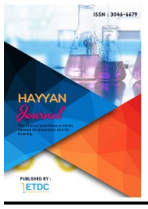

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A Review: Nanofiller for Chitosan Membrane in DMFC Application

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ABSTRACT

Chitosan, a biodegradable polysaccharide derived from chitin, is emerging as a sustainable, low-cost alternative to perfluorinated membranes (like Nafion®) in Direct Methanol Fuel Cells (DMFCs). However, pristine chitosan membranes suffer from low proton conductivity (~10^{-3} S/cm), excessive methanol crossover, limited thermal and oxidative stability, and poor mechanical strength. To address these challenges, significant attention has focused on reinforcing chitosan matrices with nanofillers—such as nanosilica, titanium dioxide (TiO_2), carbon nanotubes (CNTs), graphene oxide (GO), and sulfur- or phosphorous-doped nanoparticles—to tune hydrophilicity, proton transport pathways, and mechanical integrity.This review evaluates synthesis strategies, nanofiller types, and their concentration effects on key membrane properties. Fabrication techniques center on dispersion of nanofillers into chitosan–acid solutions, casting, drying, and crosslinking with agents like glutaraldehyde or tetraethyl orthosilicate (TEOS). Characterizations include SEM/TEM imaging for morphology, mechanical testing for tensile strength and elongation, proton conductivity via electrochemical impedance spectroscopy, methanol permeability assays, and thermal/oxidative resilience through TGA and Fenton's reagent exposure. Findings demonstrate that silica and TiO_2 nanocomposites can elevate proton conductivity to ~10^{-2} S/cm, while reducing methanol permeability to the order of 10^{-7} cm^2/s. Conductive carbon nanofillers (CNTs, GO) introduced interconnected proton channels, further enhancing conductivity, though at potential cost to homogeneity.

Keywords: Chitosan, Direct Methanol Fuel Cell, Proton transport

I. INTRODUCTION

The global pursuit of efficient and sustainable energy alternatives has grown more urgent due to the dual crises of climate change and the depletion of fossil fuel resources. Among various technological advancements, fuel cells—especially proton exchange membrane fuel cells (PEMFCs)—have shown immense promise owing to their high power density and environmentally clean operation (Zhang et al., 2018). Within this category, Direct Methanol Fuel Cells (DMFCs) are considered particularly suitable for portable electronic devices due to the convenience of methanol as a liquid fuel. However, DMFCs still face significant drawbacks, particularly methanol crossover and the high cost of conventional membrane materials like Nafion® (Rosli et al., 2020).

Nafion® is widely recognized for its outstanding proton conductivity (~10^{-1} S/cm)

and good thermal stability up to 80 °C (Singh & Ghosh, 2019). Despite these advantages, its widespread application is hindered by its high cost, environmental non-degradability, and high methanol permeability, which reduces fuel efficiency (Abdullahi et al., 2022). These limitations have encouraged researchers to explore biopolymer alternatives that are more affordable and sustainable. One of the most promising is chitosan—a polysaccharide derived from chitin, which is abundant in crustacean shells.

Chitosan is composed of β-(1→4)-linked D-glucosamine and N-acetyl-D-glucosamine units, and when highly deacetylated (>85%), it becomes water-soluble and film-forming (Rinaudo, 2006). It contains free amine groups that offer numerous modification possibilities, including protonation, crosslinking, and functionalization, which enhance its mechanical, thermal, and barrier properties (Ismail et al., 2019). However, native chitosan membranes are still limited by relatively low proton conductivity (~10^{-3} S/cm), high methanol permeability, and insufficient mechanical strength (Zhang et al., 2021).

To overcome these drawbacks, nanofiller integration into chitosan matrices has emerged as an effective strategy. Inorganic nanofillers such as silicon dioxide (SiO_2) and titanium dioxide (TiO_2) are known to enhance mechanical properties and reduce methanol crossover by introducing tortuous paths that hinder molecular transport (Mousa et al., 2020; Zhang et al., 2021). On the other hand, carbon-based nanofillers like graphene oxide (GO) and carbon nanotubes (CNTs) introduce high surface area and functional groups (–OH, –COOH) that improve hydrophilicity and create proton-conducting channels (Liew et al., 2020; Lee et al., 2018).

Crosslinking also plays a pivotal role in membrane enhancement. Agents such as glutaraldehyde (GA), sulfosuccinic acid, and tetraethyl orthosilicate (TEOS) have been used to stabilize the membrane matrix, reduce swelling, and improve oxidative durability (Sani et al., 2017; Mahalingam et al., 2019). Proper dispersion and integration of these nanomaterials are crucial, as agglomeration can compromise the membrane's uniformity and mechanical properties (Hosseini et al., 2020). These nanofillers are not merely structural additives; they actively influence the physicochemical behavior of the chitosan membranes. Through hydrogen bonding and water retention, they enable more efficient proton transport, which is essential for fuel cell operation (Al-Saadi et al., 2021). In light of these developments, this review aims to consolidate and critically analyze recent research over the past decade related to nanofiller-reinforced chitosan membranes for DMFC applications. It covers synthesis techniques, nanofiller types, membrane characterizations, and their electrochemical performances, while highlighting the challenges and future directions for transforming chitosan into a viable, eco-friendly membrane material for next-generation fuel cells.

II. METHODS

This review was conducted through a systematic analysis of peer-reviewed journal articles published between 2013 and 2024, sourced from reputable academic databases including Scopus, ScienceDirect, MDPI, Wiley, and Springer. The selection of literature was guided by specific keywords such as "chitosan membrane," "nanofiller," "DMFC," "proton exchange membrane," and "methanol crossover." An initial screening yielded over 60 relevant publications. From these, 35 articles were selected based on their scientific relevance, clarity in methodology, and the impact of their findings on the field of direct methanol fuel cell (DMFC) membrane development.

To facilitate a structured comparison, the selected studies were categorized based on several key aspects. These included the type of nanofiller used—such as inorganic, carbon-based, or hybrid composites—the concentration of the filler materials, the crosslinking strategy employed, and the resulting membrane performance characteristics. This categorization enabled a comprehensive evaluation of how each modification influenced the overall functionality of the chitosan-based membranes. The studies chosen for review

demonstrated clear experimental procedures, detailed characterization of membrane properties, and direct application to the DMFC context. The performance of the membranes discussed in the literature was evaluated based on a set of core indicators. These included proton conductivity, typically measured using electrochemical impedance spectroscopy; methanol permeability, assessed via diffusion cell techniques; and mechanical strength, determined through tensile and Young's modulus testing. Additionally, the thermal stability of the membranes was analyzed using thermogravimetric analysis (TGA), while their oxidative durability was assessed by exposure to Fenton's reagent. These performance metrics were used to compare the advantages and limitations of different nanofiller integration methods, as well as to identify trends and trade-offs inherent in the design of chitosan-based nanocomposite membranes for DMFC applications.

III. RESULT AND DISCUSSION

1. Nanofiller Influence on Membrane Performance

Inorganic nanofillers such as silica (SiO_2) and titanium dioxide (TiO_2) have gained considerable attention as effective reinforcement materials for chitosan-based membranes, particularly in the context of Direct Methanol Fuel Cells (DMFCs). These nanoparticles contribute significantly to the structural and functional performance of the membranes due to their unique physicochemical characteristics. Silica, for example, is well known for its high surface area and abundance of hydroxyl groups, which allow it to form hydrogen bonds with chitosan chains. This interaction leads to the formation of a dense and interconnected network within the polymer matrix, thereby enhancing the membrane's mechanical strength and reducing methanol permeability by introducing tortuous diffusion pathways. Similarly, titanium dioxide contributes not only as a physical reinforcement but also improves the thermal and photocatalytic stability of the membrane. Its presence has been associated with increased membrane crystallinity, which in turn enhances proton selectivity and membrane longevity under fuel cell operating conditions.

Carbon-based nanofillers, particularly carbon nanotubes (CNTs) and graphene oxide (GO), offer a different mechanism of performance enhancement. Due to their high aspect ratio and unique electronic properties, these materials act as effective proton-conducting channels when properly dispersed in the chitosan matrix. Functional groups such as carboxyl (–COOH) and hydroxyl (–OH), which are abundant on the surface of GO and functionalized CNTs, facilitate the formation of continuous hydrogen-bonded networks that promote the Grotthuss mechanism of proton transport. This enhancement is especially valuable in low-humidity environments where traditional water-mediated conduction is less efficient. Moreover, the inclusion of these nanofillers increases the hydrophilicity of the membrane, promoting water uptake that is essential for sustaining high proton conductivity. When uniformly distributed, GO and CNTs can elevate proton conductivity from $\sim 10^{-3}$ S/cm (typical for neat chitosan) to values approaching $\sim 10^{-2}$ S/cm, which is comparable to commercial membranes like Nafion®.

However, challenges arise when these nanomaterials are not well-dispersed. Agglomeration can occur at higher filler loadings, which may compromise mechanical integrity and create non-uniform proton conduction pathways. Therefore, advanced dispersion techniques such as ultrasonication, surface functionalization, and surfactant-assisted blending are often employed to ensure homogeneity. Surface-modified CNTs, for instance, exhibit better compatibility with chitosan due to improved interfacial bonding, thereby allowing for higher loading levels without significant performance penalties.

To further improve membrane properties, recent studies have employed hybrid nanofiller strategies—a combination of inorganic and carbon-based materials. These hybrid composites leverage the distinct benefits of both classes: the rigidity and methanol-blocking

ability of inorganic nanoparticles, along with the proton-conducting and high surface area attributes of carbon-based materials. For example, combining GO with silica results in membranes that not only resist methanol crossover more effectively but also offer interconnected pathways for proton transport. These synergistic effects are evident in performance metrics such as increased proton conductivity (~1.3×10^{-2} S/cm) and decreased methanol permeability (~10^{-7} cm^2/s), as shown in several experimental studies including those by Zhang et al. (2018) and Abdullahi et al. (2022).

Furthermore, such hybrid membranes often exhibit enhanced mechanical properties, including tensile strength and elasticity, which are crucial for their operational stability during long-term use in DMFC systems. The combination of multiple nanofillers also allows for more tunable properties, enabling membranes to be tailored for specific application requirements—whether targeting high conductivity, low permeability, or superior thermal resistance.

In conclusion, the incorporation of nanofillers—both inorganic and carbon-based—has shown tremendous potential in overcoming the inherent limitations of chitosan membranes. Through thoughtful selection, surface modification, and strategic combination of fillers, researchers are progressively engineering multifunctional membranes with the right balance of properties for efficient and sustainable DMFC operation.

2. Role of Crosslinking and Fabrication

Crosslinking is one of the most pivotal strategies employed to enhance the physicochemical performance of chitosan-based membranes, particularly for applications in Direct Methanol Fuel Cells (DMFCs). Chitosan, although biocompatible and easily modifiable, suffers from limitations such as high swelling in aqueous environments and relatively poor mechanical strength. Crosslinking agents—particularly glutaraldehyde (GA) and tetraethyl orthosilicate (TEOS)—have been extensively utilized to mitigate these shortcomings and create a more stable membrane structure without significantly compromising ionic conductivity.

Glutaraldehyde is a widely used chemical crosslinker that interacts with the free amino groups on chitosan through Schiff base formation. This reaction produces a networked matrix that improves tensile strength, reduces water and methanol uptake, and minimizes dimensional instability. One of the key advantages of using GA is its ability to form flexible yet durable crosslinks that do not disrupt the intrinsic hydrophilicity of chitosan. This allows the membrane to retain sufficient moisture, which is crucial for effective proton transport via the vehicular mechanism. Additionally, the presence of crosslinked sites restricts the free volume within the polymer network, thereby limiting the diffusion of methanol molecules and reducing crossover—one of the primary concerns in DMFC performance. TEOS, on the other hand, serves a dual role as both a crosslinking agent and an inorganic precursor. Upon hydrolysis and condensation, TEOS forms a silica-like network that integrates with the polymer chains. This siloxane network not only reinforces the mechanical integrity of the membrane but also acts as a methanol barrier due to its dense structure and low permeability. Moreover, TEOS-based crosslinked membranes often show improved thermal and oxidative stability, making them suitable for prolonged operation under fuel cell conditions. Compared to glutaraldehyde, TEOS offers a more rigid and inorganic framework, which is especially useful when combined with nanofillers like SiO_2 or TiO_2.

In addition to chemical crosslinking, the fabrication method of the membrane plays a critical role in determining its overall morphology and performance. Ultrasonic dispersion is commonly used during the membrane preparation process to ensure uniform distribution of nanofillers within the chitosan matrix. This method utilizes high-frequency sound waves to break down agglomerates and disperse nanoparticles evenly, leading to better interaction between fillers and the polymer backbone. A homogeneous dispersion of nanofillers not only

contributes to improved mechanical properties but also creates continuous pathways for proton conduction. Conversely, inadequate dispersion may result in cluster formation, causing stress points and disrupting proton transport channels.

Solvent casting is another fundamental technique used in the fabrication of chitosan-based membranes. It involves dissolving chitosan and its additives in a solvent—typically dilute acetic acid—followed by casting the solution onto a flat surface and allowing it to dry slowly. The drying process enables the formation of a uniform membrane film. Parameters such as solvent concentration, drying temperature, and casting thickness influence the final morphology of the membrane, including pore size distribution and surface smoothness. Membranes fabricated using optimized solvent casting conditions exhibit fewer defects, more consistent thickness, and superior barrier properties.

Taken together, the synergy between crosslinking chemistry and advanced fabrication methods determines the success of chitosan nanocomposite membranes in DMFC applications. Crosslinking agents like GA and TEOS significantly improve dimensional stability and reduce methanol permeability, while fabrication processes such as ultrasonic dispersion and solvent casting ensure optimal nanofiller integration. When precisely controlled, these strategies lead to membranes that are not only mechanically robust but also ionically conductive and methanol-resistant—crucial qualities for long-term DMFC operation.

3. Optimization and Future Prospects

In the development of nanofiller-reinforced chitosan membranes for Direct Methanol Fuel Cells (DMFCs), performance optimization frequently encounters unavoidable trade-offs. While increasing nanofiller content often enhances the membrane's mechanical strength and methanol barrier properties, excessive loading may lead to adverse effects such as reduced flexibility, increased brittleness, and disrupted proton conduction pathways. This is particularly critical in membranes where the continuous transport of protons relies on the availability of hydrated ionic channels. Agglomeration of nanoparticles at high concentrations can obstruct these pathways, leading to a decline in ionic conductivity and structural homogeneity. To address these limitations, precise control over filler concentration and uniform dispersion is essential. Incorporating nanofillers at optimized levels—typically below 5–7 wt%—has been shown to achieve a balance between mechanical reinforcement and proton conductivity. Surface modification techniques such as sulfonation, carboxylation, or grafting with functional groups are increasingly applied to nanofillers like graphene oxide (GO), carbon nanotubes (CNTs), and silica nanoparticles. These modifications improve the interfacial interaction with the chitosan matrix, promote better dispersion, and enhance the proton-conducting nature of the filler.

In terms of future prospects, the incorporation of bio-based nanofillers such as cellulose nanocrystals (CNCs) offers an eco-friendly and renewable alternative with remarkable mechanical properties and abundant hydroxyl groups for hydrogen bonding. Furthermore, the integration of ionic liquids into the chitosan matrix has emerged as a promising strategy to elevate proton conductivity, especially under low humidity conditions, due to their intrinsic ionic nature and plasticizing effect. Crucially, laboratory-scale improvements must be validated under realistic fuel cell operating conditions. Thus, real-world testing of these membranes in working DMFC modules is vital to assess long-term durability, fuel efficiency, and performance stability. Such steps will determine the practical viability of chitosan-based nanocomposite membranes and facilitate their transition from research to application in commercial fuel cell technologies.

IV. CONCLUSION

Chitosan has emerged as a highly promising biopolymer for membrane development in Direct Methanol Fuel Cell (DMFC) applications due to its abundance, biodegradability, and modifiable chemical structure. However, its inherent limitations—including low proton conductivity, high methanol permeability, and modest mechanical stability—have necessitated the incorporation of nanofillers and crosslinking strategies to achieve performance suitable for practical use. This review has demonstrated that nanofillers such as silica (SiO_2), titanium dioxide (TiO_2), carbon nanotubes (CNTs), and graphene oxide (GO) can significantly enhance membrane performance when properly integrated. Inorganic fillers improve mechanical strength and act as methanol barriers, while carbon-based materials introduce proton-conducting pathways through functionalized surfaces. Hybrid approaches that combine multiple filler types have shown synergistic effects, achieving a better balance between conductivity and durability. Surface modification of fillers, such as sulfonation or carboxylation, further enhances interfacial compatibility and proton transport. Crosslinking agents like glutaraldehyde and TEOS strengthen the membrane matrix and mitigate swelling without sacrificing conductivity. Additionally, membrane fabrication techniques such as ultrasonic dispersion and solvent casting have a profound effect on nanofiller dispersion and, ultimately, membrane homogeneity and performance. Despite these advances, several challenges remain. High filler loadings can lead to agglomeration and decreased flexibility, necessitating precise optimization of concentrations and processing conditions. Moreover, the translation of laboratory findings to commercial viability requires extensive testing under realistic DMFC operating conditions. Looking forward, future research should focus on sustainable nanofillers such as cellulose nanocrystals, incorporation of ionic liquids for humidity-independent conductivity, and industrial-scale fabrication strategies. With these developments, chitosan-based nanocomposite membranes may evolve into a cost-effective and environmentally friendly alternative to conventional materials like Nafion®, enabling cleaner and more efficient energy systems.

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