A Novel Polymer Electrolyte Membrane PES/SPEEK-TiO_2 Potential for Direct Methanol Fuel Cell

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Keywords: Polymer Electrolyte Membrane (PEM), Direct Methanol Fuel Cell (DMFC), Polyeugenol Sulfonate (PES), Sulfonated Polyether Ether Ketone (SPEEK), Titanium Dioxide (TiO_2).

Abstract: A novel polymer electrolyte membrane (PEM) has been developed by combining polyeugenol sulfonate (PES), which is derived from clove oil, SPEEK, and TiO_2 for direct methanol fuel cell (DMFC), its was characterized using various analytical techniques, including FTIR and SEM. Additionally, the membrane's ion proton conductivity (σ) , water(W_{upt}) and methanol uptake (M_{upt}), Ion exchange capacity(IEC) , and water contact angle(W_{CA}) were tested. The study demonstrated that the PES/SPEEK- TiO_2 membrane, containing 3 wt.% PES, 20 wt.% SPEEK, and 5 wt.% TiO_2, Showed better results in terms of performance when compared to the Nafion 117 membrane, particularly in terms of IEC, water uptake, proton conductivity, and methanol barrier properties. Overall, the study shows the promising potential of the PES/SPEEK- TiO_2 membrane as an efficient PEM for DMFC applications.

1 INTRODUCTION

Indonesia, as a developing country, is facing a critical energy crisis due to several factors, including a persistent increase in household demand, a substantial population growth rate, and an uneven distribution of energy sources. Indonesia has long relied on fossil fuels to generate electrical energy, which has resulted in an over-reliance on these non-renewable resources. In recent years, the country has experienced frequent power outages due to the insufficient energy supply, particularly in remote areas where the infrastructure is lacking. As of 2016, the country had an estimated 7.25 billion barrels of fossil fuel reserves, representing a decline of 0.74% from the previous year, with natural gas reserves also dropping by 5.04%. Despite the fact that the government has been transforming 92.1% of the country's complete energy reserves into petroleum, relying solely on fossil fuels is not a viable option due to their adverse environmental impact and limited availability.(Sihombing, Susilawati, Rahayu, & Situmeang, 2023). Given the challenges faced by Indonesia in the energy sector, it is imperative to explore alternative technologies for energy production. Fuel cells (FCs) offer a promising solution as they are environmentally friendly and can contribute towards mitigating global warming and other climate-related issues.(Braz, Moreira, Oliveira, & Pinto, 2022; Godula-Jopek & Westenberger, 2022). The Direct Methanol Fuel Cell (DMFC) is one type of FC example of an alternative green technology that can promote environmental sustainability. DMFC using a liquid methanol solution as fuel can convert chemical energy into electrical energy to power various applications, all while minimizing any negative environmental impact(Biswas & Wiberforce, 2023).

The DMFC system consists of several essential components that work together to generate electrical energy. The fundamental structure of a DMFC system typically includes a fuel cell stack, which is composed of individual cells that contain the anode and cathode electrodes, a PEM positioned between the electrodes. Bipolar plates are used to separate individual cells and create electrical connections between them.

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Asri, N. and Muliawati, E.
A Novel Polymer Electrolyte Membrane PES/SPEEK-TIO2 Potential for Direct Methanol Fuel Cell.
DOI: 10.5220/0012106100003680
In *Proceedings of the 4th International Conference on Advanced Engineering and Technology (ICATECH 2023)*, pages 173-179
ISBN: 978-989-758-663-7; ISSN: 2975-948X

Gaskets, current collectors, and end plates are also included to complete the assembly and ensure proper functioning of the system. Overall, the DMFC system is a complex, yet highly efficient technology that offers several advantages over traditional energy sources.(Das, Dutta, Nessim, & Kader, 2020). The fundamental composition of the DMFC system is illustrated in Figure 1, where the primary function of the PEM is to enable the efficient transportation of H^+ ions through the membrane from anode to cathode, while preventing the passage of electrons, essentially acting as an insulator (Junoh et al., 2020).

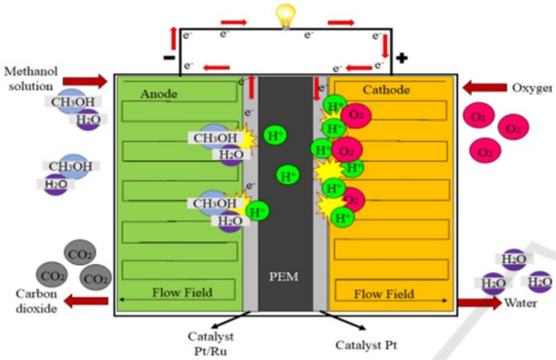

Figure 1: The fundamental composition of DMFC (Junoh, 2020).

The electrons, in order to achieve a stable state, attempt to recombine on the opposite side of the membrane and are consequently compelled to travel through an external electrical circuit to reach the cathode. Simultaneously, the protons are conveyed through the electrolyte to the cathode. This process of exchanging protons and electrons generates electrical energy. (Walkowiak-Kulikowska, Wolska, & Koroniak, 2017).

DuPont Company in the mid-1960s developed a cation-exchange membrane, which is now known as Nafion®. It comprises a polytetrafluoroethylene backbone and ionic sulfonate groups that replace the perfluorinated vinyl ether suspended side chains. Nafion® possesses exceptional thermal and chemical durability, along with a high proton-conducting capability, making it an ideal material for commercial use (Sazali, Wan Salleh, Jamaludin, & Mhd Razali, 2020). Despite its excellent properties, Nafion® has a drawback in that its performance diminishes at temperatures above 80°C. There are several factors that can be attributed to the decrease in membrane performance, such as membrane dehydration, decreased ionic conductivity, weakened air affinity, diminished mechanical properties, swelling issues, reduced fuel permeation, and evaporation. Therefore, several research studies have been conducted to enhance the membrane's performance for FC applications.. Moreover, Nafion®'s high cost, which ranges from US$800 to US$2,000 per square meter, has impeded the commercialization of PEMs and DMFC. (Aburabie, Lalia, & Hashaikeh, 2021; Nicotera, Simari, & Enotiadis, 2020; Shaari et al., 2018).

Abundant natural resources present a significant opportunity for the development of alternative and renewable energy sources, including fuel cells. Clove oil, which primarily comprises eugenol, is one such resource that is readily available. Eugenol makes up 70-96% of the oil, highlighting its potential as an energy source (E. C. Muliawati, Budianto, & Hamid, 2021; E. C. Muliawati et al., 2017). Various polymers have been synthesized in previous studies using eugenol as a raw material, and one such example is Polyeugenol sulfonate (PES) (E. C. Muliawati et al., 2021, 2017; Ngadiwiyana, Gunawan, Prasetya, Kusworo, & Susanto, 2022). TiO_2 is an affordable inorganic material non-flammability and corrosion resistance with adaptable characteristics that can be blended into a polymeric matrix to boost thermal stability and mechanical strength. TiO_2 can be employed as a co-catalyst in energy applications such as FC and batteries, or as a doping agent in PEM.(Abdullah & Kamarudin, 2015; Haragirimana, Li, Ingabire, Hu, & Chen, 2020; Jiang, 2014; Eka Cahya Muliawati et al., 2019).

This study involved the incorporation of PES material into SPEEK to produce several composite PEM. SPEEK was chosen because it offers various benefits, such as affordability, excellent chemical stability, and low methanol permeability.(Fu, Manthiram, & Guiver, 2007)(Gutru, Peera, Bhat, & Sahu, 2016; Liu et al., 2014; Salarizadeh et al., 2019; Yin et al., 2021). The objective of this project is to develop a polymer electrolyte membrane (PEM) matrix suitable for DMFC by incorporating TiO_2 as a filler. TiO_2 is a promising option for a hydrophilic filler in PES/SPEEK as it can ensure appropriate hydration of the membrane during fuel cell operation. The outcomes of the PES/SPEEK-TiO_2 composite membranes indicate that the filler's morphological features significantly impact the performance of the membranes at elevated operating temperatures.

2 MATERIALS

The basics materials or polymers employed in this study are eugenol and Poly ether ether ketone obtained from Sigma Aldrich is subjected to a sulfonation process involving the usage of sulfuric acid, deionized water, and ice cubes. N-Methyl-2-pyrrolidone (NMP) solvent from Merck is used. TiO_2 from Sigma Aldrich is utilized as an additive filler.

2.1 Polyeugenol Sulfonated (PES) Preparation

PES was synthesized by applying the techniques outlined by MuliawatI (20170, utilizing Sulfuric acid (H_2SO_4).

2.2 Sulfonated Poly Ether Ether Ketone (SPEEK)

The SPEEK polymer will be obtained through the process of sulfonation reaction of PEEK and following methods described by Jaafar (Jaafar, Ismail, Matsuura, & Nagai, 2011).

2.3 Fabrication Membranes

The process of producing PES/SPEEK-TiO_2 involves dissolving its constituents in a solvent via stirring until complete dissolution. The resulting solution is then heated at 90°C for 12 hours with continuous magnetic stirring, Following this, the direct casting method is utilized to transform it into a thin membrane, then its dried at 800°C for 30 hours to ensure its complete curing. To improve the membrane's proton conductivity, it is soaked in 10M H_2SO_4 for 100 hours. Finally, the thickness of the resulting membranes ranges between 0.2-0.3mm.

2.4 Characterization of the Membrane

Several techniques were utilized to analyze the ionic properties of the membrane, such as:

2.4.1 Proton Conductivity

Electrochemical Impedance Spectroscopy was used to measure the Proton conductivity membrane, its was hydrated by soaking in 10 M Sulfuric acid for 36 hours, and then placed into a membrane clamping chip and heated to temperatures ranging between 80^0-90^0C. The analysis was performed by using the two-probe method at frequencies ranging from 1-10^6 Heartz.

$$\sigma = L/(R \times A) \quad (1)$$

Equation (1) calculates, where σ represents the proton conductivity in S/cm of the membrane. The membrane's thickness is represented by the symbol L and measured in centimeters (cm), while A represents its surface area in cm^2. The resistance value of the membrane is represented by R in Ω.

2.4.2 Water and Methanol Uptake

To determine the membrane's water and methanol uptake, it was observed under both dry and wet conditions. The measurements were taken for both water uptake (W_{Upt}) and methanol uptake (M_{Upt}). The first step was to dry the membrane at 60°C for 18 hours and record its baseline weight. Afterward, the membrane was soaked in either water or methanol for a period of 36 hours until complete hydration was achieved. Before being weighed again, any remaining liquid present on the surface of the membrane was wiped off using a tissue.

$$W_{Upt} \text{ and } M_{Upt}\ (\%) = \left(\frac{W_{wet} - W_{Dry}}{W_{Dry}}\right) \text{X } 100\% \quad (2)$$

W_{Upt} and M_{Upt} were calculated using Equation (2), W_{dry} and W_{wet} denotes the mass of the membrane before soaking and after has been soaked in grams represents the mass of the membrane.

2.4.3 Ion Exchange Capacity (IEC)

The titration method was used to determine the ion exchange capacity (IEC) of the membrane. The membrane was first dried at 60°C for 18 hours and weighed. Then, it was immersed in a 100 mL solution containing 1M NaCl to facilitate the exchange of H^+ ions with Na^+ ions. Phenolphthalein indicator was added to the solution, which was then titrated with 0.01M NaOH until the equivalence point was reached. Subsequently, the IEC was determined using Equation (3).

$$\text{Uptake } (\%) = \left(\frac{W_{wet} - W_{Dry}}{W_{Dry}}\right) \text{X } 100\% \quad (3)$$

In Equation (3), In the titration process, M_{NaOH} represents the molar concentration of NaOH used, measured in mol/L. V_{NaOH} represents the Volume and W_{dry} represents the dry mass of the membrane in grams.

2.4.4 Water Contact Angle (WCA)

In order to assess the hydrophilicity and water uptake of the membrane, the Water Contact Angle test (WCA) using the OCA15 Pro by Data Physics, membrane samples measuring (4 X 30) mm were prepared in a dry and flat state and clamped securely in a straight position. The sessile drop method was employed during the test, and the angle between the water droplet and the membrane surface was measured to determine the membrane's hydrophilic characteristics.

2.4.5 Methanol Permeability

To determine the membrane's methanol permeability, a two-compartment diffusion cell was employed. The initial section (A) contained a methanol solution with a concentration of 1 mole per liter, whereas the second section (B) was occupied by water that had been deionized. The flat and unmoistened membrane was placed between the two sections. Within a time frame of 2 hours, samples were taken from section B every 20 minutes, using a pipette.

The extracted solutions were then examined using High Performance Liquid Chromatography (HPLC).

$$P = \left(\frac{\Delta C_B}{\Delta t}\right)\left(\frac{LV_B}{AC_A}\right) \quad (4)$$

Equation (4) is utilized to determine the methanol permeability of the membrane. P is expressed in units of cm2.s-1 and is calculated by dividing the rate of change of methanol concentration in compartment B per unit time (mol.L-1.s-1), denoted by C_B/Δt, by L multiplied by VB and divided by A multiplied by CA.

Here, L represents the thickness of the membrane in cm, VB indicates the volume of water in compartment B in cm3, A is the surface area of the membrane in cm2, and CA denotes the concentration of methanol in compartment A in mol/L.

2.4.6 Swelling Ratio (*SR*)

In order to evaluate the extent of swelling in the membrane, its length is measured in both dry and wet states. Initially, the membrane is subjected to drying in an oven set at 60°C for a duration of 12 hours, and its length is measured and recorded. Subsequently, the membrane is soaked in deionized water for 36 hours until it attains complete hydration. After removing the membrane from the water, any residual droplets on its surface are wiped away with a tissue before measuring its length.

$$SR = \left(\frac{L_{wet} - L_{Dry}}{L_{Dry}}\right) X\ 100\% \quad (5)$$

The *SR* (%) using Equation (5), which calculates the percentage increase in length between the wet L_{wet} and dry L_{dry} states.

3 RESULTS

Table 1: Value of membrane properties.

Blend Membrane	Uptake of water (%wt)	Uptake of methanol (%wt)	Ratio of Swelling (%)	Ion-exchange capacity (mmol/g)	Contact Angle (°)
20% PEEK	5.1	6	5	0.7	88
20% SPEEK	25.5	19	14.9	1.27	79
20% SPEEK – 3% TiO_2	49.7	31	13	1.8	68.91
20% SPEEK – 5% TiO_2	48.2	28.5	11	2.2	67.36
20% SPEEK – 7% TiO_2	38	28	8	2.1	67.23
20% SPEEK- 3% PES – optimum (5%) TiO_2	51.6	32	14	2.6	59.31
20% PEEK- 3% PES – optimum (5%) TiO_2	26.5	18	7	2.2	72.15
Nafion 117	19.3	41	16.4	0.98	80

Table 2: Membrane performance.

Membrane	Proton Conductivity ($S.cm^{-1}$)	Methanol Permeability ($\times 10^{-7}\ cm^2.s^{-1}$)
SPEEK 20%	0.0071	11
20% SPEEK – 3% TiO_2	0.00160	12
20% SPEEK – 5% TiO_2	0.00180	18
20% SPEEK – 7% TiO_2	0.00181	19
20% SPEEK- 3% PES – optimum (5%) TiO_2	0.00203	6
20% PEEK- 3% PES – optimum (5%) TiO_2	0.00043	8
Nafion® 117	0.090	25

Tables 1: Value properties membrane and Table 2: Membrane performance reveal that the PES/SPEEK-TiO_2 membrane loading with 3%wt PES, SPEEK 20%wt, and 5%wt TiO_2 is the most suitable composition for PEM in DMFC. In order to ensure that PEMs function effectively in DMFCs, it is important to assess key properties such as Water and methanol uptake demonstrate the exchange of ions and methanol within the membrane, respectively, while the swelling ratio assesses the membrane's stability in aqueous solutions. IEC, measured in milli equivalents per gram of polymer, indicates the number of proton transfer sites. The contact angle indicates whether the material is hydrophilic or hydrophobic. Proton conductivity is essential for proton-conducting membranes used in fuel cells, and the proton transport mechanism can be explained through various mechanisms such as "proton hopping," "Grotthus mechanism," "diffusion mechanism," or "vehicular mechanism." High water uptake, low methanol uptake, high IEC, low swelling ratio, and a more hydrophilic contact angle are essential factors for achieving optimal performance of a membrane in a fuel cell. Creating hydrophilic domains by increasing water uptake promotes proton transport.

Excessive water uptake can result in swelling and an increase in methanol permeability, which can weaken the membrane's mechanical stability. The water uptake and proton conductivity of the membrane are affected by its IEC value, which is determined by the number of sulfonic acid groups in its chemical structure. Agglomerate formation leads to a decrease in the IEC value as the filler content increases.

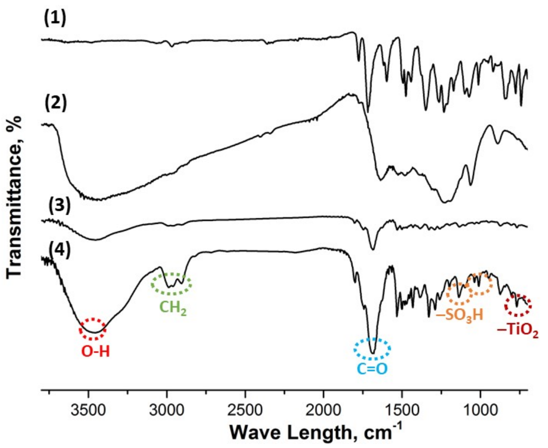

Figure 2: FT-IR spectra of (1) PEEK, (2) PES, (3) SPEEK and (4) PES/ SPEEK-TiO_2 membranes.

The FT-IR spectra of PEEK, PES, SPEEK, and SPEEK/PES- TiO_2 membranes are presented in Figure 2. The bands at 701 cm^{-1}, 1075 cm^{-1}, and 1270 cm^{-1} signifies the existence of sulfonic acid groups within the polymer, which play a critical role in facilitating proton transfer across the PES/SPEEK membrane structure. The wide absorption band observed at 3600 cm^{-1} provides further proof of the connection between water molecules and sulfonic acid groups, indicating their interaction with each other. Additionally, the stretching vibration of the sulfonate ester groups in SPEEK is observed at 1365 cm^{-1}, and the stretching vibration at 1165 cm^{-1}.of the C=O groups in SPEEK and PES is observed at 1659 cm^{-1}. The band at 701 cm^{-1} confirms the presence of TiO_2 in the membrane. The FT-IR analysis demonstrates the successful incorporation of sulfonic acid groups into the polymer.

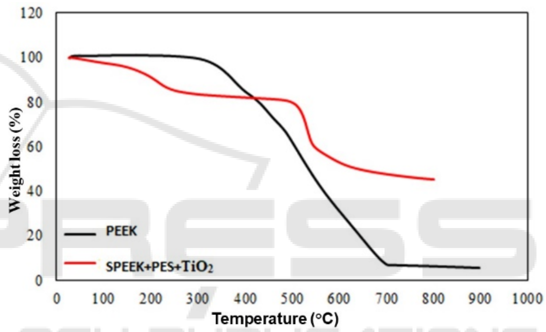

Figure 3: Thermo-Gravimetric Analysis (TGA).

The Thermogravimetric Analysis (TGA) results depicted in Figure 3 shed light on the thermal stability of the SPEEK/PES-TiO_2 membrane. The TGA curve indicates that the membrane undergoes three degradation stages, whereas PEEK membranes experience only one. The first stage is observed at about 100°C, resulting from the evaporation of water molecules from the polymer. The second stage occurs around 200°C, where the NMP solvent evaporates, and the sulfonate groups bound to the polymer are lost, as reported by Abbasi, Antunes, and Velasco in 2015. The final stage occurs before 500°C, suggesting that the SPEEK/PES- TiO_2 membrane is ideal for high-temperature applications, as its degradation temperature is approximately 500°C. In summary, the TGA results validate the membrane's remarkable thermal stability and its potential for use in high-temperature applications.

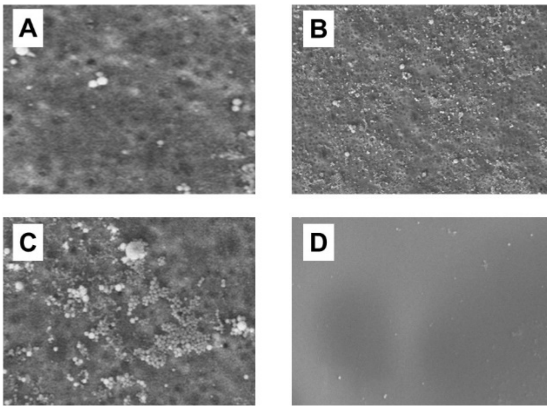

Figure 4: SEM image of (A) 20% SPEEK– 3% TiO_2, (B) 20% SPEEK – 5% TiO_2, (C) 20% SPEEK – 7% TiO_2, (D) 20% SPEEK/3% PES – 5% TiO_2

The roughness of the PES membrane is likely a result of its inherent properties and its interaction with the SPEEK and TiO2 filler. The Figure 4 SEM images also reveal that the TiO2 filler is uniformly dispersed throughout the SPEEK/PES- TiO_2 membrane, which suggests good compatibility among the components. The smooth surface of the SPEEK/PES- TiO_2 membrane may help reduce contact resistance and improve proton conductivity, making it well-suited for use in fuel cell applications.

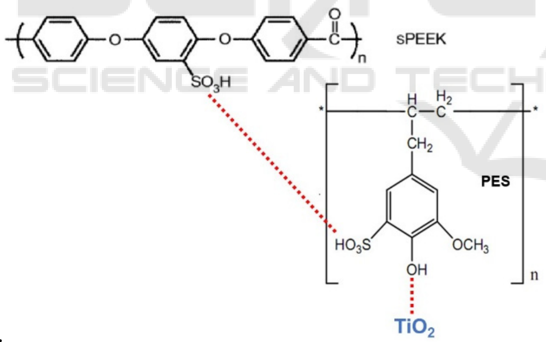

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Figure 5: Proton transport mechanism between PES, SPEEK and TiO_2.

Furthermore, the SPEEK/PES- TiO_2 membrane exhibited superior methanol resistance compared to the SPEEK/PES membrane without TiO_2, which can be attributed to the interaction between TiO_2 and PES, forming a barrier against methanol permeation. This is a crucial feature for DMFCs as it reduces the crossover of methanol from the anode to the cathode, which can lead to a decrease in cell performance. Therefore, the addition of TiO_2 not only enhances proton conductivity but also improves the membrane's resistance to methanol, making it a highly promising material for DMFC applications.

4 CONCLUSIONS

The solution casting method was used to prepare the SPEEK/PES- TiO_2 membrane, and it was found to be successful through SEM imaging, which revealed its homogeneity. Incorporating TiO_2 into the SPEEK/PES membrane is expected to enhance the number of proton transfer sites that are available, The membrane's ability to absorb water greatly aids in the creation of hydrophilic areas, thereby promoting the transfer of protons. The findings indicate that the PES/SPEEK- TiO_2 membrane has considerable potential as a PEM for DMFC applications, offering higher proton conductivity and lower methanol permeability than the Nafion® 117 membranes. These results provide a strong foundation for further research into developing PEMs with superior properties and performance for DMFCs. Additionally, Figure 5 illustrates the likely proton transport mechanism involving PES, SPEEK, and TiO_2 in the membrane.

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