An overview of synthetic polymer-based membrane modified with chitosan for direct methanol fuel cell application

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Abstract. The materials used for fuel cell membrane must have a high proton conductivity, a strong enough wall to block the reactant flow rate and be chemically or mechanically stable in the environment around the fuel cell. To improve the effectiveness of fuel cell membranes and reduce production costs, several synthetic polymer membranes have been developed, including polyethersulfone, polysulfone, polyvinyl alcohol, and polystyrene. Membranes from this polymer have the advantage of being cheap, commercially available, and allowing its structure to store moisture so it can operate at higher temperatures, yet it has low hydrophilic property. Chitosan, as a biopolymer that has strong hydrophilicity property resulted from numerous hydrophilic groups (e.g. –OH, –NH2 and –NR3 þ), can be used for various chemical modifications including to increase mechanical and chemical stability and modification to the possibility of producing ion exchange and increasing ionic conductivity which is a requirement for fuel cell membrane. The purpose of this study is to review the use of chitosan as synthetic polymer-based membrane modification from its structure and properties. Recent achievements and prospect of its applications have also been included.

1. Introduction
The rapid growth of population and industry contributes to the demand and availability of energy which is increasingly depleted and has led the world to an energy crisis. New and renewable energy sources in the future will increasingly have a critical role in meeting energy needs. This is because the use of fossil fuels for conventional power plants in the long term will deplete the sources of oil, gas and coal whose reserves are getting decreasing over time [1]. Fuel cells are one of potential energy sources generating electricity through chemical pathways, as for the recent decades many incredible researches and developments of compact fuel cells have been conducted for various stationary and mobile applications [2], [3]. Polymer electrolyte membrane fuel cells have gained huge consideration, particularly within the automobile and portable power source industries, because of their high efficiency, power density, fast on-off, and low pollution [4]. DMFC is a type of proton exchange membrane fuel cell (PEMFC) which uses methanol as fuel which is fed directly to the anode compartment [5]. Polymer electrolyte membrane (PEM) is one of the essential components in DMFC, which is expected to have high proton conductivity and low methanol permeability [6], [7]. This membrane in the DMFC functions as a transport agent for hydrogen ions (H+) that generated from anode to cathode and also as a separator between anode and cathode compartment [8]. The membrane that is commercially used today is a perfluorinated sulfonic acid membrane known by its trade name Nafion. However, Nafion membrane
still has several disadvantages including high cost, high methanol permeability which results in reduced cell performance, methanol crossover, and loss of conductivity above 80 °C in DMFC [9], [10]. Therefore, development and research on membranes for DMFC applications will always continue so that global problems regard to energy can be resolved with appropriate and environmentally friendly solutions through the DMFC application [5]. To overcome the deficiency of Nafion, membranes made from synthetic polymers with various modifications have been created. There are numerous advantages to polymeric membranes, such as an excellent mechanism for pore-forming control, good mechanical strength, reasonable cost, and more flexible [11]. Some examples of modified synthetic polymers are poly (vinylalcohol) (PVA) [12], poly (ether ketone) [13], poly (ether ether ketone) (PEEK) [14], poly (ether sulfone) (PES) [15], poly (vinylidene fluoride) (PVDF) [16][17], polyetherimide (PEI) [18] and many have been studied further for their potential as membranes in DMFC application [19].

2. Direct Methanol Fuel Cell

One type of fuel cell based on the type of electrolyte used, which is being studied extensively is the methanol fuel cell, so it is widely known as the Direct Methanol Fuel Cell (DMFC)[20]. One of the crucial components of DMFC is the membrane, which functions as a proton conductor from the anode to the cathode and as a separator between anode and cathode space[21]. DMFC offers a simple plan design and possibly higher in general productivity than the reformate-fed fuel cells by removing the reformer. Significant signs of progress in H₂ or air polymer electrolyte fuel cells and high power density have been noticed in the application of DMFC[22].

![Figure 1. Basic illustration of the direct methanol fuel cell (DMFC) system][23].

In DMFC, methanol is oxidized at the anode to produce protons and electrons. Protons arrive at the cathode through the electrolyte and meet oxygen at the cathode to produce water, thus providing the electricity[24]. The proton transfer from anode to cathode is ascribed to the proton-exchange membrane, also maintaining methanol and air (oxygen) separated in the two electrode compartments. The primary problem of DMFCs are their efficiency and performance because of the methanol crossover through the membrane, with consequent efficiency losses[25]. Therefore, it is needed to develop functionalized membranes that can diminish the methanol crossover and at the same time to ensure an effective proton move to the cathode compartment is important [26]. The electrochemical reactions taking place in a DMFC as follows:

Anode: \( \text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \) [27]

Cathode: \( 3/2\text{O}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow 3\text{H}_2\text{O} \) [28]

Overall: \( \text{CH}_3\text{OH} + 3/2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \) [27]
The free energy change, $\Delta G$, also known as free enthalpy is a thermodynamic potential which can be used to calculate the maximum reversible work that a thermodynamic system can perform at constant temperature and pressure [29].

$$\Delta G = - nFE$$

where $n$ is expressed as the number of electrons present in the chemical reaction ($n = 6$ electrons per mole of methanol), $F$ is the Faraday constant (96,487 coulombs per mole), and $E$ is the equilibrium (reversible) cell potential [30].

3. Synthetic Polymer Based Membrane

Making process of membranes from natural polymers has been studied in recent years [31]. In general, the membrane that is often used for membrane is made of cellulose and chitin and their derivatives, which two of them are the most well-known because of their accessibility and their existence is abundant in nature[32]. In Direct Methanol Fuel Cell (DMFC), membrane functions as a transport medium for hydrogen (H+) ions resulting from the oxidation reaction at the anode and a barrier between the two electrodes. The electrolyte membrane requirements for DMFC applications are chemical, electrochemical, mechanical, acidic, good proton conductor, water adsorption, and as small as possible methanol permeability. The proton transport in the electrolyte membrane is determined by the negatively charged groups (usually sulfonates, SO$_3$H). The larger the sulfonate groups, the greater the conductivity. In addition to the presence of sulfonate groups in the membrane, water is also needed to facilitate proton transport, which can increase proton conductivity [33].

Polymer electrolyte membrane (PEM) is an essential part of a DMFC. A variety of PEMs have been developed and studied for DMFC applications. PEM offer verified long-term performance (60,000 h), high proton conductivity, remarkable mechanical strength, and long-term stability. Nevertheless, they are more expensive. Besides, high methanol permeation limits their application and creates a barricade for the DMFC technology commercialization. These factors have added additional motivation for preparing other varieties of PEMs[32].

The most desired properties of polymer electrolyte membranes are:

- High perm selectivity
- Low electrical resistance
- Good mechanical and form stability and
- High chemical and thermal stability

However, the properties depend on numerous factors determined by the parameters such as the membrane material, polymer network density, hydrophilic and hydrophobic nature of the polymer matrix, type, and concentration of ions. The polymeric membrane is the vital part of the fuel cell. It uses as the main component for the conduction of protons and effective separation of the electrodes and reactants. In general, properties such as (a) heat and chemical resistance, (b) fire safety, (c) lightweight, (d) high strength and accuracy, and (e) The feasibility of manufacturing in high volumes with low processing costs make them well suited for a broad range of applications [34]. Some of the modified synthetic polymers that have been studied as potential membranes in DMFC include poly(vinyl alcohol) (PVA)[12], poly (ether ketone) [13], poly (ether ether ketone) (PEEK)[14], poly (ether sulfone) (PES)[15], poly (vinylidene fluoride) (PVDF) [16][17], polyetherimide (PEI)[18], and many more. The common modification made to the making of the proton exchange membrane is the modification using a sulfonation reaction and consolidation of inorganic fillers [19].

4. Synthetic polymer-based membrane modification with chitosan

One form of polymer membrane composite membrane, which is widely used in DMFC is electrolyte polymer membrane. The type of membrane that is usually used is polyethylene oxide (PEO) with added KOH because it shows good voltage-current density characteristics. However, due to the high degree of crystallinity of the PEO membrane, the resulting fuel cell current density cannot be increased [35]. Chitosan is a natural carbohydrate biopolymer derived from the deacetylation process of chitin, a significant component of shrimp shells. Chitosan has biocompatible, biodegradable, and non-toxic
properties. Chitosan is also an alkaline polyelectrolyte and has good chemical, mechanical and thermal stability. The addition of chitosan which is a biopolymer that has an amine (-NH₂) functional group allows it to be modified physically and chemically, where it can improve the properties of the electrolyte membrane such as proton conductivity and reduce methanol permeability[36]. However, suppose the chitosan membrane is used as the fuel cell. In that case, the resulting current density is still low because the ion delivery of the chitosan membrane is still relatively low. Besides, the crystallinity of the chitosan membrane influences the ionic conductivity of the membrane. To increase the ionic conductivity of the membrane and particularly to trigger the rate of ion migration through the membrane, it is necessary to modify the chitosan membrane [37]. Several studies have been carried out on the manufacture of DMFC application membranes by combining synthetic polymers with chitosan. Most studies combined chitosan with other materials that function as fillers to increase overall conductivity because in actual conditions, chitosan has a low conductivity due to its hydrogen atoms being tightly bound to its monomers, so it cannot be immobilized under the influence of electric fields [38]. Alam [39], made a membrane using chitosan biopolymer extracted from waste shrimp shell as a matrix and montmorillonite as a filler. Chitosan or montmorillonite composite membranes have been successfully prepared by modifying the silane coupling agent where the increase in the proton conductivity of the membrane, along with the increase in silane concentration and the operating temperature was found. Ari et al. [40] have synthesized a membrane made from chitosan by adding silica modified by cetyl trimethyl ammonium bromide. Modification is made by adding hydrophobic organic filler such as silica. Nur Fatin et al. [41] have conducted a study to make chitosan bio composites with a mixture of cellulose with various amounts of sulfosuccinic acid (SSA). The membranes were prepared using the casting method to improve their properties as well as the conductivity of the membrane. In this study, the results show that the membranes have better hydrophilic characteristic when compared to the Nafion membrane. This is due to the existence of three polar functional groups where chitosan is also highly capable of forming a hydrogen bond with water. In addition, summary of the chitosan-based membrane for DMFC is discussed in Table 1.

Table 1. Summary of the chitosan-based membrane for DMFC applications.

| Membrane Material                      | Methanol Concentration (mol/L) | Ionic conductivity (mS/cm) | Methanol Permeability (cm²/s) | Reference |
|----------------------------------------|--------------------------------|---------------------------|------------------------------|-----------|
| Quaternized Chitosan                   | 3                              | 0.17                      | 2.1 × 10⁻⁷                   | [42]      |
| Chitosan/SPVDF                         | 2                              | 2.85                      | 5.7 × 10⁻⁷                   | [43]      |
| Quaternized Chitosan/PVDF              | 2                              | 4.1                       | 12.6 × 10⁻⁷                  | [44]      |
| Zeolite/Chitosan                       | 5                              | 2                         | 1.162 × 10⁻⁶                 | [45]      |
| H₂SO₄ modified chitosan                | 1                              | -                         | 1.4 × 10⁻⁶                   | [46]      |
| Sorbitol-plasticized chitosan/zeolite  | 12                             | -                         | 4.9 × 10⁻⁷                   | [47]      |

4.1. Membrane fabrication
There are 2 points that need to be considered in the membrane fabrication; these are the original properties of the material and the intended morphology in the membrane. There are several techniques used in the manufacture of polymeric membranes: stretching, phase inversion, solution coating, track-etching and sintering [48]. In the DMFC application, membrane fabrication mostly uses phase inversion techniques [19].
The process of modifying chitosan on polymer membranes is carried out in several ways. First is with sulfonation. Sulfonated chitosan is obtained through the incorporation of sulfonate groups into chitosan matrix [49]. On a membrane with a sulfonate group, a sulfonation process is carried out, which is a process of attaching the sulfonate group (HSO\(^3^-\)) to chitosan. The sulfonation method for chitosan solution was done by adding acid reagents [50]. Also, the process of modifying chitosan on polymer membranes can be done by cross-linking. Cross-linking is a commonly used method of chemical modification. The purpose of cross-linking is to ensure good chemical and mechanical stability of chitosan and insoluble chitosan in the aqueous medium [49]. Cross-linking occurs when the sulfuric acid content in the chitosan membrane has been combined with protonation [18]. Vijayalekshmi and Khastgir [4] prepared chitosan-sulfonated poly(vinylidene fluoride) blend membranes by solution casting technique followed by cross-linking with sulfuric acid. In Enggita and Santos [51], also and Ambili et al. [52], the addition of the poly vinyl alcohol membrane was by dissolving chitosan in an acetic acid solution and then adding it to the PVA solution by stirring until a homogeneous solution was formed.

5. Characterization and performance of membrane

5.1. Methanol permeability
If the membrane more resistive, the permeability value will decrease[53]. Permeability was measured using a glass cell with two identical spaces. The membrane commonly used in DMFC, Nafion, has good conductivity, with a range of 0.1 Scm\(^{-1}\). However, this is due to an increase in methanol crossover and conductivity in hydrophilic membranes with the membrane hydration level (\(\lambda\)), it is necessary to improve the properties of this property in order to have better final performance results[54]. The equations used to determine methanol permeability (mS.cm\(^{-1}\)) is:

\[
P = \frac{C_B(\text{mol/L}) \times V_B \times l}{C_A \times A \times t}
\]  

(2)

Where \(C_a\) and \(C_b\) denote the concentration of methanol in each compartments A and B, \(l\) is membrane’s thickness, \(V_b\) is volume of liquid of compartment B, \(t\) as time, and \(A\) represents the area of membrane [55].

| Membrane type | Permeability (10\(^{-6}\) cm\(^2\)/s) | Temperature (°C) |
|---------------|--------------------------------------|------------------|
| Nafion 117    | 4.65                                 | 50               |
| Nafion 117    | 2.38                                 | 20               |
| MMWC          | 4.25                                 | 50               |
| MMWC          | 0.56                                 | 20               |

Table 2. Methanol permeability for Nafion 117 and MMW chitosan membranes.

Based on the experimental table 2, at a temperature of 20° C each chitosan membranes (fabricated from medium molecular weight (MMW) chitosan) at various concentrations of methanol has lower methanol permeability than Nafion (117). However, if the experiment was conducted at high temperatures, the mechanical strength of the chitosan membrane will weaken, which will increase methanol permeability[56]. From the experiment table, it can also be concluded that in the chitosan
membrane, an increase in methanol concentration will cause the methanol permeability to decrease, which is inversely proportional to what happens to membrane Nafion. Sulfonated PVDF (poly (vinylidene fluoride)) with chitosan blends as polymer electrolyte membranes showed good performance due to the ability to hydrate ion groups higher. Also, this membrane excludes organic solvents, which is one of the crucial things in polyelectrolyte membranes [4]. Permana found that the methanol permeability of composite membranes from chitosan and PVA with hematite still had a lower methanol permeability than Nafion [57]. A study by Hidayati et al. (2019) that the membrane printed from sPEEK/chitosan has a methanol permeability that is two times lower than the pure chitosan membrane at room temperature, but higher than the pure Nafion membrane. It was comparable to that of Nafion 115, although the thickness of Nafion 115 was doubled [58].

5.2. Proton conductivity
Proton conductivity (σ) is one of the most important properties for proton-conducting membranes used in a fuel cell [59]. The two mechanisms that determine proton conductivity are "proton leap" (Grotthus) and migration of hydrated protons (Vehicle). The Grotthus mechanism of proton transfer occurs through hydrogen bonds, whereas the Proton transfer mechanism occurs with the help of water[60]. If the proton conductivity value is bigger than the quality of the proton-conducting membrane will be better because the proton conductivity shows the efficiency of the cell reactions that occur in the fuel cell system. The equations used to determine proton conductivity (mS.cm⁻¹) is:

\[ \sigma = \frac{l}{A \times R} \]  

With \( l \) is distance between electrodes, \( A \) denote cross-sectional area, and \( R \) is membrane resistance [61]. Nafion, membrane usually used in DMFCs, already has high proton conductivity that is \( 4.7 \times 10^{-5} \) S/cm below 100°C, high thermal stability (280°C), and low percentage of water absorption. However, Nafion membrane still has weakness, where it has high methanol permeability, amounting to \( 27.6 \times 10^{-8} \) cm²/s [62]. Membranes made of chitosan components require a combination with other materials as a filler to increase the conductivity of the membrane because chitosan has low conductivity [38]. Kharisma et al. in their study made a membrane proton electrolyte made from a combination of polyvinyl alcohol (PVA) and chitosan and by adding clay with silica as a filler. The highest conductivity was obtained with a value of \( 6.96282 \times 10^{-7} \) S / cm, where it was known that the proton conductivity increases with increasing clay composition added to the membrane. This showed that the addition of silica into the polymer matrix affects the amount of proton conductivity [63]. A study conducted by Julian and Santoso [64] to determine the optimal ratio of chitosan/PVA composition with the addition of graphene oxide cross-linked with sulfuric acid showed that membranes with more chitosan composition required a longer immersion time in the manufacturing process to have bigger proton conductivity value.

5.3. Swelling degree
Water swelling test is used to determine the absorption capacity of the membrane to water. The water absorbed in the composite membrane does function as a proton transfer medium, but if swelling degree of the membrane is too high, the membrane will tend to be brittle. Swelling degree is determined based on the difference in membrane length in wet and dry conditions. Wet weight or length is determined after immersion of the membrane in water [65].

\[ \text{SD (by length)} = \frac{l_{\text{wet}} - l_{\text{dry}}}{l_{\text{dry}}} \times 100\% \]  
\[ \text{SD (by thickness)} = \frac{d_{\text{wet}} - d_{\text{dry}}}{d_{\text{dry}}} \times 100\% \]

Where \( l_{\text{wet}} \) is the length of the wet membrane, \( l_{\text{dry}} \) is the length of the dry membrane, \( d_{\text{wet}} \) is the thickness of the wet membrane, and \( d_{\text{dry}} \) is the thickness of the dry membrane. By knowing the swelling degree of the membrane, it can give an overview of methanol’s crossover properties and looseness of the membrane structure. If the membrane has low swelling degree, it indicates that the membrane is
denser so that it can hold the rate of methanol from anode to cathode better [65]. Hidayati [66] found that in the membrane of chitosan and acrylonitrile butadiene styrene (ABS), ABS has the lowest value on both swelling degree and water absorption; on the contrary chitosan shows the opposite performance. In membranes made of chitosan and sPEEK, pure sPEEK membranes had the lowest water absorption while membranes made of pure chitosan had the highest water absorption. Water uptake of sPEEK/chitosan membrane was in between pure membranes [58]. Some factors influence water uptake from the sPEEK/chitosan membrane; one of them is the ionic interaction between -SO\(^3\)\(^-\) and -NH\(^3\)\(^+\) groups in chitosan [67].

6. Conclusion and Future Outlook

Based on several literatures reviewed, chitosan is a suitable material for DMFC because it has thermal and chemical properties which are stable and cheap. However, mixing chitosan alone with synthetic polymer-based membranes has not provided a much more significant value than Nafion in several aspects, such as methanol permeability. It is necessary to add other materials as a filler of chitosan. The addition of material to the membrane can improve some aspects of membrane morphology, but on the other side it can also reduce other aspects. Further studies are needed to obtain the type of material and optimum composition to enhance properties and increase the performance of fuel cells by optimizing membrane structure and fabrication techniques with excellent proton and methanol barrier properties.

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