# Electrolyte Membrane Composite from Modified Chitosan-Vanillin and Zeolite Filler for Direct Methanol Fuel Cell Application

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Abstract: Fossil fuels, which are the main fuels in the world has a negative impact on the environment and must be replaced immediately with other fuels, DMFC is variant of fuel cell which works as portable to maintain daily human activity and potential to replace fossil fuels as the main source of energy. DMFC regulates as similar to an electrochemical cell in which favor of separator referred to as Polymer Electrolyte Membrane (PEM). PEM shows the main feature, such as hindering the electrons and reactants from trespassing between the electrodes while acting as a proton conductor. The main parameter of PEM for DMFC are good proton conductivity and low methanol permeability. Chitosan-Vanillin (CV) was synthesized by reacting chitosan and vanillin at 1: 2,5 wt ratio and stirred continuously to obtain the product. The membrane then cast by mixing the CV with some variations of zeolite with the compositions of 1,5%, 3%, and 6% wt towards CV. The membrane then cast into a petri dish and left it overnight. The resultant membrane then characterized with FTIR, ATR, molecular weight, water and methanol uptake, ion exchange capacity, ionic conductivity, and methanol permeability. The optimum membrane result was the 6% wt zeolite in the CV, in which ionic conductivity reached 0,1 S/cm and 1,266 x 10-3 cm2/s for methanol permeability.



## 1 INTRODUCTION

Fossil fuels still dominating in the world, especially in countries that still use transportation, which fossil fuels as the main fuel. Fossil fuels have a large negative impact on the environment. Fossil fuels had 82 percent of total global energy sources in 25 years, although any efforts to reduce still requires a lot of alternative energy because the percentage is still the same (Republika, 2013). If fossil fuels still used continuously, impacts such as acid rain and global warming will occur. Therefore, the purpose of this study is to replace the fossil fuels with fuel cells that produce more energy and fewer emissions

Direct methanol fuel cell (DMFC) is a type of PEMFC. DMFC provides good power density almost as high as PEMFC but is safe and capable. One of the main factors for this DMFC to work is electrolytes. Electrolytes known as separators as selective barriers to methanol and H+ ions pass through the membrane. DMFC will provide more energy and fewer emissions. Nafion is famous for commercial electrolytes used in PEMFC because of high conductivity and excellent chemical stability. Although the excellent performance of Nafion has made it a good choice of electrolytes, methanol permeability still occurs. Such permeability affects the efficiency of methanol in DMFC. Therefore, several developments have been made to overcome this problem.

Chitosan is a biopolymer in crustacean animals. Chitosan functions as a good biocompatibility composite and a good polycationic ability to provide chemical stability. Another feature of chitosan is that OH and NH2 backbones can be modified, so chitosan acts as a flexible matrix for any application. In electrolyte membranes for DMFC applications, parameters such as proton conductivity and methanol permeability must be considered. So, to modify chitosan, several methods are offered, such as modifying chitosan, whether inside and outside the matrix. This research was conducted by combining these methods. Vanillin is used for reagent polymers and inorganic silica materials such as zeolites as modifications outside the matrix. Both of these ingredients enhance chitosan as a DMFC electrolyte,



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which is suitable in terms of proton 2 experimental methods. Zeolite was chosen because it has good results, specifically decreased water uptake, decreased methanol uptake, and reduced methanol permeability. Whereas, vanillin was chosen as an anti-bacterial.

# 2 MATERIALS

Dried shrimp shells of Penaeus monodon as chitosan sources. Vanillin powder purchased from PT Subur Kimia Jaya. Zeolite purchased from PT Bratacho Chemica. Sodium hydroxide (NaOH), hydrochloric acid (HCl), methanol (MeOH), acetic acid, hydrogen peroxide (H2O2), sulfuric acid (H2SO4), toluene, ethanol (EtOH), phenolphthalein indicator, and sodium chloride in the pure analytical grade were purchased from Merck.

## 2.1 Chitosan Preparation

Chitosan preparation has three steps deproteinized, demineralized, and deacetylated. The first step is deproteinized, shrimp shells that have been prepared ground into a powder and then stir it at 60-70□C in NaOH 3,5% wt solution by the composition 1:10 (gr powder/mL NaOH) for about 2 hours. The shells then filtered from the solution, washed it by demineralized water (aqua dest), and dried at 100□C for about 4 hours. The shells then demineralized in HCl solution at 60-70□C by the composition 1:10 (gr powder/mL HCl) for about 2 hours. The shells turned into chitin this time and underwent the same procedure to get dried chitin. Chitin then deacetylated in NaOH 50% wt solution by the composition 1:10 (gr powder/mL NaOH) for about 1 hour at 90-100□C. Chitin was degraded into chitosan, and lastly, the same procedure is applied to get dried chitosan.

The dried chitosan underwent modification by vanillin. Chitosan first diluted by 1% of acetic acid (2% w/v ratio) and vanillin diluted by absolute ethanol (1:2 ratio). Both diluted chitosan and vanillin then mixed in one container with 1:2,5 of chitosan: vanillin ratio for about a day at 35□. The resultant solution then filtered by using a vacuum filter flask to get the chitosan powder. The product itself has a brown-yellowish.

## 2.2 Membrane Preparation

The electrolyte membrane was prepared using the sol-gel process. Initially, the experiments were performed by preparing various concentrations (1,5%, 3%, and 6% wt zeolite) chitosan membrane. Chitosan and desire filler were dissolved in acetic acid 2% v/v and then stirred at room temperature for 24 h until the solution formed a gel. The solution was placed into a petri dish for 24 h. After the thin film was formed, the membrane then poured with NaOH solution to faster the peeling. The resultant membrane then washed and dried at room temperature.

## 2.3 Chitosan and Chitosan-Vanillin Characterization

Membrane characterization was used Fourier Transport Infra-Red (FTIR) as instrumental analysis. Chitin and chitosan functional groups was identification by Fourier Transport Infra-Red (FTIR). Samples are directly exposed to electromagnetic radiation to obtain absorbance and then correlate between absorbance and functional groups.

## 2.4 Water and Methanol Uptake

Water uptake and methanol uptake determine the ability of the membrane absorbs the solution. The membrane was weighed before soaked with methanol or water for 12 hours. Then wet membranes are weighed and can be applied to the following formula:

$$\text{Uptake } (\%) = ((W_{wet} - W_{dry})/W_{dry}) \times 100\% \quad (3)$$

Where : $W_{wet}$ = Mass Membrane after immersion (gram)

$W_{dry}$ = Mass Membrane before immersion (gram)

## 2.5 Methanol Permeability

Methanol permeability to determine membrane performance for methanol crossover. The membrane is cut to the size of 1.6 X 1.6 cm and placed into the diffusion cell compartment. Compartment A contains 1M methanol, and compartment B contains water. Methanol concentration was measured using samples in compartment B every 30 minutes for 2 hours. Methanol concentration was measured using a pycnometer and corrected with a calibration curve. The sampled concentrations were regressed to get its slope. Methanol permeability formula as follows :

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

Where :

P = methanol permeability (cm2/s)

$\Delta CB/\Delta t$ = slope determined by function of time (mol/L.s)

L = membrane thickness (cm)
VB = volume of water in compartment (cm3)
A = membrane surface area (cm2)
CA = methanol concentration in compartment (mol/L)

## 2.6 Ion Exchange Capacity (IEC)

IEC is used to determine the movement of protons in membrane. Membrane is immersed into HCL for 1 hour as protonate. Then the membrane was immersed in NaCl as a second protonate for 24 hours. membrane has been titrated using 0.01 M NaOH with phenoptalein indicator as a titer after protonation. Titration data can be used in the following formula:

$$IEC\ (meq) = [V*C/m] \quad (5)$$

Where :
V = Volume of titer used to netralize the NaCl solution (mL)
C = NaOH concentration (M)
m = Dry weight of the membrane (gram)

## 2.7 Proton Conductivity

Proton conductivity is the main parameter to find out membrane quality to delivering protons. Zdata could be found from the LCR meter. Zview will be implemented Zdata to get the Rbulk value. Then Rbulk can be used into the formula :

$$\sigma = L/(R*A) \quad (6)$$

Where :
σ = Conductivity (S/cm))
R = Bulk resistance (ohm)
L = Membrane thickness (cm)
A = Area of the membrane (cm2).

# 3 RESULTS AND DISCUSSION

## 3.1 Membrane Structure

### 3.1.1 Chitosan-Vanillin Structure

FTIR assessments were to determine the group functionality of chitosan and chitosan-vanilline. Numerous wavelengths were caught in the FTIR spectrum. There is numerous vibration of functional groups as informed in the table below:

Table 1: Functional group vibrations of chitosan

| Functional Group | Absorbance Spectrum |
|---|---|
| -O-H | 3550-3100 |
| -N-H (COCH3) | 1680-1630 |
| -N-H | 1650-1580 |
| -C-H | 3000-2850 |
| -C-N | 1250-1020 |
| -C=O | 1650 |
| -C-O (Eter) | 1150-1085 |

(Beuchamp,1981)

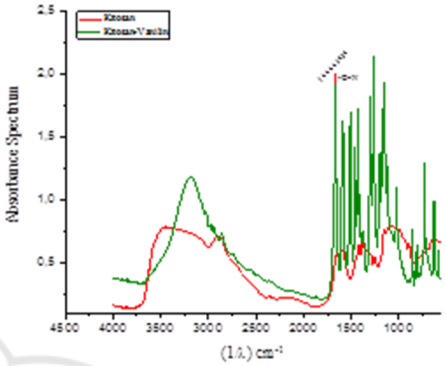


Figure 1: Infrared Spectra Chitosan and Chitosan-Vanillin

Deacetylation by compare amide absorption against water absorption. As a result, the best DD obtained of 92%. Later, the substitution of imine groups' appearance in CV was determined in wavenumber 1690-1640 cm-1. As depicted in figure 1, the –C=N group was in 1666,65484 cm-1, which indicating CV was successfully synthesized. As explained by Pramono (2014), FTIR analysis of vanillin chitosan showed peaks in the area of 1641 cm-1, including the formation of an imine (C = N) or schif base bond.

### 3.1.2 Chitosan-Vanillin Filler Zeolite Structure

The filler membrane was also be examined to determine the substitution of functional groups between CV and zeolite. When the chitosan membrane is modified with zeolite, the adhesion strength between the polymer and zeolite particles will increase and reducing the void space on the membrane (Fitri, 2016).

From figure 2, chitosan-vanillin successfully binds to the zeolite. It is proved by the vibrations peak at range 1100-980 cm-1 dan 1000-500 cm-1. This vibration is functional group Al-O and Si-O, which is chitosan-vanillin filler zeolite bonding comparable with Saikia (2010). But the highest vibrations peak at 1,5% zeolite because mixing didn't go properly.

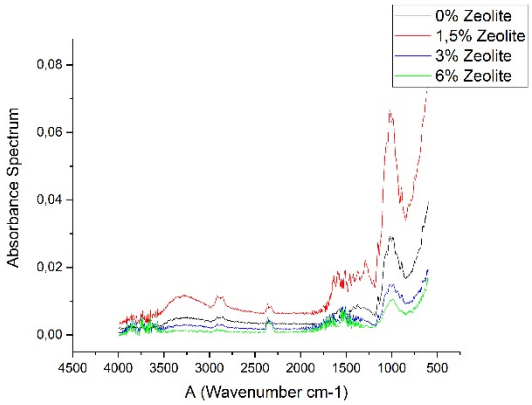


Figure 2: Infrared Spectra Chitosan-Vanillin Filler Zeolite

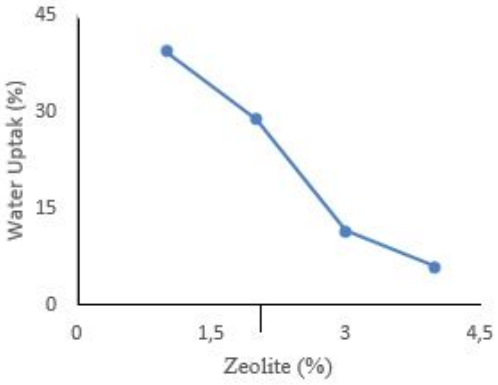


Figure 3: Water Uptake

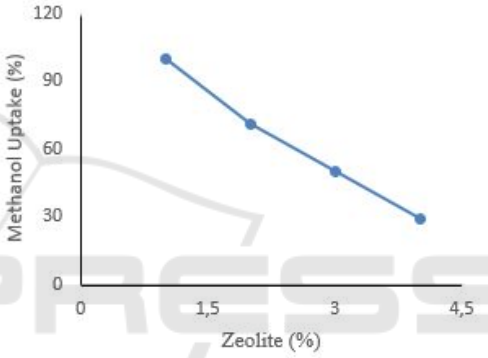


Figure 4: Methanol Uptake

## 3.2 Water and Methanol Uptake

Chitosan generally has hydrophilic and hydrophobic properties. Evidenced by the measurement of water contact angel membrane with range 100-115□ prominent in hydrophobic properties but has hydrophilic properties also. Water contact angles below 90 and hydrophobic 90-180□ (Dwivedi, 2017).Water molecules in chitosan increase the mobility of ions, but higher intensity water can be damaging membrane structure. Therefore a water uptake measurement is necessary to determine the results of the addition zeolite filler to the chitosan membrane because zeolite has hydrophobic properties. Methanol uptake measurements to determine the selectivity of the membrane against methanol as the main fuel in the direct methanol fuel cell because higher methanol uptake can affect the chemical reaction of the direct methanol fuel cell. As depicted from the figure below, the water uptake and methanol uptake of chitosan were determined.

Figure 3 showed water uptake decreased, and new molecular bonds decrease the membrane's ability to absorb water molecules from the solvent (Wang, 2010). Zeolite filler has silica molecules that increase hydrophobic properties. Further, in figure 4, methanol uptake decreased. It has two possibilities, methanol structure similar to the fenolic group, so it has a high affinity (Antony, 2019) or methanol density smaller than water molecules. This makes it easy for methanol molecules to pass through the membrane based on particle size.

## 3.3 Ion Exchange Capacity

Ion exchange capacity was conducted to determine the delivery of ions on the membrane. Therefore, an ion exchange capacity measurements are performed to compare ion delivery each variable of zeolite.

Figure 5 showed the chitosan-vanillin membrane with zeolite filler increase ion exchange capacity at concentration 3% with a value ion exchange capacity is 1,1935 milliequivalent and then decreased at a concentration of 6% of zeolite. Chitosan-vanillin filler zeolite bond makes new proton pathways. However, the silica content of zeolite reduced water molecules causes a lack of proton transport — vehicle mechanism which one requires water molecules to formed H3O+ for delivering a proton (Wang 2008).

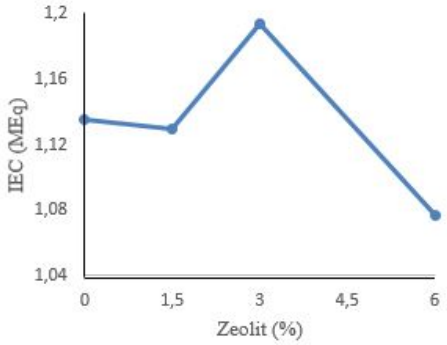


Figure 5: Ion Exchange Capacity

## 3.4 Methanol Permeability

This membrane will be applied for direct methanol fuel cells that methanol as the main fuel. The low permeability of methanol generates high fuel efficiency and reduce fuel loss. And methanol permeability is expected to be low and does not interfere with membrane performance.

Methanol permeability test can be linked with methanol uptake. The results were not enough to outrun the Nafion's. From figure 6, the best result was only 1,875, E-04 cm2/s by CV-Z 3%. Comparable with Wang (2010), high zeolite content can be affected by zeolite molecules because it has a low affinity for each other enlarges membrane pores.

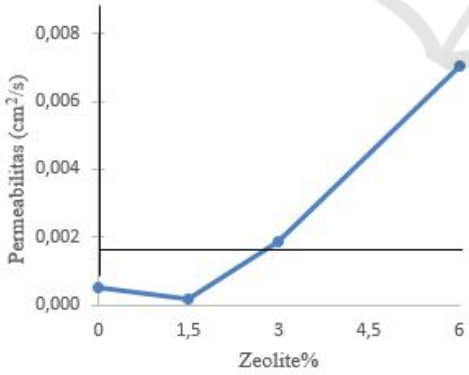


Figure 6: Methanol Permeability

Such a membrane could absorb the amount of methanol that would make this membrane-less efficient. Also, from IR spectra result was also affecting the result. These results concluded that the addition of silica content was one method to reduce the permeability of the membrane. Despite this successfully reducing methanol permeability, the optimization should be conducted for later research.

## 3.5 Ionic Conductivity

This membrane will be applied to direct methanol fuel cells, which are used as methanol to produce electrical energy. The membrane functions as a conduit of H+, which will then react with O2 and produce H2O. So, the proton conductivity test is needed to determine the ability of the membrane to deliver H+.

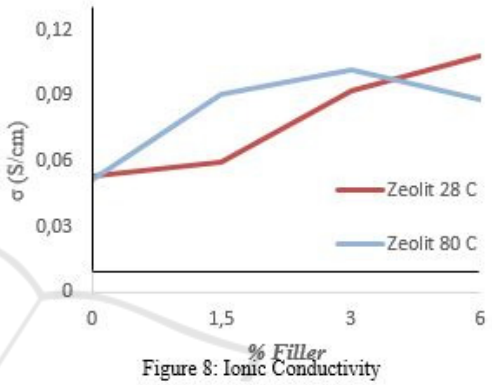


Figure 8: Ionic Conductivity

Figure 7: Ionic Conductivity

As shown in figure 7, at 28□C ionic conductivity increased along with zeolite concentration additional. Zeolites provide hydroxyl groups as pathways proton jumping mechanism. Higher temperature causes the polymer chain to fluctuate, causing a movement to the electrolyte group (Salman, 2018). Especially hydroxyl and phenolic groups in the membrane matrix. This movement causes the transferring proton at 80□C is better than 28□C. However, at 80□C, with a 6% zeolite concentration, ion conductivity was decreased because high temperature is the main problem for water content at the membrane. Proton delivery in-vehicle mechanism requires water molecules to delivers protons. This phenomenon was previously known by the measurement of ion exchange capacity. It has a connection to the delivery of protons.

# 4 CONCLUSIONS

Chitosan-Vanillin with zeolite membrane for fuel cell application was prepared with the addition of zeolite content. The best composition for this research for water uptake at CV-Z 1.5% with 28.834%, methanol uptake at CV-Z 6% with 29.03226%, ion exchange

capacity at CV-Z 3% with 1.1935 MEq, proton conductivity at KV-Z 6% with 0.088474546 S / cm, and permeability of 3% KV-Z methanol with 1,875 X 10-4 cm2 / S. The best composition in this research are methanol uptake and water uptake because the parameter decreases the point near 30% as the best composition. But needs optimization, especially in methanol permeability, because it is still higher than Nafion, which is one essential parameter for the fuel cell.

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