New Nanocomposite Membranes with blended Sulfonated Poly-Eugenol (S-PE) and Titanium Dioxide (TiO_2) as an Alternative in Direct Methanol Fuel Cells

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Abstract

This study fabricated a novel sulfonated poly-eugenol/titanium dioxide nanocomposite membrane as an alternative polymer electrolite membrane (PEM) to direct methanol fuel cells (DMFCs), addressing the high cost of PEM, a major challenge for fuel cell (FC) commercialization. Sulfonated poly-eugenol (S-PE), synthesized by polymerizing eugenol with sulfuric acid, incorporated sulfonic acid groups to improve proton flows conductivity. Titanium Dioxide nanoparticles were incorporated into the sulfonated polymer matrix, forming a mixed membrane nanocomposite. Scanning electron microscopy confirmed a homogeneous TiO_2 distribution in the polymer. The membranes' physicochemical properties, including air absorption, swelling, and methanol absorption, were evaluated and compared to commercial Nafion. The S-PE and TiO_2 nanocomposite membrane with 25% (S-PE) and 5% TiO_2 exhibited higher water and methanol absorption than Nafion, but lower proton conductivity. However, its low methanol permeability can potentially improve fuel efficiency in direct methanol fuel cells. Incorporating TiO_2 into sulfonated poly-eugenol represents a promising strategy for developing low-cost, efficient PEM for DMFCs applications.

Keywords: *Fuel cell; Nanocomposite membranes; Sulfonated poly-eugenol; Titanium dioxide*

1. Introduction

In recent years, the strategic development of organic polymers as proton conducting materials have gained significant attention within the fuel cell research community. This is largely due to their inherent structural robustness and the relative ease of fabricating polymer-based membranes, which are critical characteristics for practical fuel cell applications[1]. Advancing the research on efficient, cost-effective, and durable polymer electrolite membrane materials has been a key priority in the direct methanol fuel cells [2]. Traditional perfluoro sulfonic acid based membranes, such as the widely used Nafion, have demonstrated desirable properties like high proton flows conductivity and physicochemical stability. However, these perfluorinated membranes suffer from inherent limitations, including high manufacturing costs and issues with thermal stability and membrane dehydration at higher operating temperatures[3]. To address these well-recognized limitations of the incumbent Nafion-type membranes, researchers have actively explored alternative non-fluorinated polymer systems as potential replacements for DMFC applications.

One promising class of materials that has garnered significant attention in this context is sulfonated hydrocarbon-based polymers[4]. These non-fluorinated polymers, such as polyimides [5] have demonstrated promising potential to serve as viable polymer electrolite membrane on fuel cell applications. SPEEK, in particular, has garnered significant attention due to its excellent chemical and thermal stability, as well as its ability to provide efficient proton conductivity [6]. Similarly, other hydrocarbon-based polymers like Polyarylene ethers and Polysulphone have shown promising properties, including good mechanical strength and potentially lower manufacturing costs compared to perfluorinated membranes [7], [8], [9].

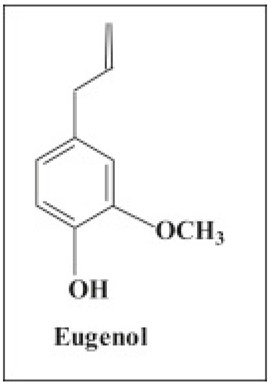

Figure 1. Chemical structure of eugenol.

The increasing reliance on synthetic polymers has been driven by the use of non-renewable resources. The limited availability of petroleum reserves, coupled with growing environmental concerns, has prompted the development of novel polymers derived from biological sources [10]. Ongoing efforts focus on creating innovative materials, particularly polymers, from renewable resources. Several research studies have explored modifying natural polymers such as cellulose [11], starch [12], chitosan[13], and sodium alginate [14] to fabricate polymer electrolite membrane on direct methanol fuel cells.

Eugenol like a Figure 1., a phenolic compound that is the primary constituent of clove oil (Eugenia caryophyllata), is a readily available renewable resource [15]. The presence of sulfonated groups in the poly-eugenol backbone can enhance its proton-conducting properties [16].

Ngadiwiyana et al. successfully synthesized a sulfonated copolymer of eugenol and diallyl phthalate. This copolymer exhibited the highest proton conductivity of 8.334 × 10–6 S cm^{-1}, cation exchange capacity of 0.44 meq/g, and water uptake of 73.0% [17] .Muliawati successfully synthesized a polymer blend membrane composed of 3 wt.% sulfonated polyetherimide and 20 wt.% poly-eugenol. This blend membrane demonstrated higher ion exchange capacity, water uptake, proton conductivity, and methanol barrier properties compared to Nafion117 [18].These findings suggest that eugenol, a renewable resource, is a promising candidate for the development of sulfonated poly-eugenol, a bio-based polymer with potential applications in fuel cells.

Researchers have also explored incorporating inorganic fillers into polymer matrices to develop Hybrid organic-inorganic nanocomposite materials have been investigated as potential membranes for fuel cell systems. For instance, Handayani et al. compared the effects of organic and inorganic fillers on the polymer system, SPEEK membranes with the organic ABS polymer exhibited higher crystallinity, which limited the movement of the polymer chains and decreased the flexibility and proton conductivity compared to the SPEEK membranes with the inorganic SiO_2 filler. [19]. Additionally, previous studies by Sidharthan et al. have reported the fabrication of nanocomposite membranes by incorporating varying amounts of titanium dioxide nanoparticles into sulfonated polyvinyl alcohol (PVA) solutions. The surface modification of the TiO_2 nanoparticles was found to enhance the ionic conductivity of the resulting composite membranes, reaching values in the 10^{-2} S/cm range. Furthermore, the methanol permeability of these nanocomposite membranes was observed to be in the order of 10^{-7} cm^2/s[20]. Incorporating titanium dioxide can potentially enhance the thermal, mechanical, and barrier properties of the resulting nanocomposite membranes, making them more suitable in the direct methanol fuel cell applications.

In this study, we report the synthesis and characterization of nanocomposite membranes composed of sulfonated poly-eugenol and titanium dioxide, developed in the direct methanol fuel cells. These membranes made through a solution casting method, and their physicochemical and electrochemical properties were extensively evaluated.

2. Method

2.1. Tools and materials

Analytical instruments : Bruker Scanning Electron Microscope, Solar-tron SI 1260 Electrochemical Impedance Spectroscopy, Perkin Elmer high performance liquid chromatography for membrane permeability testing, ubbelohde viscometer

Sulfonation process equipment : Three-neck flask, oil bath, condenser, stirrer, filter, electric balance, thermometer, beaker, measuring cup

Membrane fabrication equipment: Stirrer, ultrasonic, doctor blade, stir bar, glass plate, vacuum oven, Erlenmeyer flask with lid

Raw materials : Eugenol and titanium dioxide from Sigma Aldrich, sulfuric acid, ethanol, deionized water, and acetic acid.

Sulfonation reagents : Sulfuric acid, ice cubes, deionized water

Casting : Solvents such as dimethylformamide, dimethyl sulfoxide (DMSO), and ethanol

The research stages carried out are as follows**:**

2.2. Poly-eugenol Synthesis

The synthesis of poly-eugenol (Figure 2.) was conducted using the method reported by Ngadiwiyana [21]. This approach yielded eugenol-based polymers within a short timeframe of 90 to 160 seconds. The polymerization of eugenol was catalyzed by a mixture of sulfuric acid (H_2SO_4) and acetic acid (CH_3COOH).

2.3. Sulfonation Process

The synthesized poly-eugenol underwent a sulfonation reaction to present the desired sulfonic acid groups. The sulfonation process followed the Handayani method[22], where the poly-eugenol was introduced into concentrated sulfuric acid at a low temperature and stirred for 1 hours. This was followed by precipitation, filtration, and thorough washing steps with deionized water to obtain the final sulfonated poly-eugenol product. The sulfonated poly-eugenol powder was rigorously washed with deionized water in multiple cycles until the filtrate attained a neutral pH. This crucial step removed any remaining sulfuric acid or other impurities from the sulfonation process, guaranteeing the purity of the final sulfonated polymer for subsequent membrane fabrication. The meticulous washing helped to thoroughly purify the SPE.

2.4. Preparation of Sulfonated Poly-Eugenol/TiO_2 Nanocomposite Membranes

A 25 wt% polymer solution of sulfonated poly-eugenol was prepared by dissolving the sulfonated polymer in dimethyl sulfoxide (DMSO). Varying amounts 3%,5%,7% of TiO_2 nanoparticles were then dispersed within the polymer solution using an ultrasonication method to create a homogeneous mixture. The resulting homogeneous solution was cast onto a glass plate and dried in a vacuum oven at 80°C for 24 hours to facilitate the evaporation of the DMSO solvent and obtain the final sulfonated poly-eugenol/TiO_2 nanocomposite membranes.

2.5. Membrane Manufacturing

The polymer solution was meticulously cast into a thin membrane using the direct casting method. The cast membrane was then dried in a vacuum oven at 80°C for 36 hours, enabling complete evaporation of the DMSO solvent and formation of the final sulfonated poly-eugenol/TiO_2 nanocomposite membrane. To further improve the ion exchange characteristics, the dried membrane was subsequently soaked in a concentrated 9M sulfuric acid solution for an extended period of 100 hours. The fabricated membranes were carefully controlled to exhibit a thickness range between 0.1 to 0.3 millimeters[23], [24], [25].

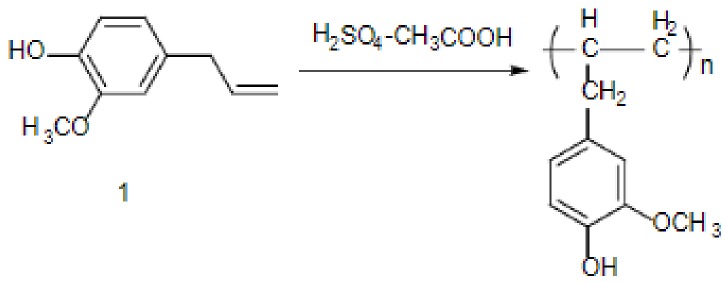

Figure 2. Synthesis of Polyeugenol

2.6. Membrane Characterization

The membranes were extensively characterized using various analytical techniques. Structural analysis was performed via scanning electron microscopy to examine the surface morphology and cross-sectional structure. Ionic properties were evaluated by measuring ionic conductivity through impedance spectroscopy. Ion exchange capacity (IEC)was determined, and solvent absorption properties were analyzed by measuring water swelling (water uptake) and methanol permeability. Additionally, the mechanism of proton transport within the membranes was investigated. The proton conductivity of the membranes was assessed using electrochemical impedance spectroscopy. Furthermore, methanol permeability was quantified employing a custom-designed permeation cell and high performance liquid chromatography.

3. Results and Discussion

The results presented in Tables 1 and 2 suggest that the 25% sulfonated poly-eugenol membrane with 5% TiO_2 is the most suitable composition for DMFC applications. The key membrane properties that must be evaluated for DMFC suitability include water absorption, methanol absorption, dimensional swelling, ion exchange capacity, surface wettability, proton conductivity, and methanol permeability[26], [27]. These parameters are crucial in determining the performance and long-term reliability of the membrane.

Water and methanol uptake are critical for facilitating the respective ionic and fuel transport through the membrane. The swelling ratio indicates the membrane's dimensional stability and resistance to structural changes in aqueous environments, which is important for long-term operational reliability. The ion exchange capacity (IEC), defined as the fixed number of exchangeable groups per unit mass of the polymer, corresponds to the available proton transfer sites for efficient proton conduction. The contact angle measurement provides insights into the hydrophilic or hydrophobic nature of the material, where lower angles signify increased hydrophilicity, which can enhance water management and proton transport [28], [29]

Proton conductivity is the most critical factors to proton conducting membranes used in fuel cells, as it directly impacts the power output and efficiency of the DMFC[30], [31]. A high proton conductivity is desirable to minimize ohmic losses and maximize the electrochemical properties of the fuel cell. Additionally, low methanol permeability is crucial to prevent fuel crossover, which can lead to reduced fuel utilization and cell voltage losses[32]. The transport of protons within hydrated polymer matrices is generally explained by two mechanisms: the "proton hopping" or "Grotthus mechanism," and the "diffusion mechanism" in which water acts as the transport medium[33]. The presence of sulfonic acid groups through the sulfonation of the poly-eugenol backbone serves as fixed charge carriers, facilitating proton transport via the Grotthus mechanism[34].

Table 1 Membrane Properties

No	Composition (%)	Water absorption (%wt)	Methanol absorption (%wt)	Dimensional Swelling (%)	EIC (mmol/g)	Wettability (°)
1	25% (S-PE) +3% TiO_2	27	33	35	1.5	61
2	25% (S-PE) +5% TiO_2	27.5	32	36	1.4	60
3	25% (S-PE) +7% TiO_2	33.7	31	37	1.2	59
4	Nafion 117	20	15	17	0.9	80

Table 2 Methanol Permeablility and Proton Conductivity

No	Composition (%)	Metanol Permeability ($\times 10^{-7} cm^2.s^{-1}$)	Proton Conductivity ($S.cm^{-1}$)
1	25% (S-PE) +3% TiO_2	22.5	0.0008
2	25% (S-PE) +5% TiO_2	23.5	0.0009
3	25% (S-PE) +7% TiO_2	23	0.0009
4	Nafion 117	25.5	0.09

The proton conductivity of high-performing membranes generally increases alongside factors such as high water absorption, low methanol absorption and permeability, elevated ion exchange capacity, minimal swelling ratio, and reduced contact angle. Increased water absorption enhances the formation of hydrophilic domains, facilitating efficient proton transport through the membrane. The water absorption of polymers can be improved by presence ionic groups, such as sulfonic acid moieties. However, excessive water uptake may lead to excessive swelling, compromising the mechanical stability of the membrane and increasing methanol permeability, which is undesirable in the direct methanol fuel cell applications[26], [35], [36].

The scanning electron microscopy analysis confirms that the pristine (S-PE) membrane forms a smooth surface[37]. However, the incorporation of TiO_2 filler alters the surface morphology, and the concentration of the filler is a crucial factor in determining the surface characteristics. Based on Figure 3 (A), the 25% sulfonated poly-eugenol ((S-PE))-3% titanium dioxide (TiO_2) membrane exhibits a less uniform surface, suggesting that the fabrication process requires further optimization and the TiO2 filler is not distributed evenly throughout the material. In contrast, Figure 3. (B) the 25% (S-PE) + 5% TiO_2 membrane demonstrates a well-dispersed TiO_2 filler. Conversely, significant TiO_2 agglomeration was observed on Figure 3. (C), the surface of the 25% (S-PE)+7% TiO_2 membrane. Figure 3. (D). SEM proves that (S-PE) forms a smooth surface on the pristine (S-PE) membrane.

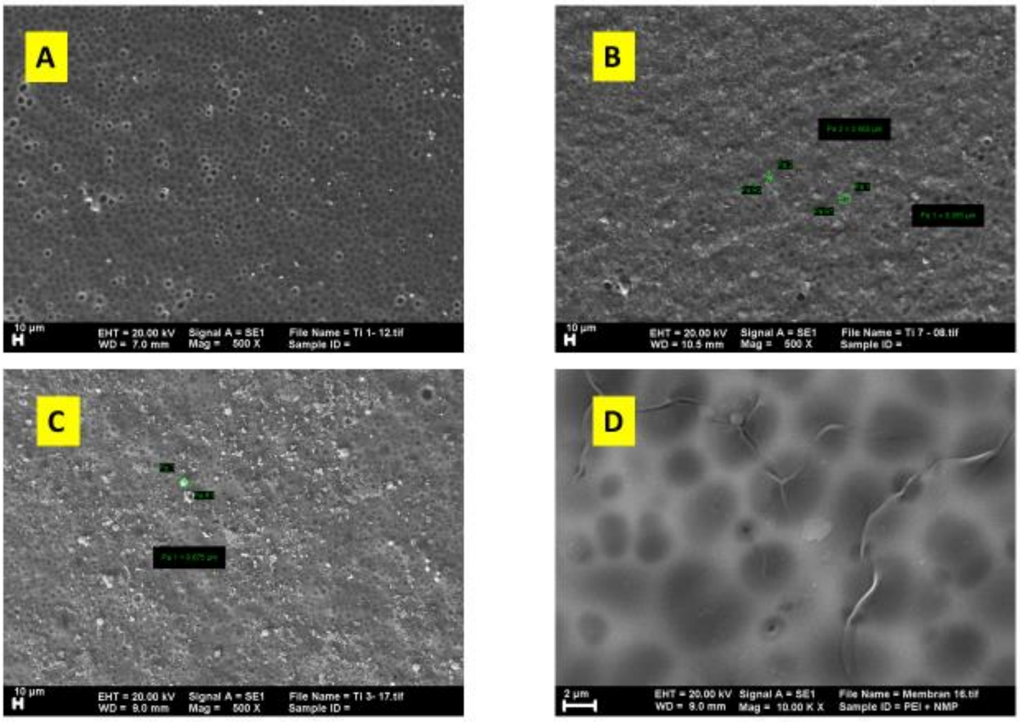

Figure 3. SEM Surface Analysis of membranes (A) 25% (S-PE) + 3% TiO_2, (B) 25% (S-PE) +5% TiO_2, (C) 25% (S-PE) + 7% TiO_2, (D) 25% (S-PE)

4. Conclussion

The study found that a 25% w/w (S-PE) membrane with 5% TiO_2 is a alternative candidate in the direct methanol fuel cell applications. This nanocomposite membrane exhibited lower methanol permeability compared to the commercially used Nafion membrane, which is a critical parameter for DMFC performance. While the proton conductivity of the (S-PE)- TiO_2 membrane was relatively lower than that of Nafion, the researchers suggested that it could be improved by incorporating other polymers into the composite. The detailed synthesis and comprehensive characterization of these (S-PE)-TiO_2 nanocomposite membranes were investigated, evaluating their key properties, including water absorption, methanol permeability, ion exchange capacity, dimensional swelling, and surface wettability. These parameters are crucial in determining the suitability and performance of the membrane for DMFC applications, as they directly influence the ionic and fuel transport, dimensional stability, and overall electrochemical performance of the fuel cell.

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