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Valorisation of Shrimp Waste into Chitosan/Montmorillonite-Sulfosuccinic Acid Composite Membrane for DMFC Application

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Abstract

Composite membranes have been synthesized from biopolymer chitosan (CS) and nanosized montmorillonite (MMT) filler crosslinked with sulfosuccinic acid (SSA) as an alternative electrolyte membrane for direct methanol fuel cell (DMFC) application. All prepared membranes were obtained by solution casting technique. Prepared membranes were systematically characterized in terms of water uptake, methanol uptake, and methanol permeability as membrane performance parameter for DMFC application. Fourier transform infrared spectroscopy was used to confirm the structures of the CS/MMT-SSA composite electrolyte membranes. The addition of sulfosuccinic acid evidently decreased the value of methanol permeability with the lowest value of 2.9973×10^{-7} cm^2/s *was obtained from CS/MMT-SSA 16% membrane. The addition of sulfosuccinic acid also decreased the absorption of methanol with the lowest value of 45.9459% while the water absorption of 53.6424% occurred in the membrane with the addition of 16% sulfosuccinic acid. As a result, the CS/MMT-SSA composite membrane appears to be a potential candidate for the DMFC applications.*

Keywords: *direct methanol fuel cell; proton exchange membrane; methanol permeability; chitosan*

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INTRODUCTION

Fuel cells are the most promising alternative power source today because it has several advantages such as, high efficiency, producing clean energy with no pollutants, and economical benefits (Kakati *et al.*, 2015; Sasikala, Gopi and Bhat, 2016). Among various types of fuel cells, the direct methanol fuel cells (DMFCs) is one type of fuel cell which is very promising because it can be used for portable applications resource such as cell phones, laptops, and personal digital accessories (Wasmus and Küver, 1999). In addition, the direct methanol fuel cell has other advantages such as being able to operate at low temperatures (40-120 °C), easy handing, limited toxicity, stable against chemical compounds and does not cause environmental pollution (Aricò *et al*., 2009).

Meanwhile, proton exchange membrane (PEM) is an important component to determine the performance of DMFC (Mohanapriya *et al.*, 2011). It has a very important role in the transport of protons from anode to cathode during cell operation (Kim *et al.*, 2012). A good electrolyte membrane that used for DMFC applications is a membrane that has high proton conductivity, low methanol permeability, and derived from cheap raw material (Tripathi and Shahi, 2011). Currently, one of the membranes for DMFC applications available in the market is sulfonated polytetrafluoroethylene (PTFE), known as Nafion (Tsai and Wang, 2008). However, for DMFC applications, Nafion has several disadvantages, such as decreased performance of the membrane due to permeation of methanol through the membrane (methanol crossover) often occurs if operate at high temperatures (Ma and Sahai, 2013), has a high methanol permeability value at 27.4×10^{-7} cm^2/s (Tsai and Wang, 2008), and the price is relatively expensive (Smitha *et al*., 2005). So, it is a challenge for researchers to develop electrolyte membranes that have better performance.

Presently, several researchers have been developed chitosan based membrane as alternatives for DMFC application (Cui *et al.*, 2009; Xiao *et al.*, 2013; Purwanto *et al.*, 2016a). Chitosan is a material that is abundant in nature, environmentally friendly, inexpensive, hydrophilic, has a regular chemical structure, easy to modify chemically, excellent biodegradability, and non- toxic, so chitosan is one of the materials that can be used as membrane materials that have high performance for fuel cell applications (Pillai *et al*., 2009). Chitosan can be obtained from the extraction of shrimp shell waste (Vilar Junior *et al.*, 2016). Interestingly, Purwanto et al., (2016) recently prepared chitosan and montmorillonite composite membrane (CS/MMT) using 3-glicidoxy propyltrimethoxysilane (GPTMS) as crosslinking for DMFC application. They reported that CS/G-MMT-5 membrane showed the best methanol permeability with the value of $3{,}03 \times 10^{-7}$ cm^2/s. Furthermore, this proves that adding MMT in chitosan matrix has a significantly surpassed Nafion in terms of methanol permeability.

Montmorillonite (MMT) is well known layered silicate, which was used as the nano-fillers added into the composite membranes for DMFC application (Herrera *et al.*, 2009; Sainul *et al.*, 2017). The layer structure and high aspect ratio of MMT clays are expected to be able to decrease the methanol permeability owing to a winding diffusion path for methanol (Yang and Lee, 2019). However, the weakness of MMT as an inorganic material is that it cannot collaborate perfectly with organic polymers, because the montmorillonite surface layer cannot interact optimally with the organic part of the polymer. Furthermore, to solve this drawback can be used crosslinking technique. The sulfosuccinic acid (SSA) crosslinker can provide a major source of proton conduction. Kakati *et al.*, (2015) reported that the effect of crosslinking using crosslinker SSA on the PVA/SMMT/IL composite membrane has shown the way to balance between water uptake and proton conductivity, at the same time has the methanol permeability value of $8{,}76 \times 10^{-6}$ cm^2/s. In addition, crosslinking is very important in perfecting polymer and incorporate functionalized additives for performance of DMFC (Sasikala, Gopi and Bhat, 2016).

The prime objective of this work is to develop a low cost and environmental friendly chitosan/montmorillonite-sulfosuccinic acid (CS/MMT-SSA) composite membrane from shrimp shell waste (*Litopenaeus vannamei*) prepared by simple solution casting method. The performance of the prepared membrane for DMFC applications has been considered by water uptake, methanol uptake, and methanol permeability parameter.

EXPERIMENTAL METHODS

Materials

Raw shrimp shell waste (*Litopenaeus vannamei*) was obtained from a home industry of "Petis" (a traditional Indonesian sauce) in Sidoarjo city, Indonesia. Aquades was purchased from (SAP chemical, Indonesia). Sulfosuccinic acid (SSA) and Montmorillonite (K-10) were procured from Sigma-Aldrich. Sulfuric acid (98% H_2SO_4), Acetic acid (CH_3COOH 99,9%), Sodium Hydroxide pellets (NaOH pure), Hydrochloric acid (HCl), and Methanol (CH_3OH) were supplied by Merck Chemicals

Extraction of chitosan from shrimp shell waste

Extraction of chitosan from shrimp shells divided into four steps: shrimp shell preparation, deproteination, demineralization, and deacetylation.

Shrimp shell preparation. Shrimp shells were obtained from the Petis Industry waste in Sekardangan, Sidoarjo, East Java, Indonesia. Shrimp shells waste were cleaned from impurities and shrimp fleshs that were still attached, then dried in the sun until completely dry. The dried shrimp shells waste was sorted to separate the shrimp shells from the tails and legs and other impurities. The shrimp shells were mashed with a blender and then filtered through a 100 mesh sieve. Shrimp shells that pass 100 mesh sieve were stored.

Deproteination. The prepared shrimp shell powder was dissolved in 3.5% NaOH (m/v) with a ratio of 1:10 (m: v) shrimp shell powder: 3.5% NaOH (m: v). The solution was heated to a temperature of 65°C then stirred with a magnetic stirrer for 2 hours at a temperature of 65°C. After stirring, the solution was cooled, then filtered through a cotton cloth filter. The resulting precipitate was washed with aquades until the pH was neutral. The precipitate with neutral pH was then dried in an oven at 105°C for 4 hours.

Demineralization. The mineral removal process was carried out by dissolving the deproteinized shrimp shell powder in 1 M HCl with a ratio of 1:15 (m: v) 1 M shrimp shell powder: 1 M HCl.

The solution then was heated at a temperature of 65°C and stirred using a magnetic stirrer for 30 minutes. The solution was cooled at room temperature and then filtered using a cloth filter and the filtrate was discarded. The precipitate formed was washed with aquades until the pH was neutral. The solids were dried in an oven at 105°C for 4 hours to evaporate the remaining aqua demineralized. The dry powder obtained was analyzed by FTIR to determine the formation of chitin.

Deacetylation. Chitin was added to 50% NaOH with a ratio of chitin: NaOH 50% of 1:10 (m: v). The mixture was heated to 120 °C while stirring for 4 hours. After stirring, the mixture was cooled at room temperature and then filtered to separate the solids from the filtrate. The solids were then washed to a neutral pH, then dried in an oven for 4 hours at 105°C. The final dry powder obtained was analyzed by FTIR to determine the formation of chitosan.

Determination of the Deacetylation Degree (DD%)

The degree of deacetylation of chitosan was calculated using equation (1) from (Baxter *et al.*, 1992). Applying the band A_{1655}/A_{3450} of infrared ray spectroscopy.

$$\%DD = \left\{ 100 - \left[\frac{A_{165}}{A_{3450}} \times 115 \right] \right\} \qquad (1)$$

Preparation of nanosized montmorillonite

To prepare montmorillonite nanoparticles used method according to previous report (Thuadaij and Nuntiya, 2008; Mor *et al.*, 2017). First, a total of 15 grams of montmorillonite (MMT) was added to 100 mL of 6 N HCL, then stirred for 6 hours. The mixture was filtered and the solids obtained were washed to a neutral pH. Solids which have a neutral pH are dried in an oven at 105°C for 2 hours. The dry solids were then dissolved in 2.5% NaOH (m: v) and stirred for 8 hours. After that, the solution was dripped with 5 M H_2SO_4 until the pH was neutral and formed a colloid, then filtered and washed with warm aquades followed by room temperature. The solids were dried in an oven at 50°C for 48 hours and then ashed at 700°C for 6 hours. The montmorillonite ash was then characterized using a Particle Size Analyzer (PSA) to determine its size.

Preparation of composite membranes

A total of 2 grams of chitosan powder was dissolved in 75 mL 2% (v/v) acetic acid in a beaker at 80°C and stirred for 30 minutes. In different beakers, 0.04 grams of montmorillonite were prepared and dissolved in 25 mL of 2% acetic acid for further ultrasonication process for 30 minutes. The contents of the two beakers were mixed and then stirred with a magnetic stirrer at 80°C for 30 minutes. After stirred, the mixture was ultrasonicated for 30 minutes. Then the mixture was allowed to stand for 30 minutes and then re-ultrasonicated for another 30 minutes. After the second ultrasonication process, sulfosuccinic acid was added to the mixture with variations of 0, 4, 8, 12, 16% (v/m). The mixture is then stirred for 6 hours constantly after stirring, the mixture is poured into the mold and leveled and then allowed to stand for a few days to dry.

The dried membrane was immersed in a 2.5% (m/v) NaOH solution and aquades for 24 hours, respectively. The membrane was then allowed to stand at room temperature to dry. The membrane was then left at room temperature for drying of the remaining distilled water. The synthesized membrane was then coded CS/MMT-SSA %. CS/MMT is the code for chitosan (chitosan) composite with montmorillonite while SSA is the code for sulfosuccinic acid (sulfosuccinic acid) and (%) is the amount of sulfosuccinic acid added. Furthermore, all membranes were characterized by their functional groups using the FTIR instrument and their physical properties included methanol permeability, methanol absorption, and water absorption.

Fourier Transform Infrared Spectroscopy (FTIR)

The chitin, chitosan, and composite membrane samples were analyzed at wavelength of 400-4000 cm^{-1} using a Fourier Transform Infrared Spectrometer. A KBr disc was used as reference. To determine the maximum absorption intensity of bands, the baseline was used.

Water uptake and methanol uptake

Measurement of water and methanol absorption of the membrane that has been made determined by measuring the weight of the membrane after (W_{wet}) and before (W_{dry}) immersion in water and methanol (for methanol uptake test) at room temperature for 24 hours. Before immersion, a dry membrane is immersed in water and 5 M of methanol for 24 hours to see the water and methanol absorption. After immersion, the membrane surface is dried with a tissue and re-weighed as the weight of the wet membrane. Percentage of water absorption calculated using the following equation (2).

$$\%Water\ uptake\ (methanol\ uptake) = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\% \qquad (2)$$

Methanol permeability

Compartments A and B are filled with methanol and distilled water, respectively, as shown in Fig. 1, then a circular sample is placed between them (Wu *et al.*, 2007). In the next steps, each compartment containing methanol and distilled water was stirred. To determine the permeability of methanol, a 5M methanol solution will be used. Every 20, 40, 60, 80, 100 minutes, the compartment containing distilled water is taken as much as the volume of the pycnometer to determine the methanol concentration through a technique using a pycnometer. The permeability value of methanol is obtained using the equation of (Yang and Chiu, 2012):

$$Methanol\ permeability : \frac{SV_B L}{AC_{A0}} \times C_{A0} \qquad (3)$$

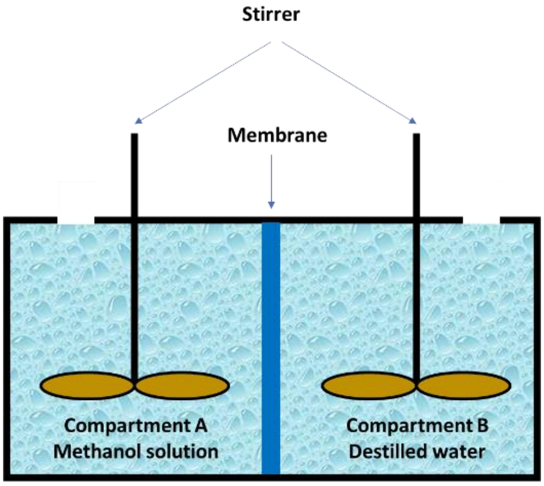

Figure 1. Illustration of methanol permeability test scheme (Neburchilov *et al.*, 2007)

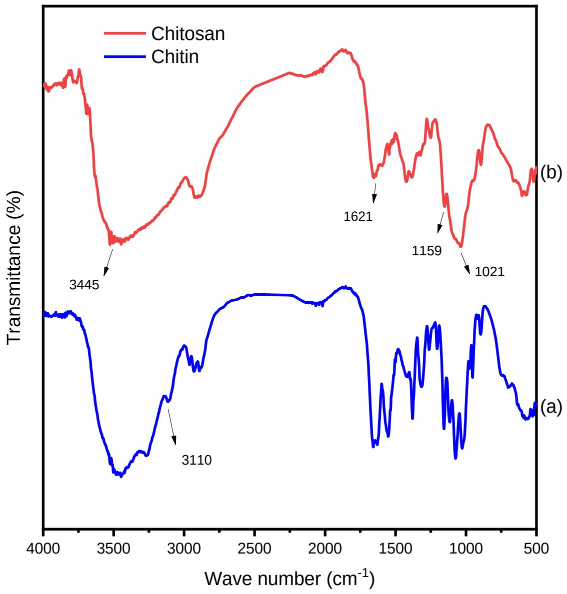

Figure 2. Spectrum FTIR of (a) chitosan dan (b) chitin

S is the slope of the chart; V_B (mL) is the volume of compartment B (distilled water); C_{AO} (mol / L) is the initial concentration of methanol in compartment A (methanol); L (cm) is the thickness of the membrane; and A (cm^2) is the area of the membrane.

RESULTS AND DISCUSSION

Extraction of chitosan from shrimp shell waste

The process of extracting chitin from shrimp shells divided into two steps, deproteination and demineralization. The process that occurs in deproteination is that there is a breakdown of protein and it becomes Na-proteinate which is soluble in water. Then demineralization, is a step that aims to remove inorganic compounds in shrimp shell waste. The final step that must be done to obtain pure chitosan powder is the deacetylation process. In this stage there is the transformation of chitin into chitosan through the process of removing the acetyl group ($-COCH_3$) from chitin by using a strong base reagent, such as NaOH with a high concentration to turn it into an amine group ($-NH_2$). To ensure pure chitin and pure chitosan powder produced, FTIR spectra were tested. The absorption of chitin and chitosan functional groups on FTIR can be seen in Fig. 2.

Based on Figure 2, it can be seen that the FTIR spectra of chitin showed an absorption peak at a wave number of 3445 cm^{-1} which indicated the stretching vibration of the –OH group. The appearance of absorption at 1660 cm^{-1} indicates the amide I band (C=O stretching vibration) and indicates the presence of an acetyl group. The wave number of 3110 cm^{-1} which is the absorption of amide II (asymmetric buckling –NH) is also evidence of the presence of an acetyl group (Branca *et al.*, 2016). Then, the presence of chitosan biopolymer was indicated by a change in the absorption peak of about 3445 cm^{-1} which became wider and shifted towards a smaller wave number, and the absence of absorption at 3110 cm^{-1} which indicated that a deacetylation process had occurred. The appearance of smaller amide I absorption (C=O stretching vibration) in the FTIR spectra of chitosan at 1621 cm^{-1} indicates the release of the acetyl group from chitin (Pearson, Marchessault and Liang, 1960; Sheppard, 1995). In addition, the appearance of absorption in the 1159 cm^{-1} region (asymmetric C-O-C stretching) and absorption in the 1029 cm^{-1} region (C-O stretching vibration) is a typical absorption band of saccharide group compounds. Several studies on chitosan found peaks in similar locations (Kim *et al.*, 2006; Lavorgna *et al.*, 2010). Based on the functional group analysis above, it can be concluded that the product prepared in this study is chitosan.

The degree of deacetylation is a quality parameter of chitosan which shows the quantity of the percentage of acetyl groups that can be removed from the chitin product. The mechanism for releasing the acetyl group ($-COCH_3$) is then converted into a free amino acid group ($-NH_2$) which is the product of chitosan itself. The more acetyl groups released, the higher the degree of deacetylation, and indicates that the quality of the purity of chitosan is getting better (Khan *et al.*, 2002). The high purity of chitosan indicates that the free amino groups are formed, which means that the crosslinked products formed in the next process will be better. According to (Khan *et al.*, 2002), the degree of deacetylation of chitosan produced affects the quality and application of chitosan in various fields.

The deacetylation degree of chitosan from shrimp shell

In this study obtained chitosan with a degree of deacetylation of 74.45%. Furthermore, the chitosan produced have characteristics comparable to commercial chitosan, the degree of deacetylation ranged between 70 and 95% (Guibal *et al.*, 1995; Ishii *et al*., 2014). For the comparison, the other study (Vilar Junior *et al.*, 2016) tried to extract chitosan using the same type of shrimp source (*Litopenaeus vannamei*) by using the method of Zamani *et al.*, (2007) resulting in a degree of deacetylation of 76%.

To calculate the degree of deacetylation of chitosan from shrimp shell waste using the following method from (Baxter *et al.*, 1992).

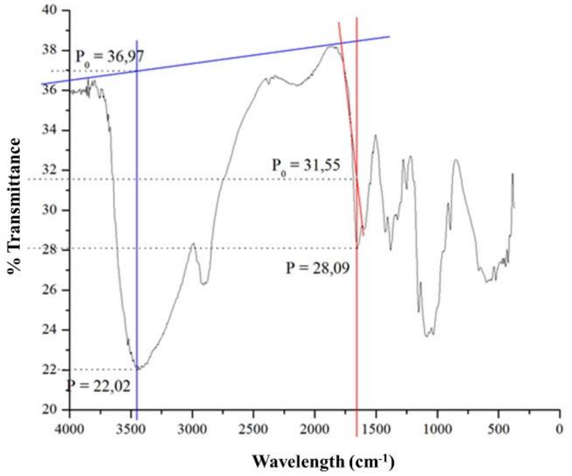

Figure 3. Determination of the deacetylation degree of chitosan using the FTIR baseline method

The formula for calculating the degree of deacetylation based on that proposed by (Baxter *et al.*, 1992) is:

$$A = \log\frac{P_0}{P} \text{ dan } \%DD = \left\{100 - \left[\frac{A_{1655}}{A_{3450}} \times 115\right]\right\} \qquad (4)$$

Where:

A = absorbance
P_0 = % Transmittance on baseline
P = % Transmittance on maximum peak
A_{1655} = amide group absorption
A_{3450} = hydroxyl group absorption

Based on the FTIR spectra of chitosan above, the percentage of DD can be calculated as follows:

$$A_{3450} = log\frac{36{,}97}{22{,}02} = 0{,}225$$

$$A_{1655} = log\frac{31{,}55}{28{,}09}$$
$$= 0{,}05$$

so that:

$$\%DD = \left\{100 - \left[\frac{0{,}05}{0{,}225} \times 115\right]\right\}$$
$$= \{100 - 25{,}55\}$$
$$= 74{,}45\%$$

Preparation of nanosized montmorillonite

In this study, modifications were made to montmorillonite which was used as a filler in the membrane. Montmorillonite which was originally measuring 1213,666 nm was reduced to nano size following the precipitation method that has been carried out by Thuadaij and Nuntiya (Thuadaij and Nuntiya, 2008). The treated montmorillonite was then characterized using PSA (Particle Size Analyzer) to determine its size. The characterization results show the average particle size of montmorillonite is 128.4706 nm with a size distribution as shown in Fig. 3. In the picture, the prepared montmorillonite is shown which has a size between 50 nm to 275 nm.

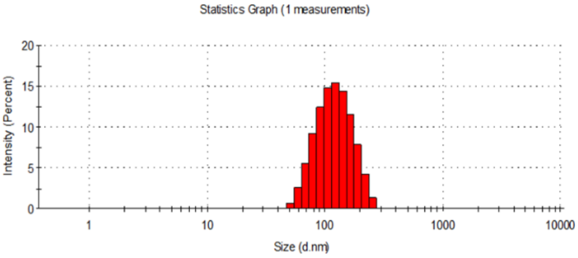

Figure 4. PSA measurement of prepared montmorillonite nanoparticles

Characterization of composite membranes using Fourier Transform Infrared Spectroscopy (FTIR)

The chitosan-montmorillonite composite membrane crosslinked with sulfosuccinic acid has been successfully synthesized and the FTIR spectra show the typical functional groups of chitosan-montmorillonite and sulfosuccinic acid. The FTIR spectra of chitosan/montmorillonite-sulfosuccinic acid (CS/MMT-SSA) composite membranes are represented in Figure 6. In Figure 5 it is seen that there are several peaks the characteristics of the chitosan matrix that appear are in the area of number waves 3400-3470 cm^{-1}, 2877 cm^{-1}, 1647 cm^{-1} and 1589 cm^{-1}, each of which indicates the presence of stretching vibrations –OH, stretching vibrations –CH_2, stretching vibration of the carbonyl group (C=O), and the bending vibration of N−H of the group amine (−NH_2), similar spectrums were also found in other studies (Ramadhan *et al.*, 2014; Purwanto *et al.*, 2016b). The characteristic vibration bands of montmorillonite (MMT) MMT are shown near 1075 cm^{-1} (Si–O) (Zhang *et al.*, 2007; Faghihi *et al.*, 2013) and vibrations around 618 cm^{-1} Al-O-Si (Ayyubi and Admaja, 2020).

The characteristic peak that indicates the presence of sulfosuccinic acid seen in the wave number near 1257 and 1033 cm^{-1} which showed a symmetrical S=O stretching vibration of the sulfonic acid group in the sulfosuccinic acid compound. This corresponds to reported by Balbasi et al (2010) that the stretching S=O vibration of the group sulphonic acids are generally found in the wave number region 1030-1090 and 1160-1260 cm^{-1} (Balbaşi and Gözütok, 2010), the absorption indicated that sulfosuccinic acid was successfully bound to the synthesized membrane. Meanwhile, at a wave number of 3420 cm^{-1}, the transmittance increased for the addition of 0%, 4%, 8%, and 12% SSA but decreased with the addition of 16% SSA. This also occurs at wave numbers 2877 cm^{-1} and 1647 cm^{-1}. Based on the facts from the FTIR spectra that have been described, it can be assumed that there has been a fairly strong interaction between the chitosan matrix and the filler montmorillonite and also crosslinking occurs between chitosan and sulfosuccinic acid crosslinking agent in a composite membrane indicated by the appearance of characteristic peaks of each compound in the FTIR spectra. All prepared membranes are shown in Figure 5.

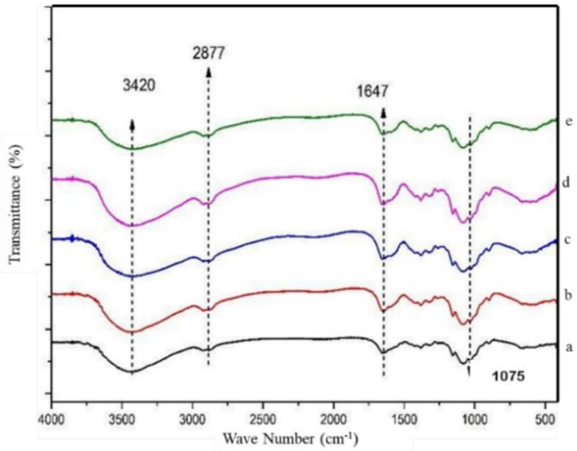

Figure 5. FTIR spectra of CS/MMT-SSA 0 % (a), CS/MMT-SSA 4 % (b), CS/MMT-SSA 8 % (c), CS/MMT-SSA 12% (d), and CS /MMT-SSA 16% (e)

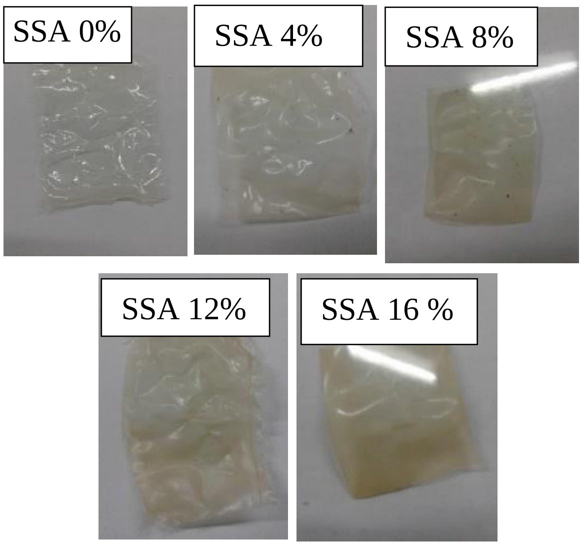

Figure 6. All prepared CS/MMT-SSA composite membranes that have been synthesized

Water uptake and methanol uptake

Water uptake and methanol uptake are important characteristics of Proton Exchange Membrane used in DMFC. Water absorption is related to proton conductivity, while methanol absorption affects methanol permeability. In general, the higher the water absorption capacity can obtain the higher proton conductivity and smaller methanol absorption effects to smaller the methanol permeability. The membrane for a good DMFC has a high proton conductivity and low methanol permeability. The highest water absorption value was obtained on the CS/MMT-SSA 4% membrane of 69.6%, while the lowest methanol absorption was found in the CS/MMT-SSA 0% membrane of 17.8% and CS/MMT-SSA 4% of 48.0%. The water absorption and the methanol absorption of the synthesized membrane are presented in Fig. 6.

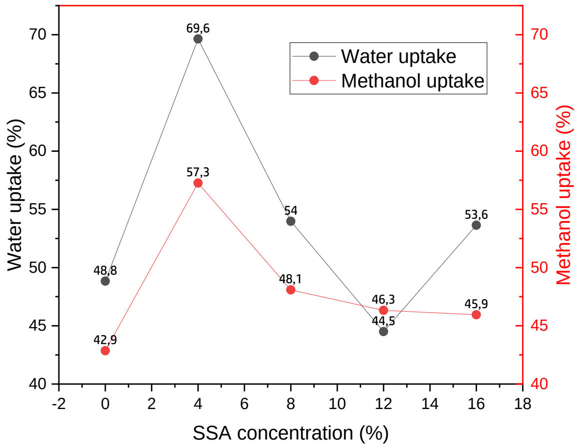

Figure 7. Graph of the water and methanol uptake of the CS/MMT-SSA composite membranes based on the addition of SSA concentration

Figure 7 shows the correlation between water absorption and methanol absorption as a function of the amount of sulfosuccinic acid (SSA) added. When added 4% SSA water absorption increased, then gradually decreased to 12% SSA and again increased when added 16% SSA. A good membrane for DMFC is one that has high water absorption value and low methanol absorption. The highest water absorption was shown by the membrane with the addition of 4% sulfosuccinic acid. Meanwhile, the lowest absorption of methanol was shown by the membrane with 16% SSA when sulfosuccinic acid was added.

When the addition of sulfosuccinic acid there is an increase in the percentage of water absorption as the concentration of sulfosuccinic acid increases. This is due to an increase in the content of sulfonate groups ($-SO_3$) which can interact well with water molecules can increase water absorption on the membrane (Seo *et al.*, 2009). In addition, the addition of sulfosuccinic acid as a crosslinking agent can reduce stiffness in the chitosan chain so that the interaction between the chitosan matrix and the montmorillonite filler becomes weak thereby increasing the ability of the membrane in absorbing water. This is in accordance with the research reported by Witt et al (2010) that the formation of crosslinking can reduce the bond hydrogen and weakens the interactions in the chitosan chain, causing water molecules can pass through the membrane easily (Witt *et al.*, 2010). Furthermore the addition of sulfosuccinic acid can increase the hydrophilic properties of the membrane (Tsai and Wang, 2008). In addition, the role of montmorillonite as a filler in the membrane also has an effect in increasing the value of water uptake due to the hydrophilic properties of the clay (Purwanto *et al.*, 2016b; Sainul *et al.*, 2017).

The percentage of water absorption of membrane is greater than the absorption capacity of methanol which indicates that the membrane absorbs water more easily than methanol. This corresponds to research reported by Wu et al (2007) that if the value of absorption methanol is lower than water absorption, so water absorption by the membrane is more priority than methanol (Wu *et al.*, 2007).

Methanol permeability

One of the important parameters to determine membrane performance for Direct Methanol Fuel Cell (DMFC) applications is methanol permeability. Since DMFC uses methanol as fuel, the low permeability of methanol in PEM will contribute to high fuel efficiency and low fuel loss (Purwanto *et al.*, 2016a). Based on Figure 8, it is known that the largest methanol permeability value is owned by the CS/MMT-SSA 4% membrane of 13.112 × 10^{-7} cm^2/s. This value is lower than the Nafion® membrane methanol permeability reported by Wang et al. (2008) that is equal to 27.40 × 10^{-7} cm^2/s, this may be due to differences in physical and chemical properties between chitosan and Nafion® (Wang *et al.*, 2008). The lowest methanol permeability value was obtained by the CS/MMT-SSA 16% membrane at 2.9973 × 10^{-7} cm^2/s.

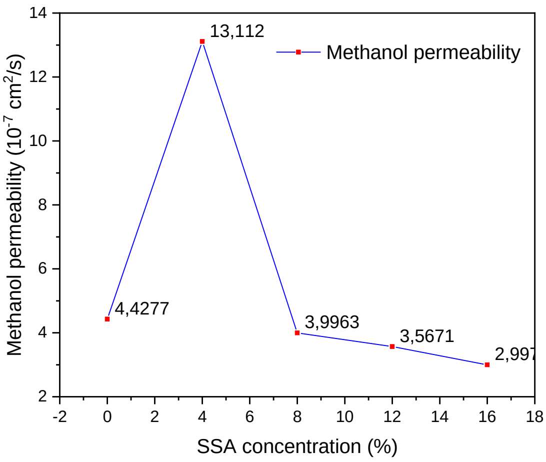

Figure 8. Graph of the permeability value of the CS/MMT-SSA composite membranes based on the addition of SSA concentration

In general, the addition of sulfosuccinic acid can reduce the value of methanol permeability of the composite membranes. This may be caused by 2 things : (i) the formation of a winding path (thoutorus pathway) for methanol diffusion and increased membrane compatibility due to formation of cross-links between the polymer matrix and sulfosuccinic acid and, (ii) the presence of a hydrophilic group (sulphonic group) derived from sulfosuccinic acid which causes the membrane to be hydrophilic so that it can reduce the value of methanol permeability of the composite membranes (Kim *et al.*, 2004; Kakati *et al.*, 2015). Montmorillonite as a filler has a role in decreasing the permeability of methanol because it can hold methanol from passing through the membrane and can physically make the membrane harder (Ayyubi, 2021).

CONCLUSION

Chitosan can be obtained by extraction from shrimp shell waste. Characteristics of the extracted chitosan from shrimp shell waste (*Litopenaeus vannamei*) has a degree of deacetylation of 74.5%. Chitosan from shrimp shell waste can be used for several applications, one of which is as a composite membrane matrix for Direct Methanol Fuel Cell (DMFC).

The chitosan-montmorillonite composite membranes crosslinked with sulfosuccinic acid (SSA) have been successfully synthesized and the FTIR spectra show the typical functional groups of chitosan-montmorillonite and sulfosuccinic acid. The addition of sulfosuccinic acid decreased the value of methanol permeability with the lowest value of 2.9973 × 10^{-7} cm^2/s obtained from CS/MMT-SSA 16% membrane. The addition of sulfosuccinic acid also decreased the absorption of methanol with the lowest value of 45.9459% while the water absorption of 53.6424% occurred in the membrane with the addition of 16% sulfosuccinic acid.

Based on results, it can be concluded that chitosan composite membranes prepared from shrimp shell waste, consisting of MMT, and SSA has a high potential to be a promising low cost and environtmental friendly polymer electrolyte membrane for DMFC applications.

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