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ENHANCED IONIC CONDUCTIVITY OF SULFONATED CHITOSAN–SILICA COMPOSITE MEMBRANES DERIVED FROM PALM OIL SHELL WASTE FOR DIRECT METHANOL FUEL CELL APPLICATIONS

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ABSTRACT

The electrolyte membrane, as a proton passage medium, plays an important role in the direct methanol fuel cell (DMFC) system. In this study, an alternative electrolyte membrane was developed through the fabrication of a composite membrane using the biopolymer chitosan and silica filler derived from palm oil shell waste. The membrane synthesis employed the vasa inversion technique with varying amounts of filler (5%, 10%, 15% wt.%) in an acetic acid solution. Initially, a sulfonation treatment with H_2SO_4 was applied to enhance the functional groups in the membrane structure. Examination of SEM images and FTIR analysis shows the success of combining silica with chitosan biopolymer in the composite membrane structure. The most favorable composite membrane was identified in the Ch/Silica 15 variant, exhibiting water uptake and methanol uptake values of 79% and 57%, respectively. Additionally, the methanol permeability test indicated a value of 0.05 $mg.cm^2.s^{-1}$. The sulfonation treatment contributed to an increased number of functional groups, serving as ion exchange media for membrane performance in fuel cells. The optimal ion exchange capacity was achieved in the Ch/Silica 15 variant with a value of 4.45 $mmol.g^{-1}$. Overall, the findings suggest that the composite membrane, consisting of chitosan biopolymer and silica filler, is promising as an electrolyte membrane in DMFC applications.

Keywords: Membrane, Chitosan, Silica, Palm Oil Shell, DMFC

INTRODUCTION

The extensive use of fossil fuels by society has resulted in major environmental challenges. Currently, more than 80% of the world's primary energy consumption still relies on fossil fuels, contributing significantly to environmental pollution and accelerating global warming. In response to these challenges, there is a growing urgency to explore alternative energy options that are sustainable, economically viable, and environmentally friendly.[1] Fuel cells have emerged as a promising solution, attracting significant attention for several years. In this electrochemical system, a redox reaction occurs directly, producing electrical energy.[2,3] Among the different fuel cells being developed, direct methanol fuel cells (DMFC) have stood out for their ability to deliver high energy, ease of use, low environmental impact, and convenient mobility. Notably, DMFC holds significant promise in portable applications.[4] The substantial progress in DMFC development can be attributed to its unique advantages, including a straightforward operating system, lightweight construction, compact design, and rapid recharge capability. Operating efficiently at low temperatures, up to 90°C, DMFC utilizes renewable methanol as its fuel source.[5,6] As a

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result, DMFC has emerged as a green energy solution with a user-friendly design that can support SDG 7, namely, affordable and clean energy.[7] At the core of the DMFC system lies the electrolyte membrane, serving a dual purpose as both a separator between the cathode and anode and a conduit for transporting protons generated during the oxidation reaction at the anode to the cathode.[8] Currently, the commercial membrane most extensively utilized as an electrolyte is Nafion, celebrated for its high proton conductivity. Nevertheless, this barrier encounters various obstacles, including a relatively elevated cost, susceptibility to dehydration, and the predicament of methanol permeation, commonly referred to as methanol crossover. This latter poses an important challenge as it can adversely affect the cathode reaction rate, ultimately reducing fuel cell efficiency.[9] Given these difficulties, there is increasing demand for replacement membranes made from economical yet high-quality polymer materials suitable for fuel cell applications. Membrane poly-mers designed for fuel cell systems must fulfill specific criteria, including high chemical stability, good proton conduction pathways, low methanol cross-over, and the utilization of economically viable materials. The exploration of such alternatives aims to overcome the constraints associated with the current Nafion membrane, providing a more economical and effective resolution for DMFC technology.[10] A promising material that shows potential for use as an electrolyte membrane is chitosan, a biopolymer derived from waste shrimp shells. Chitosan stands out due to its easy regulation, biodegradability, non-toxicity, hydrophilic properties, film-forming capability, and accessibility from fishery waste.[11,12] Through effective combinations with other substances, chitosan can be utilized to create composite membranes aimed at improving essential properties for fuel cell applications. In a prior investigation[13], it was found that when chitosan was combined with CaO, the membrane exhibited lower methanol permeability, owing to the methanol-blocking effect of CaO's hydrophobic properties, alongside an increase in ion exchange capacity. Another study[14] utilized silica filler from rice husks in chitosan-based membranes, demonstrating that a 15% silica content exhibited favorable methanol permeability and ion exchange capacity. However, there are interesting research challenges in exploring sulfonation techniques for composite membranes that integrate silica fillers derived from palm oil shell waste into a chitosan biopolymer matrix intended for use in DMFC applications. This study aims to fill this void by investigating membranes produced with chitosan obtained from shrimp shells serving as a polymer matrix and incorporating silica derived from palm oil shells as a filler to achieve increased ionic conductivity, which contributes to improved fuel cell performance. Furthermore, the application of sulfonation treatment using sulfuric acid is implemented to enhance the presence of $-SO_4^{2-}$ groups within the membrane's structural layer, creating a pathway for protons.[15] A comprehensive evaluation of various electrolyte membrane properties is conducted to strengthen its potential as a fundamental material for DMFC applications.

EXPERIMENTAL

Materials

Dried shrimp shells from fishery waste were used as the primary source of chitosan, while silica was obtained from palm oil shell waste. Chemicals, including hydrochloric acid (HCl), methanol (MeOH), sodium hydroxide (NaOH), sodium chloride (NaCl), sulfuric acid (H_2SO_4), acetic acid (CH_3COOH), and phenolphthalein indicator, were of analytical grade and supplied by Merck.

Extraction of Chitosan

The extraction of chitosan from shrimp shell powder involves three main steps: deproteinization, demineralization, and deacetylation. First, the shell powder is soaked in a 3.5% NaOH solution (1:10 w/v), stirred at 400 rpm, and heated for 2 hours, then washed to neutral pH and dried at 105 °C for 4 hours. Next, the dried material is mixed with 1 M HCl (1:15 w/v), stirred at 400 rpm, and heated at 65 °C for 30 minutes, followed by washing and drying to obtain chitin. In the final step, chitin was subjected to 50% NaOH treatment (1:10 w/v), followed by stirring and heating for 4 h, then thoroughly washed and dried to yield white chitosan powder. This stepwise process ensures efficient extraction and conversion of chitosan.

Preparation of Silica

The process begins by soaking 50-mesh dry palm shell powder in 4 M HCl for 3 hours, followed by rinsing to neutral pH and drying at 100 °C. The dried powder is then burned at 300 °C for 3 hours to

produce charcoal, which is further ashed at 900 °C for 2 hours. The resulting ash is soaked in 3 M HCl for 3 hours, neutralized, then dissolved in 3 M NaOH and heated for 2 hours. After washing and filtering, the filtrate is titrated with 3 M HCl to pH 7.5–8.5, centrifuged at 4000 rpm for 4 minutes, and dried at 80 °C for 24 hours. Finally, the silica powder is activated by heating at 900 °C for 2 hours. This step-by-step method ensures efficient extraction, purification, and activation of silica from palm shell waste.

Membrane Fabrication

In the initial step, silica powder (5%, 10%, and 15% w/w) was mixed with 25 mL of 2% acetic acid and sonicated for 30 minutes. Simultaneously, chitosan powder was dissolved in 25 mL of 2% acetic acid, stirred, and heated at 60 °C for 30 minutes. Both mixtures were then combined and stirred at 60 °C for another 30 minutes, followed by three cycles: 30 minutes sonication, 30 minutes resting, and another 30 minutes sonication. The final mixture was poured into molds and dried at room temperature. The prepared membrane was soaked in 0.1 M NaOH for 1 hour, rinsed with deionized water, and dried. Sulfonation was carried out by immersing the membrane in 3 M H_2SO_4 for 24 hours, followed by thorough rinsing and drying. Pure chitosan membranes were also prepared using the same procedure, without the addition of silica. The membrane fabrication process stages are as shown in Fig.-1.

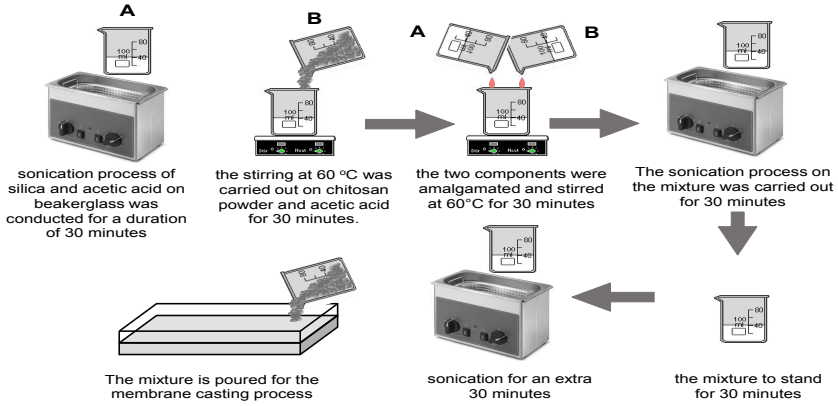


Fig.-1: Chitosan-Based Composite Membrane Fabrication Process

Membrane Characterization

Structural, Functional, and Morphological Characterization of the Composite Membrane

The composite membrane was characterized using FTIR to analyze its structural and functional groups within the 600–4000 cm^{-1} range, providing insights into its chemical composition and bonding. Morphological analysis was conducted using SEM, where gold-coated samples were examined to obtain high-resolution images of the membrane surface, revealing detailed microstructural features.

Water and Methanol Uptake

Water and methanol uptake of the membrane were measured by comparing its weight before and after 24-hour immersion. Membranes (1×1 cm) were dried at 35 °C to obtain the dry weight (W dry), then soaked in water and 1 M methanol separately. After immersion, the wet weight (W wet) was recorded, and uptake values were calculated using Equation (1).

$$Uptake\ (\%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\% \qquad (1)$$

W_{dry} and W_{wet} represent the membrane's weights in grams before and after immersion, respectively.

Ion Exchange Capacity (IEC)

The membrane's proton conductivity was evaluated through its Ion Exchange Capacity (IEC) using a titration method. Dried 1×1 cm membrane pieces were weighed, then soaked in 50 mL of 1 M NaCl solution. Phenolphthalein indicator was added, followed by titration with 0.01 M NaOH. IEC was calculated using Equation (2).

$$IEC\ (mmol\ g^{-1}) = \frac{M_{NaOH}\ x\ 1000\ x\ V_{NaOH}}{W_{dry}} \quad (2)$$

M_{NaOH} (mol·L^{-1}) and V_{NaOH} (L) represent the concentration and volume of NaOH utilized during titration, respectively, while W_{dry} denotes the membrane's dry weight (g).

Methanol Permeability

Methanol permeability was assessed in two sections: A with 1 M methanol and B with water. A 3×3 cm membrane was placed between the sections, and samples from section B were collected every 30 minutes for 2 hours to measure density. Methanol permeability was then calculated using Equation (3).

$$P = \left(\frac{\Delta C_B}{\Delta t}\right)\left(\frac{L\,V_B}{A\,C_A}\right) \quad (3)$$

P represents methanol permeability (cm^2/s), $CB/\Delta t$ represents slope, L represents membrane thickness (cm), V_B represents water volume in compartment B (mL), C_A represents methanol concentration (M), and A represents membrane contact/diffusion area interconnected in compartments (cm^2).

Proton Conductivity

Proton conductivity of the membrane was determined using a proton conductivity tester employing the two-probe method. The membrane was positioned between two sample plates, each measuring 1 × 1 cm, and the voltage was adjusted on the device. The proton conductivity was then calculated using Equation 4.

$$\sigma = \frac{L}{(R \times A)} \quad (4)$$

Where σ is defined as the membrane's proton conductivity (S·cm^{-1}), L as its thickness (cm), A as its surface area (cm^2), and R as the membrane resistance (Ω).

RESULTS AND DISCUSSION

Characterization of Sulfonated Chitosan/Silica Membrane

Fourier Transform Infrared Spectroscopy testing was carried out to analyze the functional groups in the sulfonated Ch/Silica membrane, covering the wavelength range of 4000 – 600 cm^{-1}, as depicted in Fig.-2. In the Ch/Silica 15 Sulfonation membrane, the presence of the N-H and O-H functional groups is shown at wave numbers of 3342 cm^{-1} and 3284 cm^{-1}, respectively. Additionally, the C=O and S=O groups are also shown by absorption at 1644 cm^{-1} and 1009 cm^{-1}, respectively. Within this composite membrane, absorptions at 1052 and 1055 cm^{-1} were detected, signifying a Si-O bond with the stretching of the C-O bond. This peak suggests the inclusion of silica in the composite membrane, confirming the successful addition of the filler. Therefore, the incorporated filler continues to bestow crucial properties to the composite membrane.[16,17]

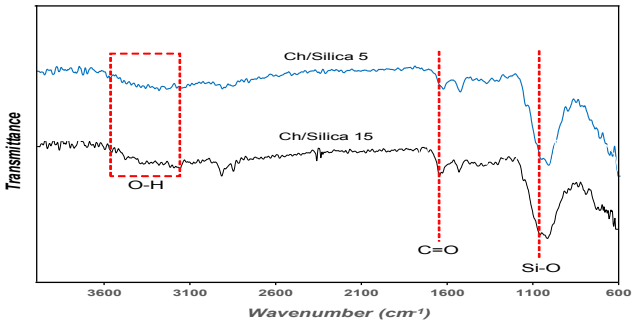


Fig.-2: FTIR Spectra of sulfonated Ch/Silica Composite Membrane

The membrane consisting of sulfonated Ch/Silica 5 demonstrated absorption peaks at wave numbers 3288 cm^{-1} and 3336 cm^{-1}, which indicate the O-H and N-H functional groups, respectively. The functional group C=O was identified at wavenumber 1636 cm^{-1}, while the S=O functional group appeared at 1015 cm^{-1}. These findings validate that the sulfonation process applied to the combined membrane resulted in the integration of sulfonate groups into the structural layer of the membrane, establishing a pathway for

proton movement in applications such as fuel cells. A prior investigation[18] highlighted the significant influence of sulfonation treatment on proton conductivity in composite membranes.

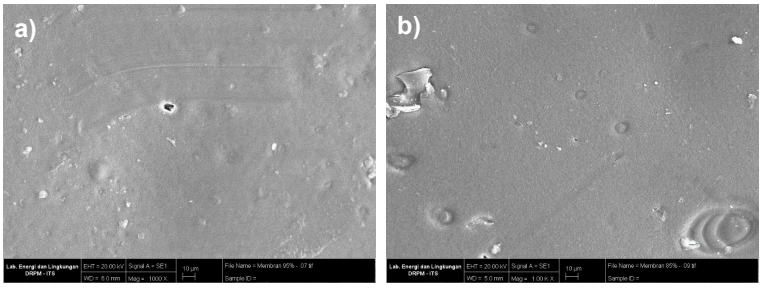


Fig.-3: SEM Images of Ch/Silica 5 (a) and Ch/Silica 15 (b)

The results of morphological analysis on the composite membrane of sulfonated Ch/Silica, conducted using SEM, are illustrated in Fig.-3. The Ch/Silica 5 membrane demonstrates a solid structure that is smooth and dense, with a slight distribution of granules observed on the membrane surface. The improvement in interfacial morphology is evident when increasing the quantity of filler incorporated into the structural layer of the membrane.[19] In contrast, the Ch/Silica 15 composite membrane exhibits a diverse distribution of silica filler on the membrane surface, presenting a more compact and tightly structured morphology. The presence of silica increases the density of the membrane structure so that the chance of methanol crossover decreases. A previous investigation.[20] It is indicated that the addition of silica into Nafion could increase the membrane density in its structural layer, resulting in a more condensed composite membrane.

Water and Methanol Uptake

The characteristics of the membrane in absorbing water or methanol are evaluated using specific uptake tests. The membrane's ability to preserve water within its layers plays a key role in facilitating proton transfer from anode to cathode in DMFC devices. A membrane exhibiting favorable water bulk phase characteristics signifies superior performance in proton movement, thereby enhancing the overall functionality of the membrane.[21,22] The results of the water uptake test show that increasing the filler load increases the water uptake value of the composite membrane, as shown in Fig.-4. The sulfonated Ch/Silica membrane recorded the highest water uptake value, reaching 79%. This highlights the membrane's effective water absorption capacity, a critical parameter for optimizing proton movement and overall performance in fuel cell applications.

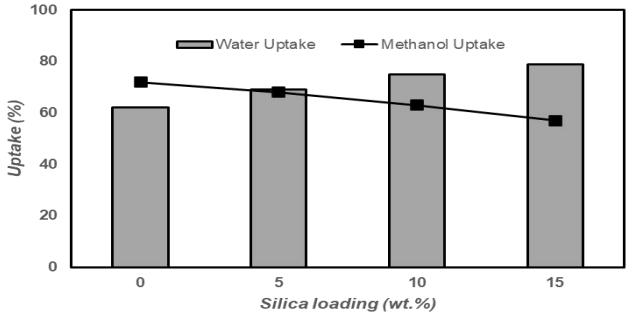


Fig.-4: Water and Methanol Uptake of Sulfonated Ch/Silica Composite Membrane

The properties of the composite membrane are significantly enhanced by the sulfonation process. The introduction of $-SO_3$ groups, marked by highly electronegative oxygen atoms, supports the formation of hydrogen bonds with water passing through the membrane, leading to greater water absorption by filling available void spaces.[23–25] The addition of sulfonate groups leads to a more hydrophilic membrane, simplifying water absorption. The water molecules contained in the membrane structure layer help facilitate the proton transport process, which ultimately contributes to increasing membrane performance. Figure-4 illustrates that as the silica content increases in the membrane; the methanol uptake value also decreases. The sulfonated Ch/Silica 15 composite membrane shows the lowest methanol uptake value,

specifically at 57%. This suggests that the incorporation of silica and the modification of the membrane contribute to a reduction in methanol crossover within the membrane. Consistent with previous research, the morphological structure plays a pivotal role in influencing the membrane's ability to retain methanol.[26] A lower methanol absorption value indicates a reduced likelihood of crossover within the membrane. Methanol crossover is characterized by the movement of methanol molecules from the anode across the membrane, towards the cathode, potentially consuming some of the fuel and causing cathode flooding. This, in turn, leads to a slower reaction rate at the cathode, ultimately diminishing fuel cell performance.[27] Additionally, a decreasing trend in the value of methanol absorption can indicate the possibility of low membrane permeability values, highlighting the membrane's capability to withstand the movement of methanol that passes through.

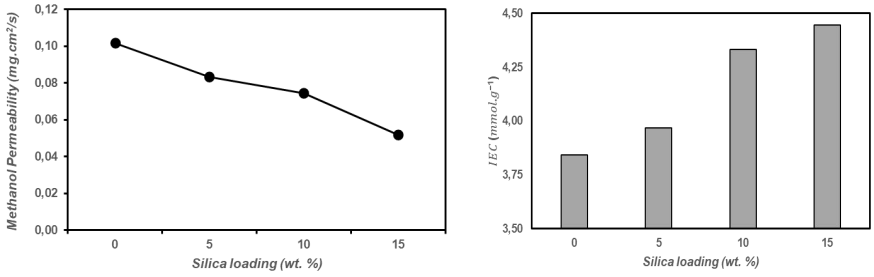
Methanol Permeability, Ion Exchange Capacity, and Proton Conductivity

The methanol permeability value plays a crucial role in evaluating the potential occurrence of methanol crossover in the electrolyte membrane. Higher methanol permeability values indicate an increased probability of methanol diffusing across the membrane. Methanol permeability data for membranes containing sulfonated Ch/Silica from measurements are summarized in Table-1. The most favorable outcome was observed in the Ch/Silica 15 membrane variant, with a methanol permeability of 0.05 mg. cm^2/s. The positive impact of the dispersed silica filler on both the membrane surface and within its layers effectively hindered methanol entry, resulting in reduced methanol passage through the membrane. Furthermore, the membrane modification through the sulfonation process induces cross-linking, leading to the densification of the polymer structure. This increased density poses a challenge for methanol permeation, contributing to a lower permeability value.[28]

Table-1: The Properties and Capabilities of Sulfonated Chitosan/Silica Membrane

Membrane	Methanol Permeability ($mg.cm^2/s$)	Ion Exchange Capacity ($mmol.g^{-1}$)	Proton Conductivity (mS/cm)
Ch Pristine	0.10	3.84	0.56
Ch/Silica 5	0.08	3.97	2.09
Ch/Silica 10	0.07	4.33	0.65
Ch/Silica 15	0.05	4.45	2.82

The sulfonation procedure plays a crucial role in developing a composite membrane that exhibits strong compatibility with the layers constituting the membrane structure. Polymer electrolyte membranes (PEM) with low methanol crossover are indispensable for achieving optimal performance in Direct Methanol Fuel Cell (DMFC) applications. Essential attributes required for this purpose encompass favorable morphology/topography and thermal properties, ensuring the membrane's resilience against methanol movement and minimizing methanol crossover.[29] The existence of methanol diffused into the membrane can disrupt the effectiveness of the membrane electrolyte during fuel cell system processing, and uncontrolled movement of methanol can result in a swift depletion of the methanol fuel.[21,30] The methanol permeability value for membranes with different silica loading variations can be shown in Fig.-5 (a). The test results show that the methanol permeability value of the membrane shows a decreasing pattern as the filler content increases.



(a) (b)

Fig.-5: Results of Methanol Permeability Testing (a) and IEC Value (b) of Sulfonated Chitosan/Silica Composite Membranes

The membrane composed of sulfonated Ch/Silica exhibits a compact and pore-free structure, effectively obstructing the mobility of methanol. This resistance to methanol movement is ascribed to the absence of pathways within the membrane's structural layer. Consistent with findings from previous investigations[31]Increasing the amount of filler content in the composite membrane increased the structural resistance, leading to a decrease in methanol permeability. Composite membranes with optimal density can successfully impede the penetration of methanol into the membrane layer. A membrane possessing these characteristics plays a crucial role in addressing the methanol crossover phenomenon. Recognized challenges, such as methanol interference with the electrolyte membrane's functionality during fuel cell operations and rapid methanol depletion, are well-documented.[7,32,33] Consequently, achieving low methanol permeability emerges as a pivotal factor in achieving high performance in applications of Direct Methanol Fuel Cells. Figure-5 (b) depicts a pattern where the IEC values show an increase with the introduction of silica into the membrane. The membrane, which contains 15 wt.% silica, demonstrates the highest ion exchange capacity value, reaching 4.45 mmol.g^{-1}. The relationship between the IEC value and water uptake in the membrane is evident, as higher water uptake values correspond to an augmented ion exchange capacity.[34] Chitosan contains NH_2 groups that undergo protonization in water, transforming into NH_3^+ ions. The quantity of NH_3^+ ions is influenced by chitosan's capacity to bind protons (H^+). Furthermore, the sulfonation process in composite membranes introduces sulfonate groups into the structural layer of the membrane. These groups create opportunities for ion exchange within the membrane structure, contributing significantly to the ion exchange capacity value.[35] A previous study[36] reported that sulfonation treatment on composite membranes increased the IEC value compared to membranes without sulfonation. A heightened ion exchange capacity value indicates that the sulfonated Ch/Silica membrane serves as an efficient medium for proton transport, underscoring its potential as an electrolyte membrane in DMFC application. Proton conductivity is the main property that determines proton transport in electrolyte membranes for direct methanol fuel cell applications. Previous analysis showed that the ability of the membrane to absorb water is very important because water acts as the initial medium for proton transport through the liquid phase.[37] However, the main factor in selecting a membrane for a fuel cell system is its ability to conduct protons. The more protons that can pass through the membrane, the smoother the flow of electrons moving from the anode through the external circuit, so that the energy produced becomes greater.[38,39] Proton conductivity on Ch/silica composite membranes with variations in the amount of filler is shown in Table-1. The test results show that the membrane with the highest proton conductivity, which is 2.82 mS.cm^{-1}, was obtained on the Ch/silica 15 membrane. The presence of silica in the membrane structure causes the proton pathway to become denser, thereby increasing the efficiency of proton transport. In addition, modification of the membrane structure through the sulfonation process can increase the number of electron-conducting groups, which can accelerate the movement of protons and increase the proton conductivity value.[40] These improvements in proton conductivity directly contribute to advancing clean and efficient energy conversion technologies, thereby enhancing the performance and sustainability of direct methanol fuel cells. This advancement supports the objectives of SDG 7, affordable and clean energy, by fostering the development of alternative, low-emission energy systems that can reduce reliance on fossil fuels, increase energy efficiency, and promote wider access to environmentally friendly power solutions. The high proton conductivity value on the membrane is a promising phenomenon for obtaining high performance in direct methanol fuel cell applications.

CONCLUSION

The sulfonated chitosan–silica composite membrane, synthesized from shrimp shell chitosan and silica derived from palm oil shell waste via solvent evaporation, demonstrates enhanced ionic conductivity and structural integrity as confirmed by FTIR and SEM analyses. The Ch/Silica 15 variant shows optimal water and methanol uptake (79% and 57%), low methanol permeability (0.052 mg·cm^{-2}/s), and the highest ion exchange capacity (4.45 mmol·g^{-1}), indicating superior proton transport for direct methanol fuel cell (DMFC) applications. By utilizing renewable waste resources and achieving high ionic conductivity, this study contributes to sustainable, high-performance membrane technology aligned with

SDG 7, Affordable and Clean Energy, with recommendations for further scale-up and long-term stability assessments.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

The present work is related to *SDG-7: Affordable and Clean Energy*. 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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