The Effect of Silane Addition on Chitosan-Fly Ash/CTAB as Electrolyte Membrane

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Abstract. Electrolyte membrane is an important component in fuel cell system, because it may influence fuel cell performance. Many efforts have been done to produce electrolyte membrane to replace commercial membrane. In this research, electrolyte membrane is composed of chitosan as an organic matrix and fly ash modified with CTAB and silane as inorganic filler. Fly ash is modified using silane as coupling agent to improve interfacial morphology between organic matrix and inorganic filler. This research aims to determine the best membrane performance based on its characteristics such as water uptake, mechanical properties, proton conductivity, and methanol permeability. The steps that have been done include silica preparation from fly ash, modification of silica surface with CTAB, silica coupling process with silane, synthesis of membranes with inversion phase method, and membrane characterization. The result shows that membrane C-FA/CTAB-Silane 10\% (w/w) has the best performance with proton conductivity 8.00 x 10\(^{-4}\) S.cm\(^{-1}\), methanol permeability 3.37 x 10\(^{-7}\) cm.s\(^{-1}\), and selectivity 2.12 x 10\(^{-3}\) S.s.cm\(^{-1}\). The result of FTIR analysis on membrane C-FA/CTAB-Silane 10\% shows that there is only physical interaction occurred between chitosan, fly ash and silane, because there is no peak differences significantly at wave number 1000-1250 cm\(^{-1}\), while morphology analysis on membrane with Scanning Electron Microscopy (SEM) shows good dispersion and there is no agglomeration on chitosan matrix.

Keywords: chitosan, coupling agent, electrolyte membrane, fly ash, silane

1. Introduction

Electrolyte membrane is a critical component in the fuel cell because it serves as a proton conductor and also as a barrier between the two electrodes (anode and cathode) \cite{1}. Currently, the wide use of membrane material is Nafion. The ability of Nafion as a proton conductor is very good with proton conductivity of 0.082 S / cm \cite{2}. The main problem of Nafion if it is used at Direct Methanol Fuel Cell (DMFC) is there is methanol passing through the membrane (methanol crossover). The methanol permeability can cause the loss of fraction of fuel and cause the rate of reaction at the cathode to be slower, which means reducing the performance of cell voltage \cite{1}. Many efforts have been done to produce the electrolyte membrane as Nafion replacement. One biopolymer that is intensively being investigated to replace Nafion is chitosan modified with inorganic fillers for example silica.

The use of inorganic filler with a smaller size can improve the performance of membranes for fuel cell applications \cite{3}. This is according to research of \cite{4} who did chitosan composite membrane/HZSM-5 with variations in particle size is 5, 2, and 0.4 lm. the results showed that there...
has been an increase in proton conductivity and methanol permeability decrease with decreasing particle size HZSM-5.

In this research, silica is coupled with silane, and then incorporated into chitosan to prepare C-FA/CTAB-Silane membrane. According to [5] the presence silane can improve the adhesion between the polymer matrix with filler, so that the interaction is stronger and can improve the electrolyte membrane properties. The proton conductivity, methanol permeability, and membrane selectivity are investigated and optimum membrane is characterized by FT-IR and SEM.

2. Experiment

2.1. Materials

Chitosan with the deacetylation degree of >80% was purchased from Bogor Agricultural Institute, Glycidoxypropyl-trimethoxysilane (GPTMS) and N, N-dimethylformamide (DMF) was purchased from CV. Wahana Hilab Indonesia (Yogjakarta), Fly ash was obtained from PLTU Tanjung Pati Jepara, CTAB, CH₃COOH, CH₃OH, NH₃, HCl, H₂SO₄ was purchased from CV. Chem-Mix Pratama (Yogjakarta).

2.2. Silica preparation from fly ash

Silica preparation from fly ash was done by washing method using HNO₃. The ratio of fly ash and HNO₃ was 1: 4, then stirred using magnetic stirrer for 3 hours at room temperature. After that, the solution was filtered and the residue was washed again with HNO₃. The residue obtained in this way was washed with distilled water to pH neutral and then was dried in an oven at 200°C for 6 hours [6].

2.3. Modification of fly ash surface with CTAB

First step, silica, CTAB and aquademin were mixed and stirred for 30 minutes at room temperature. The ammonia was added quickly until pH= 9, then the solution was stirred again for 2 hours at 60°C. After the solution was filtered, the residue was washed with aquademin to pH neutral and then was dried in an oven at 100°C for 24 hours and was dried in a furnace at 650°C for 3 hours [7].

2.4. Fly ash coupling process with silane

Fly ash and GPTMS were dissolved in 10 mL DMF at room temperature and stirred for 6 hours. Then the homogeneous solution was cast in a beaker glass and placed in an oven at 60°C, then at 100°C for 1 hour, and 120°C for 2 hours until the solvent removed [8]. After that, the residue was soaked with 0.1 M HCl solution at 80°C for 24 hours [9].

2.5. Synthesis of membranes

Chitosan powders 1.000 g were dissolved in 50 mL 2% (w/v) acetic acid and stirred for 4 hours at room temperature. Fly ash powders 0.0883 were dissolved in 50 mL 2% (w/v) acetic acid and stirred for 7 hours at room temperature. Then the two solutions were mixed and stirred for 4 hours at room temperature. The dope solution then was poured into acrylic mold and dried in oven at 60°C for 24 hours.
3. Result and Discussion

3.1. Characterization of silica preparation from fly ash

Tabel 1 shows comparison of fly ash chemical composition by X-Ray Fluorescence (XRF) before and after being washed with HNO₃.

**Table 1. The chemical composition of fly ash**

| No | Compound | Content before preparation (%) | Content after preparation (%) |
|----|----------|--------------------------------|-----------------------------|
| 1  | SiO₂     | 44.94                          | 56.61                       |
| 2  | Al₂O₃    | 19.10                          | 17.58                       |
| 3  | Fe₂O₃    | 14.25                          | 17.85                       |
| 4  | CaO      | 6.64                           | 2.72                        |
| 5  | MgO      | 4.53                           | 0.21                        |
| 6  | Na₂O     | 4.14                           | 0.05                         |
| 7  | TiO₂     | 1.11                           | 0.84                        |

Table 1 shows the SiO₂ content increased by 11.67%. It shows that the nitric acid dissolve metal impurities better than Si in fly ash. The reaction between fly ash and nitric acid is shown in the following equation.

\[
\text{Fly ash} + \text{HNO}_3(\text{aq}) \rightarrow \text{SiO}_2(s) + M(\text{NO}_3)_3(\text{aq})
\]

where, M is a metal other than Si which contained in fly ash such as Al, Mg, Fe, Na, K, Ca, Ti, Mn and other metals [6].

3.2. Characterization of CTAB-modified fly ash particle

Figure 1 shows the morphology of fly ash modified with CTAB a) 0% and b) 4.10%. Modification process of silica with CTAB have been done successfully, it was supported by the particle size of fly ash from the beginning (1-5.5 μm) become slightly smaller than fly ash after modified with CTAB (0.75 – 3.33 μm) if were. This is accordance to [6] which states that the modification of CTAB on the surface of silica can reduce the size of original silica 240.38 nm to 107.89 nm.

![Figure 1. Morphology of fly ash modified with CTAB a) 0% and b) 4.10%.](image)

In addition, agglomeration of silica particles in fly ash appeared to be smaller after they are modified with CTAB. According to [10], surfactant can reduce inter-particle agglomeration of silica, so it can facilitate silica joining the polymeric matrix.
3.3. Characterization of Fly ash coupling process with silane

Figure 2 shows the morphology of fly ash after being coupled with 10% of silane. After the fly ash is coupled with silane, it is obvious that there are silica particles that are spherical with a smaller size in fly ash. It indicates that fly ash coupling process with silane has been done successfully, because the silane that interacts with fly ash and cause coupled of silica which is contained in fly ash.

![Figure 2. SEM image of fly ash/CTAB-silane 10%](image)

Schematic representation of the coupling process of fly ash with silane can be seen in Figure 3. In the first stage, silane form silanol (Si-OH), then silanol from several silane molecules undergo condensation to form polysilane network through bonding Si-O-Si. The next process is incorporation of silane compound on the silica substrate. In this process, the hydroxyl group (OH) on polysilane is bonded to silanol (Si-OH) of the silica substrate through hydrogen bonds and releases water molecules, so it will form polysiloxane network between silica substrate with a silane compound.

![Figure 3. Schematic of the coupling process of fly ash with silane](image)

The final stage of the fly ash coupling process with silane is the soaking powders with 0,1 M HCl solution at 80°C. It is according to [9] at this stage epoxy groups deformation (ring opening) of
the silane compound will happen and produces hydroxyl (OH) that has the potential to react with the amine group on chitosan matrix.

3.4. Proton Conductivity

The proton conductivity of chitosan-fly ash (C-FA), C-FA/CTAB-Silane membranes that are in hydrated conditions at room temperature is presented in Figure 4. It is found that the proton conductivity increases after being coupled with silane, but in silane addition > 10% proton conductivity decreases. It is because the amount of added silane is strong enough to bind the chitosan amine and form a polysiloxane network with fly ash. Strong hydrogen bonds are formed between the amine group on the chitosan and epoxy silane, so it can facilitate the proton hopping.

![Figure 4. Proton conductivity membrane with various concentration of silane](image)

It is consistent with the statement of Lin et al (2010) that the polysiloxane bond formed between the silica and silane fly ash can bind with water to facilitate the occurrence of proton hopping mechanism. In addition, silane at a concentration of >10%, the hydrogen bonds formed between the silane and chitosan and polysiloxane network become saturated and therefore can not facilitate proton hopping optimally and resulting lower proton conductivity.

All proton conductivity of membrane synthesis result shows a smaller value compared to Nafion, but this membrane can still be used as an electrolyte membrane for by [11] membrane having a proton conductivity above $1 \times 10^{-5}$ S / cm can be used as an electrolyte membrane fuel cell. The result shows all membrane synthesis product can be used as an electrolyte membrane.

3.5. Methanol Permeability

The methanol permeability of chitosan-fly ash (C-FA), C-FA/CTAB-Silane membranes at 1 M methanol concentration is shown in Figure 5. All membranes show methanol permeability much lower in the range $1.77 \times 10^{-6}$ to $0.337 \times 10^{-6}$ cm$^2$.s$^{-1}$ than Nafion ($5.6 \times 10^{-6}$ cm$^2$.s$^{-1}$). With the increase of silane addition, the methanol permeability first decreases then increases when silane addition >10% is done.
Figure 5. Methanol permeability membrane with various concentration of silane

Decreasing methanol permeability is caused by the power of a strong interface that causes empty space (void) contained on the membrane surface. It is according to [9] that decreasing methanol permeability can be attributed to better interfacial morphology between chitosan matrix and fly ash filler. The transitional phase between the silane and chitosan generated by the organic chains on the surface silica is favorable for reducing the non-selective voids, and the hydrogen bonds between fly ash and chitosan connect two phases closer. Thus, more methanol molecules would diffuse through the pores in fly ash particle, rather than the fly ash-chitosan interface, which is favorable for reducing the methanol crossover. Increase methanol permeability was caused by the aggregate pore on membrane. It can increase methanol permeability, because mass transfer (methanol) could occur through aggregate pore [2].

3.6. Selectivity

Membranes for the practical usage of PEM in fuel cell are required to posses high proton conductivity and low methanol permeability. Figure 6 shows the selectivity defined the ratio of proton conductivity and methanol permeability.

Figure 6. Selectivity membrane with various concentration of silane

The selectivity C-FA/CTAB-Silane 10% membrane closely resembled with Nafion (2.04 x 10^{-3} \text{ S.s.cm}^{-3}), so the membrane can be used as electrolyte membrane.

3.7. FT-IR Spectra of membrane

The FT-IR spectra of C-FA, C-FA/CTAB, C-FA/CTAB-Silane 10 and 30% membrane are presented in Figure 7.
The characteristic bands of chitosan including the –OH stretching, C-O stretching, -NH$_2$ bending, and –CH$_2$ stretching are located at 3448, 1118, 1627, and 2924 cm$^{-1}$, while the characteristic of fly ash is found at 671 and 493 cm$^{-1}$ which shows Si-O and Al-O are stretching. The result of FT-IR analysis shows that there is physical interaction between chitosan, fly ash, and silane since there is no change significantly.

3.8. Morphology analysis of membrane

Figure 8 shows the typical surface-section SEM image of the C-FA, C-FA/CTAB, C-FA/CTAB-Silane 10 and 30% membrane.

As shown in Figure 9a) and 9b) there is obvious agglomeration of fly ash particle in the surface of membrane. If it is compared with C-FA membrane, the particle size of fly ash in C-FA/CTAB membrane is smaller than fly as in C-FA membrane, indicating that modification of surface of the fly
ash with CTAB can reduce the size particle of fly ash. In addition, in Figure 9c) no obvious agglomeration and good dispersion of fly ash particle, while in Figure 9d) obvious agglomeration happened. The result suggests that at C-FA/CTAB-Silane 10% membrane, interaction between chitosan and fly ash is good, so the membrane structure becomes compact, whereas at C-FA/CTAB-Silane 30% membrane, there is obvious agglomeration because the excess of silane addition, so interaction between chitosan and fly ash is not good.

4. Conclusion

C-FA/CTAB-Silane 10% membrane has the best performance with proton conductivity of $8.00 \times 10^{-4}$ S.cm$^{-1}$, methanol permeability $3.37 \times 10^{-7}$ cm.s$^{-1}$, and membrane selectivity $2.12 \times 10^{3}$ s.s.cm$^{-3}$. The result of Fourier Transform Infra Red (FT-IR) analysis on membrane C-FA/CTAB-Silane 0% and 10% shows that there is only physical interaction occured between chitosan, fly ash and silane, while the result of morphology analysis membrane with Scanning Electron Microscopy (SEM) shows particle distribution was spread evenly and there is no agglomeration.

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