and proton conductors is quite efficient with a conductivity of about 0.1 S/cm [17]. However, Nafion's weakness is up to 80°C so that it only affects the component resistance so that the membrane performance will decrease. This decrease is due to membrane dehydration, ionic conductivity, decreased affinity with air, mechanical properties, swelling properties, fuel permeation decreased evaporation. As a result, various studies have been carried out as an effort to improve membrane performance for fuel cell applications. Nafion is also an expensive polymer (US$800 – 2,000 m-2) so that the use of this material becomes an obstacle to commercialize PEMFC and DMFC [18]. Besides being expensive, the polymer structure is not environmentally friendly because it is not easily biodegradable in nature. In order to increase the effectiveness of membranes in fuel cells and reduce production costs, the development of membrane polyelectrolytes in fuel cells is as follows: modification of the conventional structure of polymeric PFSA membranes, alternative sulfonated polymers (hydrocarbon), acid-base complex membranes, composite membranes (organic- inorganic), polymer membrane blending [17]. Several polymers containing sulfonated aromatic substitutes that have been widely studied include polybenzimidazole, polyetherimide, polyetherketone, polysulfone, polyether sulfone because they are resistant to high temperatures and have good stability in the oxidative environment. The polymer with aromatic C-H strength has a strength of 435 kJ/mol, which is greater than the aliphatic C-H of 350 kJ/mol [19]. The greater the strength, the greater the temperature required to determine it, so that the temperature stability of the material will be greater.
The potential for abundant natural resources is a great opportunity in creating alternative and renewable energy sources such as fuel cells. One of the abundant natural resources is clove oil. The main component in clove oil which reaches 70-96% is eugenol [9]. Several previous studies have synthesized eugenol-derived polymers, one of which is polyeugenol sulfonate (PES). PES is used as an acid catalyst for citronellal cyclization reactions and lipophilic anionic additives on Ion Selective Electrodes (ESI) [10]. However, the polymer that binds the sulfonic acid group (–SO3H) has not yet been applied as an electrolyte polymer membrane material for direct methanol fuel cells. In this study, a polymer was used as a matrix, namely polyeugenol sulfonate. PES can be synthesized from eugenol containing allyl groups (-CH2-CH=CH2), phenol (-OH), and methoxy (-OCH3) [9]. The incorporation of PES with polysulfone applied to proton exchange fuel cells has been reported by previous researchers who showed proton conductivity results of 10-6 S/cm at 30 °C and the DTA thermogram showed that the membrane underwent a change in geometric structure at a temperature of 155-170 °C and SOx release at a temperature of 220-325°C[19]. The polymer that binds the sulfonic acid group (–SO3H) in pure PES as a matrix has not yet been applied as an electrolyte polymer membrane matrix. Therefore, in this research, a promising polyeugenol sulfonate membrane will be made to be applied to direct methanol fuel cells.

2. Material and Method

2.1 Material
The material or polymer used is eugenol from Merck. Sulfuric acid, ice cubes, deionization water are used for process sulfination. Sodium chloride and sodium hydroxide are used for determine Ion Exchange Capacity (IEC)

2.2 Polyeugenol Synthesis
The synthesis of eugenol polymerization was carried out using the method used by Ngadiwiyana [20]. The polymers that have been obtained are then analyzed by thin layer chromatography, molecular weight determination using the Ubbelohde Viscometer

2.3 Polyeugenol sulfonated (PES) synthesis
The sulfination process for synthesis of polyeugenol sulfonated with H2SO4 using the method of Handayani and Amri [10,19]. The obtained PES was analyzed as in the polymer obtained from polyeugenol.

2.4 Fabrication membranes
PES is stirred with solvent until dissolved. The membrane matrix components were dissolved in a beaker glass for 12 hours while heated at 80 °C and stirred with a magnetic stirrer. The finished polymer mixture was then formed into a thin membrane using the direct casting method and dried at 800 C for 36 hours. After drying, they were soaked in 9M H2SO4 for 100 hours [21]. All membranes were printed on a membrane thickness of 0.2-0.4 mm.

2.5 Characterization
Membrane characteristics were carried out in ionic property analysis by

2.5.1 Proton Conductivity
The proton conductivity of each membrane variation was analyzed using Electrochemical Impedance Spectroscopy (EIS, Autolab instrument). The membrane was prepared under the conditions hydration, namely soaking the membrane in 10 M H2SO4 for 24 hours. Then membrane is inserted in the membrane clamping chip and heated to 80-900C. The analysis process is carried out using the two probe method, in the frequency range 1-106 Hz. The proton conductivity of the membrane is calculated using Equation (1) [24, 25].
\[ \sigma = \frac{L}{R \times A} \]  

where \( \sigma \) is the proton conductivity of the membrane (S.cm\(^{-1}\)), \( L \) is the thickness membrane (cm), \( A \) is the membrane surface area (cm\(^2\)) and \( R \) is the resistance value membrane (ohms).

### 2.5.2 Water Uptake and Methanol Uptake

Water Uptake and Methanol Uptake determined by measuring the membrane in wet and dry conditions. First, the membrane was dried at 50°C for 24 hours weighed. Furthermore, the membrane is immersed in water to determine water absorption (water uptake) and immersed in methanol to determine methanol uptake (methanol uptake) on the membrane for 24 hours until the membrane is hydrated maximum. The membrane is then removed from the water or methanol bath and cleaned using a tissue to remove excess water droplets or methanol on the surface. Water and methanol uptake are then calculated by using Equation (2) [33].

\[
\text{Uptake (\%) = } \left( \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \right) \times 100 \%
\]  

where \( W_{\text{dry}} \) and \( W_{\text{wet}} \) are the mass of the membrane before and, respectively after soaking (grams).

### 2.5.3 Ion Exchange Capacity (IEC)

The membrane is analyzed for the ion exchange capacity (IEC) with using the titration method. The membrane is first dried in an oven at 50°C for 24 hours and the mass was weighed. Next membrane immersed in 50 mL of 1M NaCl solution so that the exchange of H\(^+\) ions from membrane with Na\(^+\). The solution resulting from the immersion is then dripped with phenolphthalein indicator and titrated using 0.01 M. NaOH until the equivalence point is reached. IEC is calculated using Equation (3) [4,24].

\[
\text{IEC} = \frac{V \cdot M}{W_{\text{dry}}}
\]

Where \( M_{\text{NaOH}} \) (mol.L\(^{-1}\)) and \( V_{\text{NaOH}} \) (L) are the concentration and volume of NaOH that used for the titration and \( W_{\text{dry}} \) is the dry membrane mass (grams).

### 2.5.4 Water Contact Angle (WCA)

Analysis of the absorption properties of the solvent by calculating water uptake the tendency of the material to like water or hydrophilicity in the membrane structure can be determined through analysis using the Water Contact Angle (WCA, OCA15 Pro, Data Physics). Membrane samples were prepared in flat and dry conditions with a size (5 x 40) mm. The membrane is placed on the clamp in a straight position. The test process is carried out using a water drop technique (sessile drop) and the degree is analyzed generated between the water droplet and the membrane surface. The state of the water droplets seeps into the membrane structure analogous to the tendency of hydrophilicity of the membrane.

### 2.5.5 Methanol Permeability

The permeability of methanol was measured using a two-compartment diffusion cell which illustrated in Figure 3.2. Compartment A is filled with 1M .Methanol solution and compartment B filled with deionized water. Furthermore, the membrane that has been prepared with a flat surface and condition, placed between two compartments, A and B. Samples in compartment B were taken with pipette every 30 minutes, for 3 hours. Then all the sample solutions that have been obtained in a closed container.
Next, the solution is analyzed using High Performance Liquid Chromatography (HPLC). Score methanol permeability can be calculated using Equation (4) [4,24].

\[
P = \left( \frac{\Delta C_B}{\Delta t} \right) \left( \frac{LV_B}{AC_A} \right)
\]

\[\text{Equation (4)}\]

\(P\) is the methanol permeability of the membrane \((\text{cm}^2\cdot\text{s}^{-1})\), \(C_B/\Delta t\) is the slope variation of methanol concentration in compartment B with a function of time \((\text{mol. L}^{-1}\cdot\text{s}^{-1})\), \(L\) is the thickness of the membrane \((\text{cm})\), \(V_B\) is the volume of water at compartment B \((\text{cm}^3)\), \(A\) is the membrane surface area \((\text{cm}^2)\), and \(C_A\) is concentration of methanol in compartment A \((\text{mol.L}^{-1})\), as well as studying the proton transport mechanism that occurs in the membrane.

2.5.6 Swelling ratio

The next analysis of membrane properties is the degree of swelling (swelling ratio) is determined through the process of measuring the length of the membrane in the wet and dry. First, the membrane was dried at 50°C for 24 hours then measure the length. The membrane is then immersed in deionized water for 24 hours until the membrane is maximally hydrated. The membrane is then removed of the soaking water and cleaned using a tissue to remove excess water droplets on the surface. The next degree of swelling calculated using Equation (5) [24, 25].

\[
\text{Swelling ratio} = \left( \frac{l_{\text{wet}} - l_{\text{dry}}}{l_{\text{dry}}} \right) \times 100\%
\]

\[\text{Equation (5)}\]

where \(l_{\text{dry}}\) and \(l_{\text{wet}}\) are the lengths of the membrane before and after immersion \((\text{cm})\)

3. Result and Discussion

First, eugenol was put into a beaker, then added concentrated sulfuric acid (98%) dropwise until a gel is formed. The reaction is exothermic and emits an odor. The gel that has been formed then comes to room temperature and turns into a solid. Residue obtained with water until neutral, then dried and weighed. The physical form that changes from a pale yellow liquid eugenol to a purple-black solid indicates that eugenol has been successfully polymerized and sulfonated. The appearance of the results of thin layer chromatography Fig 2 also succeeded in showing the retention factor (Retardation Factor) \(R_f\) which was different from eugenol, polyeugenol and poly eugenol sulfonate in comparison eluents of chloroform and ethanol are 3: 1.

![Figure 2](image-url)

**Figure 2.** Thin Layer Chromatography of Eugenol, Polyeugenol and Polyeugenol sulfonate in a row from left to right

The physical appearance of polyeugenol and polyeugenol sulfonate shows the similarity that they are both solid blackish purple. Over time, the gel will change its shape to solids. The difference can be seen from the Thin layer chromatography (TLC) results, namely that there is a difference in the migration distance of the analyte from the starting point or \(R_f\). It can be concluded that eugenol,
polyeugenol and poly eugenol sulfonate are different compounds. The Rf value in thin layer chromatography can be used to identify compounds. If the identification value of Rf has a different value, then these compounds have different properties or different compounds [30,31,32].

In this study, polyeugenol sulfonate membranes were produced from various compositions (12, 17, and 22) % w/w. The PES membrane that has been produced is characterized by calculating ionic conductivity, ion exchange capacity (IEC), analysis of the absorption properties of the solvent by calculating water uptake and methanol permeability. PES membrane with 22 wt.% is the best composition that promises to be a PEM for DMFC application, based on table 1 for membrane capability analysis and table 2 which presents the methanol permeability and proton conductivity of the membrane. Water absorption and methanol uptake are parameters for the membrane in diffusing ions and methanol. 

Water uptake and methanol uptake are parameters for the membrane in diffusing ions and methanol. The swelling ratio (SR) Swelling behaviors were determined by measuring the weight and dimensions (thickness and area) difference between the fully hydrated and completely dried membranes [22]. The contact angle (CA) is the degree for hydrophilic or hydrophobic materials. Ion exchange capacity (IEC) is defined as the fixed billion of exchange groups per gram of polymer, usually corresponding to the number of sites for proton transfer [23]. Proton conductivity is one of the most important factors for proton membranes used in fuel cells. In general, proton transport in a hydrated polymer matrix is described according to two main mechanisms: "proton hopping" or "Groththus mechanism" using and "diffusion. Methanol permeability of the membranes was obtained by measuring the diffusion behavior across the membranes under the concentration difference. Water uptake($W_{up}$), methanol uptake, membrane swelling ratio (SR), water contact angle (CA), ion exchange capacity (IEC), proton conductivity and methanol permeability are the main characteristics of membranes that need to be calculated for DMFC application.

| Data | Composition | Membranes PES (%) | Water uptake (%wt) | Methanol uptake (%wt) | swelling ratio (%) | IEC (mmol/g) | Contact Angle (°) |
|------|-------------|--------------------|--------------------|-----------------------|--------------------|--------------|------------------|
| 1    | 12          | 28                 | 34                 | 32                    | 1                  | 61            |                  |
| 2    | 17          | 29.5               | 35                 | 33                    | 1.3                | 60            |                  |
| 3    | 22          | 32.6               | 36                 | 34                    | 1.6                | 59            |                  |
| 4    | Nafion 117  | 19.3               | 41                 | 16.4                  | 0.98               | 80            |                  |

| Data | Composition | Membranes PES (%) | Methanol Permeability ($\times10^{-7}$cm$^2$.s$^{-1}$) | proton conductivity (S.cm$^{-1}$) |
|------|-------------|--------------------|-------------------------------------------------------|----------------------------------|
| 1    | 12          | 21                 | 0.0007                                                |                                  |
| 2    | 17          | 22                 | 0.0008                                                |                                  |
| 3    | 22          | 23.5               | 0.00095                                               |                                  |
| 4    | Nafion 117  | 25                 | 0.09                                                  |                                  |

Membranes which have good performance marked by high proton conductivity, water uptake, ionic exchange capacity (IEC) and low membrane swelling ratio, methanol permeability and absorption, also degrees of drop in contact angle (membrane) tend (hydrophilic) so that they are able to operate at higher temperature (> 80°C). According to Hebar [28], compounds with if < 90° is hydrophilic while > 90° is hydrophobic , PES generated in this study shows of 61.29° so PES tends to be hydrophilic. Tendency of the membrane hydrophilic properties are required in DMFC applications due to the ease of chemical structure Inner membrane material absorbs water or likes water. Water is
needed membranes in DMFC applications in maintaining proton and conductivity values maintain membrane humidity during operation. Because protons are able to pass through 51 membrane with water media, so that the water management in the DMFC application is one of the important keys in generating value high proton conductivity [29]. The rate of water absorption in the polymer can be increased by increasing the content of ionic groups (-OH and \(-\text{SO}_3\text{H}\)) in the polymer chain, but too much water absorption causes an improve in swelling of the membrane (swelling), which causes decrease of mechanical stability in the membrane and methanol permeability high [26]. The IEC value depends on the number of sulfonic acid groups in the chemical structure of the polymer membrane and can affect the water absorption and proton conduction properties of the polymer membrane [25]. The IEC value increases as the loading of the polymer composition increases [24]. Therefore, all parameters must be optimized for successful fuel cell operation.

Based on the performance parameters PES membrane at table 1 and table 2, the probability of the proton transport mechanism occurring in the membrane is as shown in Figure 4. Proton transport mechanism in the PES membrane. Protons will easily pass through the membrane structure in the \(-\text{OH}\) (phenol) and \(-\text{SO}_3\text{H}\) (sulphonate) groups.

**Figure 3. Proton transport mechanism on PES membrane**

4. Conclusion
The PES membrane with a composition of 22% w/w is promising applied for DMFC membranes because it can more down value Permeability of methanol than commercial Nafion membranes. Although the proton conductivity is quite low but have a fairly high temperature stability of >100°C. it is possible to modify it with other polymers or fillers to increase performance, the PES membrane with presence of groups (-OH and \(-\text{SO}_3\text{H}\)) possible for proton transport to occur in the structure.

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