Composite Membrane Based on Modified Chitosan and Bentonite Filler for Direct Methanol Fuel Cell Application

Mochammad Purwanto [1], Gusti Umindya Nur Tajalla [2], Anjas Badarani Syahab [3], Gugus Handika [4], Cynthia Linaya Radiman [5], Lukman Atmaja [6]

ABSTRACT

DMFC is a type of fuel cell that can be carried around and used to power daily activities, potentially replacing fossil fuels as the primary energy source. DMFC regulates similarly to electrochemical cells by using a separator known as a Polymer Electrolyte Membrane (PEM). The main feature of PEM is that it prevents electrons and reactants from passing between the electrodes while acting as a proton conductor. PEM's main properties for DMFCs are high proton conductivity and low methanol permeability. Because of the widespread methanol crossover problem in commercially available Nafion membranes, this study will investigate the ability and optimal composition of the chitosan-vanillin membrane with the silica-rich bentonite filler. The pristine chitosan was modified with vanillin to improve the organic–inorganic interfacial morphology. The chitosan vanillin (CV) was mixed with bentonite filler in an acetic solution to produce CV-B composite membrane with a phase inversion technique. FTIR and ATR analysis showed that bentonite fillers were successfully intercalated in the CV matrix. Water and methanol uptake, ion exchange capacity, methanol permeability, and photon conductivity were all measured to assess the performance of the membrane. CV-B 10 and CV-B 20 had the highest proton conductivity and methanol permeability, with values of 0.16 S/cm and 7.03 x 10-5 cm2/s, respectively. The performance test results show that the membrane has promising applications as electrolyte membrane for direct methanol fuel cell applications.

Keywords: Fuel cell; Membrane; Chitosan; Vanillin; Bentonite

1. INTRODUCTION

Fossil fuel is the primary energy. It is widely used in common machines, electrical appliances, and devices to maintain society's daily needs. However, such dependence and lack of awareness among people may result in scarcity of this fuel. In addition, using this fuel will significantly impact the environment, particularly acid rain, and global warming (Vaghari et al, 2013). Alternative energy that is sustainable, low emissions and low cost is required. Fuel cells, which have attracted attention as a promising energy source, are one alternative energy source that has the potential to be developed. Direct methanol fuel cells (DMFC) are capable of high energy production, simple design, and easy handling among various types of fuel cells. Therefore, DMFC was developed as a fuel cell green energy source with an easy-to-use device.

Direct methanol fuel cell (DMFC) is one distinct type of the Proton Exchange Membrane Fuel Cell (PEMFC). PEMFC and other fuel cells typically use H_2 as reactant fuel, whereas DMFC uses methanol as the fuel basis. DMFC has a similar power density to PEMFC, but it is safer and more capable as a portable energy source. The main component of a DMFC's working system is the ion exchange membrane, which in this context, proton exchange membrane. The proton exchange membrane acts as a selective barrier to methanol in order to prevent waste of reactant fuels for continuous energy production. This piece of membrane only allows ions to roam freely. As a result, as more H^+ ions pass through the membrane, more electrons are produced, allowing DMFC to provide more energy while emitting less. Nafion® is a well-known commercial proton exchange membrane used in PEMFC. Although Nafion®'s excellent properties (high conductivity up to 7.8 x 10^{-2} S/cm and stable) have made it a good electrolyte choice, methanol permeability still remains a prominent issue. Methanol permeability is problematic because it can result in a small amount of fuel (methanol) being lost and flooding the cathode. This phenomenon causes the reaction rate at the cathode to slow, lowering the cell's working voltage. Therefore, some developments have been made to overcome this problem while maintaining the beneficial properties of electrolytes (Lufrano, F. et al, 2013).

At least several requirements must be met by the polymer electrolyte membrane for the DMFC-type fuel cell operating system requires, including the use of inexpensive materials, good thermal stability, low methanol crossover, and high proton conductivity. Chitosan, a readily available biopolymer, has been successfully used as a Nafion modification for DMFC applications, such as in Wu et al, (2016)'s study with the collaboration of chitosan and phosphotungstic acid (PTA), resulting in high proton conductivity of 2.9 x 10^{-2} S cm-1 and low methanol permeability of 4.7 x 10^{-7} cm2s-1.

Chitosan is a biopolymer found in mostly crustacean animals and some parts of plants. Chitosan serves as a good biocompat-

ibility composite as well as polycationic ability, making it ideal for chemical stability. Despite this advantageous feature, chitosan suffers from low conductivity and mechanical strength. These deficiencies can be compensated by adding some additives to the chitosan polymer matrix. This can be accomplished through crosslinking and mixing methods, as both can potentially increase the power factor of either conductivity or mechanical strength. Horimatsu et al. (2013) reported that the incorporation of glutaraldehyde into chitosan can improve conductivity. Another compromising feature of chitosan is its modifiable OH and NH_2 backbones, which make it a flexible matrix for any application.

Tohidian et al. (2013) utilized chitosan as a matrix and montmorillonite as a filler to create a composite membrane. Because of the strong interaction between chitosan and montmorillonite that resist the movement of methanol, the permeability of methanol is low, at 8.03×10^{-8} cm^2s^{-1}, which is lower than pure chitosan at 1.0×10^{-6} cm^2s^{-1} and Nafion at 2×10^{-6} cm^2s^{-1}. This membrane can work at temperatures as high as 70 °C, so more research is needed to address this shortcoming. It is well-known that membrane fabrication using organic material as the matrix and inorganic material as the filler produces better membranes. Chitosan is a fast-regulating, biodegradable, and non-toxic biopolymer. Chitosan is also hydrophilic, has a good film shape, and can be easily obtained from fishery waste. Bentonite is a clay that is rich in silica. The electrostatic force is formed by parallel layers in a shared structure that are interconnected. Bentonite can interact with organic compounds due to its crystal structure, which includes space and hydroxyl groups on the surface.

This research proposed integrating crosslinking and composite filler into chitosan membranes to improve proton exchange membrane properties and, consequently, fuel cell performance. Vanillin is used in the cross-linking method because it is affordable and has a high ion exchange capacity. The novel aspect of this study is the modification of chitosan with vanillin. The modification of the biopolymer matrix has the potential to increase the value of proton conductivity; in addition to some silica-based fillers (bentonite), it can increase the density of the membrane, reducing the permeability of methanol.

2.   EXPERIMENTS

2.1 Materials

Dried shrimp shells were obtained from fishery waste as chitosan sources. Vanillin powder, Bentonite, hydrochloric acid, Sodium hydroxide, methanol, acetic acid, ethanol, phenolphthalein indicator, and sodium chloride in the pure analytical grade were purchased from Merck.

2.1.1 Chitosan Preparation

First, shrimp shells were ground into powder and then stirred for about 2 hours at 60-70°C in a NaOH 3,5% wt solution with a composition of 1:10 (gr powder/mL NaOH). The shells were filtered from the solution, washed with demineralized water (aquadest), and dried for about 4 hours in an oven at 100 °C. Afterward, the shells were demineralized in HCl solution at 60-70 °C for about 2 hours using a 1:10 (gr powder/mL HCl) ratio. The shells were then converted into chitin and dried using the same method. Chitin was then deacetylated in a NaOH 50% wt solution using the ratio 1:10 (gr powder/mL NaOH) for approximately 1 hour at 90-100 °C. Chitin was degraded into chitosan and, the procedure was repeated to obtain dried chitosan (Purwanto, M. et

al, 2016).

The dried chitosan underwent modification by vanillin. Chitosan was first diluted by 1% of acetic acid (2% w/v ratio) and vanillin was diluted with absolute ethanol (1:2 ratio). Diluted chitosan and vanillin were mixed in one container with 1:2,5 of chitosan:vanillin ratio for about a day at 35 °C. The resultant solution was filtered using a vacuum filter flask to obtain the desired product. The product itself has a brown yellowish color (Pramono, E. et al, 2012). The schematics are shown as the figure below:
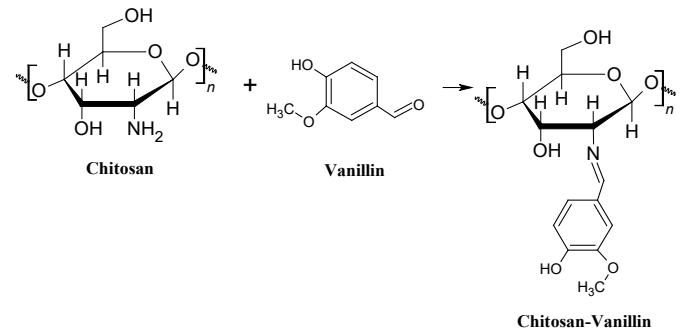

Fig. 1 Synthesis of Chitosan-Vanillin (CV)

2.1.2 Membrane Preparation

The electrolyte membrane was prepared using a sol-gel process. Concentrations of bentonite (1,5%, 3%, and 6% wt) were varied to create chitosan membrane. Chitosan and the desired filler were dissolved in 2% v/v acetic acid at room temperature for 24 hours until the solution gelled. The solution was then cast in drops in a petri dish for 24 hours. After the thin film had formed, the membrane was soaked in NaOH solution to speed up the peeling process. The resulting membrane was washed and dried at room temperature (Purwanto M. et al, 2016).

2.1.3 Characterization

Fourier Transport Infrared (FT-IR) Spectroscopy
Fourier Transport Infrared (FT-IR) Spectroscopy was used to characterize functional groups of chitin and chitosan. The sample was directly subjected to electromagnetic radiation to get the absorbance, which was then correlated with the functional group.

2.1.4 Water and methanol uptake

Water uptake and methanol uptake were determined by measuring the wet membrane and dried membrane. First, the dried membrane should be weighed as a reference. The membranes were immersed in water or methanol for 12 hours for maximum hydration. The surface of the membrane was then wiped with tissue and then weighed again. The formula for water and methanol uptake is shown below:

$$\text{Uptake (\%)} = ((Wwet - Wdry) / Wdry) \times 100\% \qquad (3)$$

Where W_{wet} and W_{dry} are the mass of the membrane before and after immersion (gram).

2.1.5 Methanol Permeability Measurements

Methanol permeability is one of parameters that evaluates membrane performance. Two diffusion cell compartments were prepared to test methano permeability. Membranes were cut into 1.6 x 1.6 cm rectangular sizes and placed between the compart-

ments. Compartment A contains a 1 M methanol solution, while Compartment B is filled with water. The methanol solution was sampled every 30 minutes for about 3 hours. Methanol concentration can be determined using a pycnometer and correcting with a calibration curve. The sampled concentrations were regressed to get their slope. The methanol permeability formula is as follows:

$$P = [\Delta CB/\Delta t] * [L*VB/(A*CA)] \tag{4}$$

Where :
P = methanol permeability (cm2/s)
$\Delta CB/\Delta t$= slope determined by a function of time (mol/L.s)
L = membrane thickness (cm)
VB = volume of water in the compartment (cm3)
A = membrane surface area (cm2)
CA = methanol concentration in the compartment (mol/L)

2.1.6 Ion Exchange Capacity Measurements

The ion exchange capacity was used to determine how many ion substitutions, particularly H^+, occurred in the membrane. First, the membrane was immersed in HCl for 1 hour to protonate fully. The membrane was immersed in 2 N of NaCl for 24 hours. After some time, the solution was taken for a titration test. NaOH 0,01 M was used as titer with phenolptalein indicator. To calculate the IEC, use the following formula:

$$IEC \text{ (meq)} = [V*C/m] \tag{5}$$

Where V is the volume of titer used to neutralize the NaCl solution (mL), C is NaOH concentration, and m is the dry weight of the membrane, respectively.

2.1.7 Proton Conductivity

Proton conductivity is one essential parameter for working fuel cell membranes. To begin, the membrane (4.4 x 2.2 cm) should be investigated under an LCR meter instrument to obtain Z data. Z data was further converted into Rbulk by using the z-view application. Lastly, to determine conductivity using this formula:

$$\sigma = L/(R*A) \tag{6}$$

Where σ is conductivity (S/cm), R is bulk resistance (ohm), L is the membrane thickness, and A is the area of the membrane tested, respectively.

3. RESULTS AND DISCUSSION

Chitosan-Vaniline (CV) membrane was investigated accordingly using FT-IR analysis to observe the potential interactions between chitosan molecules and vaniline molecules through indicative absorption peaks correlated with the literature. Figure 2 demonstrates the IR spectra of the CV membrane. The peaks are mostly depicted from chitosan as a membrane framework, as shown in Table 1. Vaniline addition only substitutes the amine group (NH) of chitosan with carboxyl (C=O) group forming C=N, which indicated an absorption peak of 1666 cm^{-1} as shown in the schematic reaction of chitosan-vaniline (Figure 1) (Dholakia et al, 2013). On the other hand, OH peak also increased, which was attributed to the additional OH of phenolic group of vaniline. Subsequently, vaniline also contributed to the high peak of C-O, C-N, and C-H, contributing to the CV membrane's overall mass. These observations showed that the CV membrane was successfully fabricated.
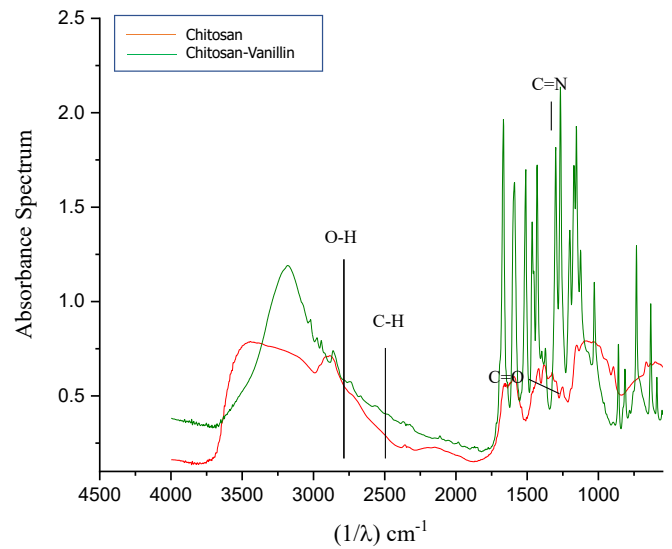

Fig. 2 Chitosan and CV Infrared Spectroscopy Wavelengths

Numerous wavelengths were caught in the FTIR spectrum. There are numerous vibrations of functional groups as summarized in Table 1 below:

Table 1 Functional Group Vibrations of Chitosan

Vibration	Wavenumber (cm^{-1})
-O-H	3550-3100
-N-H (COCH$_3$)	1680-1630
-N-H	1650-1580
-C-H	3000-2850
-C-N	1250-1020
-C=O	1650
-C-O (ether)	1150-1085

(Dholakia et al, 2013)

Bentonite variations of 0%, 1.5%, 3%, and 6% were used as fillers containing high silica and alumina, which are shown in Figure 3 in the peak of 1034 cm^{-1} and 594 cm^{-1}, respectively. As of the increase of filler, the peaks of bentonite in the CV matrix were more intense, which caused the favorability of chitosan bonding to silica and alumina in the membrane, thus releasing vaniline by sol-gel transition process (Nilsen-Nygaard, J. et al, 2015).
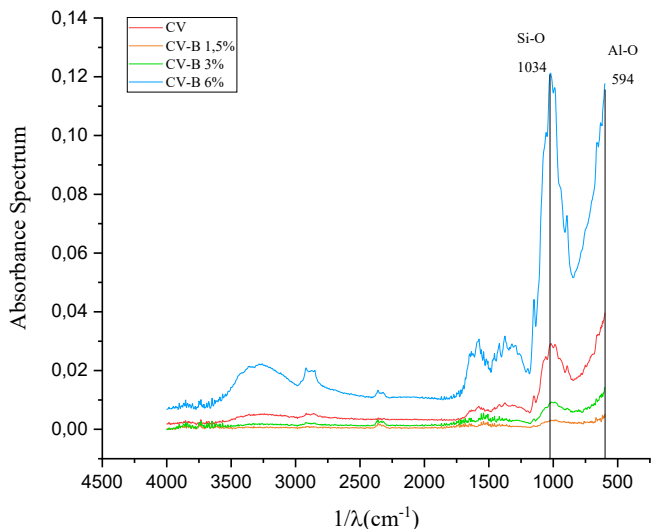
Fig. 3 Infrared Spectra of CV and its Bentonite Filler

From Figure 3, bentonite fillers were successfully intercalated in CV matrix, thus modifying the membrane. This result later became a reference for another performance test. Typically, the higher the filler, the higher the IR spectra, implying that there are more alternative silica fillers in the membrane in comparison to performance (Dholakia et al, 2013).

The water uptake graph presents a downward trend. Because the silica content acted as a water barrier, water absorption was reduced. This result is also reported in an earlier report (Ma J. et al, 2013). The same results were depicted in methanol uptake (Figure 4) because of the same factor. Nonetheless, the difference in water and methanol content was higher. Because CV's phenolic group is structurally similar to methanol, it has a high affinity for methanol rather than water (Liu, H. et al, 2016). The CV-B 6% produced the best results, with the lowest methanol and water uptake.
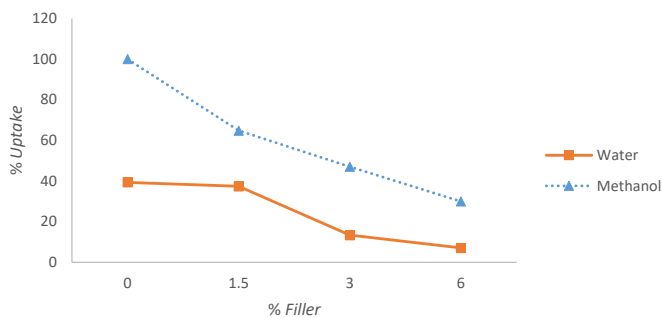

Fig. 4 Water Uptake and Methanol Uptake

The ion exchange capacity test was conducted as a precursor reflection to ionic conductivity performance. The more substitution occurred in the membrane; the more H^+ could be transferred within the membrane.
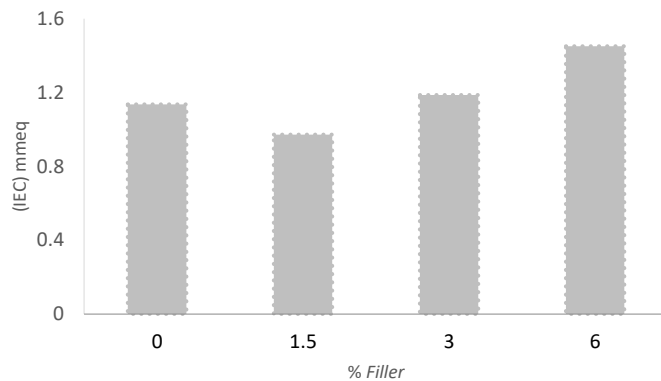

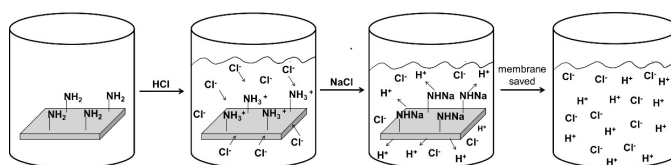**Fig. 5 Ion Exchange Capacity Test for Filler Membrane**

Fig. 6 Ion Exchange capacity scheme between membrane and NaCl solution

As depicted in Figure 5, the graphs of bentonite show the escalating results. Theoretically, adding silica content into membrane matrix enhanced the proton transport mechanism by proton hopping because of its Si-O and Al-O group. This theory explains why adding bentonite should give a higher value (Antony, R. et al, 2019). This IR spectra result is also emphasized with results. The protonation begins when the amine group (NH_2) exchanges the H^+ of HCl to become NH_3^+; later the NH_3^+ is contacted with Na^+ from NaCl to undergo an exchange H^+ and Na^+. This test implies the mechanism of proton transport within the membrane and also how well the membrane can provide pathways for the proton. As stated earlier, the probability of proton exchange is influenced by the higher deacetylation degree and the membrane structure. The higher the deacetylation degree provides more NH_2 to be protonated, and a good structure (uniformly porous) could increase the probability of proton transport, which emphasizes the role of inorganic fillers (bentonite) (Beydaghi, H. et al, 2015). A similar trend was discovered in the case of bentonite incorporation studied in literature elsewhere (Sasikala, S. et al, 2014).

Methanol permeability tests showed a comparative result which is shown in Figure 7. This permeability test can be linked with methanol uptake. There needed to be more than the results to outrun the Nafion. The best result was only 7.03 x 10^{-5} cm²/s by CV-B 6%. The methanol uptake indirectly affects methanol permeability (Liu, H. et al, 2016). Such a membrane that could absorb methanol would make this membrane less efficient. From IR spectra result was also affecting the result. These results concluded that adding silica content was one method to reduce the membrane's permeability. Despite successfully reducing methanol permeability, the optimization should be conducted for later research. For additional information, generally, a fuel cell needs water to become operational. For proton hopping or vehicle transport, water is essential for proton transport. Even so, water should be kept as minimum as possible to prevent the membrane from swelling or fuel leakage (Purwanto, M. et al, 2016).
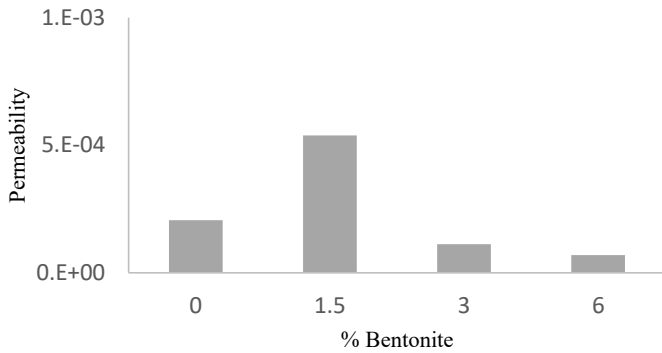
Fig. 7 Methanol Permeability Test of Filler Membrane

The ionic conductivity test was carried out twice. The ambient temperature comes first, followed by the 80°C FC operational temperature. Bentonite would increase only small conductivity (Sasikala et al, 2014) dependent on silica distribution in the membrane matrix. The CV-B membrane complied with the theory. The higher temperature increased the movement of protons within the matrix, as seen in Fig. 8. As a vehicle mechanism, water served as a proton carrier. Hence, the higher the temperature, there more likely the water could evaporate, causing the membrane to lose its proton carrier (Salman, Y.A.K., et al, 2018). The ionic conductivity was also connected with ion exchange capacity. The addition of silica content was critical to add a particular proton carrier. However, too much addition may cause silica interacts with another, contributing to the membrane crumbling and losing its conductivity.
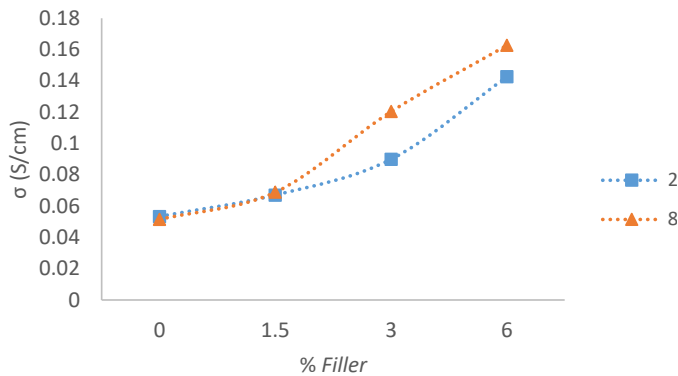

Fig. 8 Membrane Conductivity Test Results of Filler Membrane

4. CONCLUSION

Chitosan-Vanillin with bentonite membrane for fuel cell application was successfully prepared using the solution casting method. FTIR and ATR spectra demonstrated that the CV-B composite membrane was successfully synthesized. CV-B 6% was the best composition for this membrane with excellent conductivity results of 0.108 S/cm at room temperature and 0.162 S/cm at elevated temperature (80°C). The methanol permeability was reduced to 7.03×10^{-5} cm²/s. The characterization results confirmed that the CV-B composite membrane has the potential to electrolyte membrane for DMFC applications.

5. ACKNOWLEDGEMENTS

REFERENCES

Antony, R., Arun, T., and Theodore, D. M. S., 2019, A Review On Applications of Chitosan-Based Schiff Bases, International Journal of Biological Macromolecules,**159**, 615-633.

Beydaghi, H. and Mehran, J., 2015, Aligned Nanocomposite Membranes Containing Sulfonated Graphene Oxide, Industrial & Engineering Chemistry Research, **54**(48), 7028-7037.

Dholakia, Amit B., Jignesh, B. D. and Devyani, Y. M., 2013, Synthesis, characterization and application of novel biopolymeric Schiff base from chitosan and 5-chloro-3-methyl-1-phenyl-1H-pyrazole-4-carboxaldehyde, Der Chemica Sinica, **4**(5), 96-101.

Horimatsu, N, T Takahashi, D Kobayashi, A Shono, and K Otake., 2013, Development of Polystyrene Sulfonate/glycol Chitosan Hybrid Membrane for Direct Methanol Fuel Cell, Desalination and Water Treatment, **51**, 5254–59.

Liu, H., Gong, C., Wang, J., Liu, X., Liu, H., Cheng, F., Wang, G., Zheng, G., Qin, C., and Wen, S., 2016, Chitosan/Silica Coated Carbon Nanotubes Composite Proton Exchange Membrane for Fuel Cell Applications, Carbohydrate Polymers, **136**, 1379-1385.

Lufrano, F., V. Baglio, P. Staiti, V. Antonucci, and A. S. Arico', 2013, Performance Analysis of Polymer Electrolyte Membranes for Direct Methanol Fuel Cells, Journal of Power Sources, **243**, 519–34.

Ma J, Sahai Y, 2013, Chitosan biopolymer for fuel cell applications. Carbohydr Polym., **92**: 955-975.

Nilsen-Nygaard, J., Strand, S.P., Vårum, K.M., Draget, K.I., Nordgård, C.T., 2015, Chitosan: Gels and Interfacial Properties. Polymers, **7**, 552-579.

Pramono, E., Prabowo, A., and Purnawan, C., 2012, Synthesis and Characterization of Chitosan-Vanillin as Polymer Electrolyte Membrane, Journal of Chemical Research, **8**(1), 70-78.

Purwanto, M., and Atmaja, L., 2016, Biopolymer-based electrolyte membranes from chitosan incorporated with montmorillonite-crosslinked GPTMS for direct methanol fuel cell, Journal RSC Advances, **3**, 2314-2317.

Salman, Y. A. K., Abdullah, O.G., Rawad R. H., and Shujahadeen B. A., 2018, Conductivity and Electrical Properties of Chitosan-Methylcellulose Blend Biopolymer Electrolyte Incorporated with Lithium Tetrafluoroborate, International Journal of Electrochemical Science, **13**, 3185 – 3199.

Sasikala, S., Meenakshi, S., Bhat, S.D., Sahu, A.K., 2014, Functionalized Bentonite clay-sPEEK based composite membranes for direct methanol fuel cells, Electrochimica Acta, **135**, 232-241.

Tohidian, M., Seyed Reza Ghaffarian, Seyed Emadodin Shakeri, Erfan Dashtimoghadam, and Mohammad Mahdi Hasani-Sadrabadi. 2013. "Organically Modified Montmorillonite and Chitosan-Phosphotungstic Acid Complex Nanocomposites as High

Performance Membranes for Fuel Cell Applications." *Journal of Solid State Electrochemistry* **17** (8): 2123–37.

Vaghari, H., Malmiri, H.J., Zheng, X., Berenjian, A., and Anarjan, N., 2013, Recent advances in application of chitosan in fuel cells, Sustainable Chemical Processes, **1**(16), 1-12.

Wu, Q., Haining Wang, Shanfu Lu, Xin Xu, Dawei Liang, and Yan Xiang. 2016. "Novel Methanol-Blocking Proton Exchange Membrane Achieved via Self-Anchoring Phosphotungstic Acid into Chitosan Membrane with." *Journal of Membrane Science* 500: 203–10.