

Utilization of nanosilica from boiler ash sugar cane industry for filler of chitosan sulfate membrane on direct methanol fuel cell

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Abstract. Nanosilica from boiler ash sugar cane industry can be utilized as filler electrolyte membrane of Direct Methanol Fuel Cell (DMFC). The aim of the study was to determine the influence of ammonium sulfate addition on chitosan and nanosilica addition to performance of chitosan sulfate membrane. This research was conducted through three stages: synthesis of nanosilica using presipitation method, synthesis of chitosan sulfate with ammonium sulfate in various concentration of 0.1 M, 0.5 M, 1 M, 1.5 M, and synthesis of chitosan sulfate membrane by adding nanosilica of 1%, 3%, 5% level. The result showed that nanosilica produced had characteristics of amorphous, 330 nm of particles size, 47.49 nm of crystal size, 64% of crystallization degree, and 0.3 of Polydispersity Index (PDI). The degree of sulfonation produced by chitosan sulfate was 15.86%, 19.00%, 22.84%, and 24.75%. The sulfonation of chitosan and nanosilica addition gave significant effect ($\alpha = 0,05$) of membrane characteristics. Membrane with 0.1 M of ammonium sulfate and 3% of nanosilica had the highest performance with 40.75% of water absorption, 44.22% of methanol absorption, 0.66 meq/g of ion exchange capacity, and 6.48×10^{-4} S/cm of ion conductivity. The composite membrane can be applied for DMFC.

1. Introduction

Sugar industry produces boiler ash approximately 0.3% of canes that utilized for sugar production. Boiler ash is by product of sugar industry from the combustion of bagasse on the boiler with the content of SiO_2 , Al_2O_3 , and Fe_2O_3 more than 70% [1]. According to [2], the result of boiler ash characterization using XRF showed that the largest contain of boiler ash is silica of 56.36%. Silica is an inorganic polymer composed of silicon and oxygen with chemical formula of SiO_2 [3]. Silica can be transformed into nanosilica with nanotechnology to improve the characteristics because nanosilica had the larger surface area than silica [3]. Nanosilica from boiler ash can be used as a filler material of ceramic production, filler of rubber production [4], ultrafiltration membrane, composite porous buffer layer [5], and composite of electrolyte membrane on DMFC [6].

DMFC is a kind of fuel cell from methanol. Membrane which commonly used on DMFC series is polytetrafluoroethylene (PTFE) known as trade name of Nafion. PTFE is an expensive polymer and thus becomes an obstacle to commercializing DMFC [7],[8]. The previous study have been developed to explore the alternative electrolyte membrane from other polymer. One of natural polymer that used



to substitute Nafion is chitosan. Chitosan had high thermal stability but the capacity of ion exchange was low.

Addition of filler had important role to increase the characteristic and performance of electrolyte membrane. The addition of filler may result membrane with required characteristics. The requirements of membrane for DMFC should have high proton conductivity and low methanol permeability. The objective of this research were to measure the effects of nanosilica addition and enhancement of ammonium sulfate towards the performances of chitosan-nanosilica electrolyte membrane.

2. Materials and methods

2.1. Materials

Materials which used in this research were boiler ash from sugar factory, natrium hydroxide (Merck/technic), sulfat acid (Merck/PA), amonium hydroxide (Merck/PA) to produce silica, chitosan with DA 93.80%, amonium sulfate, methanol (Merck/PA), technical HCL, acetic acid 2%, and aquadest. The equipments used in this research were glass apparatus, oven, and refluks equipments. Analitical tools included X-Ray Fluorescence (XRF) ARL OPTX-2050 Analyzer, Particle Size Analyzer (PSA) Vasco, X-Ray Diffraction (XRD) Emma GBC, Fourier Transform Infrared (FTIR), and LCR-meter HIOKI 3532.

2.2. Synthesis of nanosilica

Boiler ash was filtered and then heated at a temperature of 700 °C for 6 hours using a furnace [9], and the result was furnace ash. 10 g furnace ash was extracted using 80 ml of 2.5 N NaOH for 3 hours. The solution was filtered and the residue was washed using 20 ml of boiling distilled water. The filtrate was cooled at room temperature. The filtrate was titrated using H₂SO₄ 5 N to pH 2 and added NH₄OH 2.5 N to pH 8.5. The solution was aging at room temperature for 3.5 hours, then dried at 105 °C for 12 hours to obtain dry silica [9],[3],[10]. Silica was hydrolyzed using 3 N HCl for 6 hours. The solution was filtered and the residue was washed with distilled water to pH neutral. Furthermore, the residue was dissolved in NaOH 2.5 N. After a homogeneous solution was added by H₂SO₄ 5 N to pH 7. The solution was allowed to aging at room temperature for 3 hours, then washed with hot water and dried at 105 °C for 12 hours [9],[1],[6].

2.3. Synthesis of chitosan sulfate

Chitosan was added with amonium sulfate at various concentrations 0.1 M, 0.5 M, 1 M, and 1.5 M and ratio 2 : 20 (w/v) then stirred for 4 hours. The mixture was filtered by filtering paper, the sediment was washed with aquades water until neutral and dried for 4 hours in oven in 60 °C [11].

2.4. Synthesis of chitosan sulfate membrane

Chitosan sulfate was dissolved in acetic acid 2%. Nanosilica was added into the solution with various concentration of 1%, 3%, and 5% (w/w). The solvent was stirred until completely mixed by magnetic stirrer. After completely dissolved and no bubbles, the solvent of composite membrane was given ultrasonic for 30 minutes. The solvent was molded into plate of glass with size 10 × 15 cm and dried in oven in 40 °C for 24 hours. The dried membrane was saved in desiccator before use it.

2.5. Characterization

Mineral content in the boiler ash and furnace ash were analyzed using X-Ray Fluorescence (XRF) [6]. Nanosilica which produced in this research was tested with Particle Size Analyzer (PSA) and X-Ray Diffraction (XRD) Emma GBC [6]. The membrane performances was tested by water and methanol absorption test [12], ion exchange capacity [13], ion conductivity, and functional group test [10].

3. Result and discussion

3.1. Characteristics of nanosilica

Based on analysis using XRF, the largest mineral content in boiler ash and furnace ash was silica with amount of 57.4% and 56%. Nanosilica which produced from boiler ash using precipitation method with pH 7 and aging time 3 hours had purity 97.75%. Based on the result of analysis with PDF card (Powder Diffraction File), the characteristic of nanosilica was amorphous. Amorphous properties will provide a large area of proton transport in the membrane [14]. Nanosilica which produced had crystal size, crystallinity degree, particle size, and PDI of 47.49 nm, 64%, 330 nm, and 0.3 respectively. The particles size of nanosilica in this research was included in nano-sized particles according to [15] who stated that nanoparticles size was in the range of 10-1000 nm. PDI showed the uniformity of particles size. The lower PDI value will minimize the agglomeration process [3]. According to [6], the characteristics of nanosilica produced in this research can be applied as filler of membranes for DMFC.

3.2. Water absorption and methanol absorption

Water absorption describes membrane's ability to bind polar groups [10]. The synthesis of chitosan sulfate increased the hydrophilicity of chitosan, thus it facilitated to release proton on DMFC membrane. According to [16], the water which absorbed into membrane can facilitate to transfer proton, and the addition of silica particles can increase hydrophilic parts in polymer structure. Nanosilica additions to membrane also increased the water absorption because of its hygroscopic and amorphous properties. However the addition of nanosilica more than 3% decreased the water absorption. It was because nanosilica can cover existing sulfate groups on chitosan membrane. The value of water absorption can be seen in figure 1.

Methanol absorption was related to methanol permeability. It was the characteristic that inhibit the performance of DMFC. Similar with water absorption, the absorption of methanol was increased with the addition of nanosilica up to 3%. It was caused by the polarity of methanol, thus the water and methanol can be absorbed by hygroscopic silica and have largest surface area [12]. The value of water absorption can be seen in figure 2.

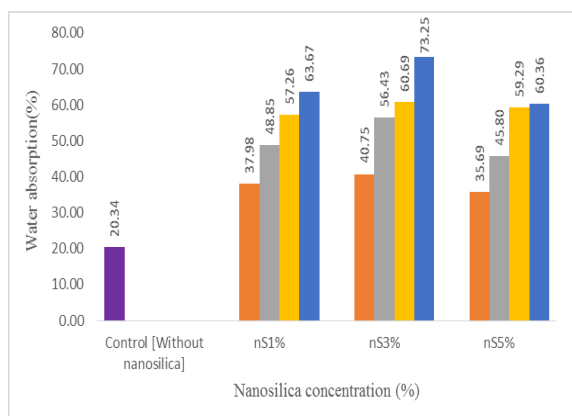


Figure 1. The influence of nanosilica addition and (NH₄)₂SO₄ concentration to water absorption. (■) control without (NH₄)₂SO₄, (■) (NH₄)₂SO₄ 0.1 M, (■) (NH₄)₂SO₄ 0.5 M, (■) (NH₄)₂SO₄ 1 M, (■) (NH₄)₂SO₄ 1.5 M.

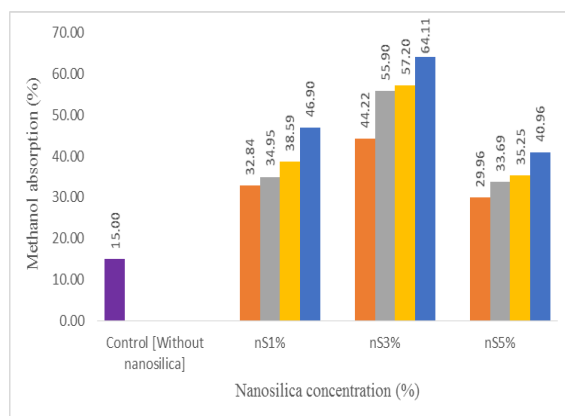


Figure 2. The influence of nanosilica addition and (NH₄)₂SO₄ concentration to methanol absorption. (■) control without (NH₄)₂SO₄, (■) (NH₄)₂SO₄ 0.1 M, (■) (NH₄)₂SO₄ 0.5 M, (■) (NH₄)₂SO₄ 1 M, (■) (NH₄)₂SO₄ 1.5 M.

3.3. Ion exchange capacity and ion conductivity

Ion exchange capacity (IEC) indicates the number of protons that can be transported from the anode to the cathode. The IEC test results (figure 3) showed that the higher concentration of $(\text{NH}_4)_2\text{SO}_4$ that used, increased the ion exchange capacity. The value of IEC increased with by the addition of the sulfate groups in chitosan. The sulfate groups facilitated membrane to release H^+ thus it can increased ion exchange capacity. According to [2], Sulfonate group is able to release H^+ easily, thus can be used as aktif groups into proton conductive membranes to be fuel cell. The existence of SiO_2 groups in chitosan solution will increase the ion exchange capacity [10].

Ion conductivity play an important role in a DMFC membrane. The larger proton conductivity, quality of proton conductive membranes will better. Ion conductivity showed the efficiency of the cell reaction that occurs in the fuel cell system [17]. Figure 4 showed the influence of different concentrations of nanosilica and different concentrations of $(\text{NH}_4)_2\text{SO}_4$ for chitosan toward the ion conductivity. Membrane chitosan sulfate with $(\text{NH}_4)_2\text{SO}_4$ concentration of 0.1 M and addition of 3% nanosilica had the highest ion conductivity. The addition of nanosilica up to 3% increased proton conductivity. Ion conductivity decreased with addition of nanosilika more than 3%. This was caused by nanosilica covered the role of sulfate groups as proton conductor. The membran which have ionic conductivity/proton larger than $1 \times 10^{-5} \text{ S/cm}$ can be used to fuel cell utilization [18]. Nanosilica composite membrane based on chitosan sulfate can be applied as a DMFC membrane.

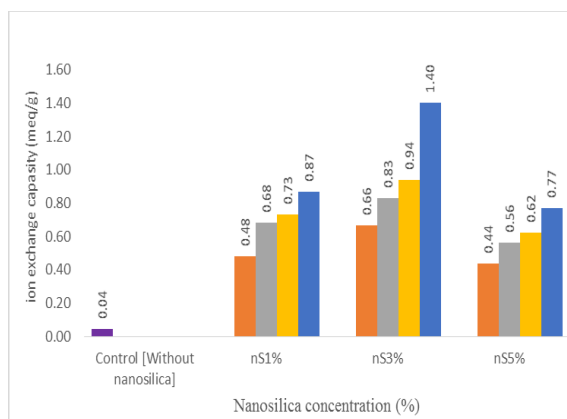


Figure 3. The influence of nanosilica addition and $(\text{NH}_4)_2\text{SO}_4$ concentration to ion exchange capacity. (■) control without $(\text{NH}_4)_2\text{SO}_4$, (■) $(\text{NH}_4)_2\text{SO}_4$ 0.1 M, (■) $(\text{NH}_4)_2\text{SO}_4$ 0.5 M, (■) $(\text{NH}_4)_2\text{SO}_4$ 1 M, (■) $(\text{NH}_4)_2\text{SO}_4$ 1.5 M.

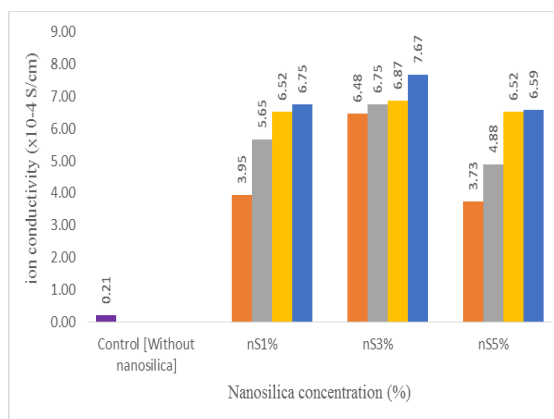


Figure 4. The influence of nanosilica addition and $(\text{NH}_4)_2\text{SO}_4$ concentration to ion conductivity. (■) control without $(\text{NH}_4)_2\text{SO}_4$, (■) $(\text{NH}_4)_2\text{SO}_4$ 0.1 M, (■) $(\text{NH}_4)_2\text{SO}_4$ 0.5 M, (■) $(\text{NH}_4)_2\text{SO}_4$ 1 M, (■) $(\text{NH}_4)_2\text{SO}_4$ 1.5 M.

3.3.1. Membrane functional groups

The addition of sulfate groups in the polymer chitosan was able to improved the performance of the membrane, because the sulfate group was rich with electrons thus it able to release H^+ . The addition of nanosilica in chitosan sulfate solution to produce of a DMFC membrane was able to affect the performance of the membrane. Silanol groups of nanosilica in the membrane makes it easier to absorb the water thus it can easily transfer protons. In addition, nanosilica had pores that can hold methanol permeation.

The functional groups that presented in membrane chitosan sulfate with 0.1 M $(\text{NH}_4)_2\text{SO}_4$ and nanosilica 3% can be seen at figure 5. The absorption peak appeared at the wave number 613 cm^{-1}

indicating the presence of S-O bond. According to [19], a peak of about 618 cm⁻¹ is a sign of S-O bond. The wave number of 890 cm⁻¹ showed the presence of Si-OH groups of silica. The peak at the 1150 cm⁻¹ wave number indicates the presence of a siloxane (Si-O-Si) functional group.

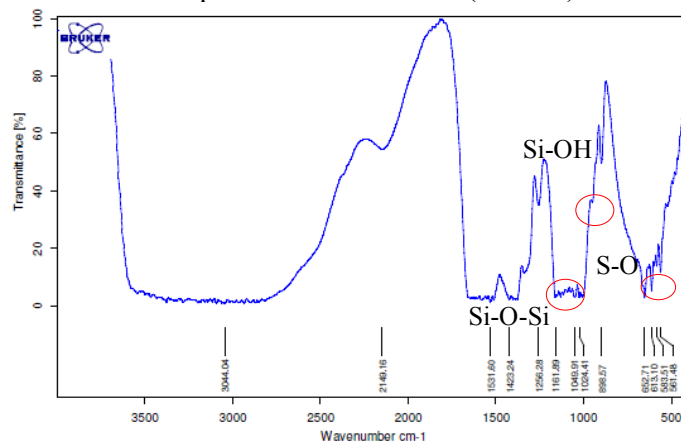


Figure 5. The result of FTIR test on membrane chitosan 0.1 M (NH₄)₂SO₄ and nanosilica 3%.

4. Conclusion

The addition of sulfate groups in chitosan and the addition of nanosilica in membrane chitosan sulfate was able to improve the performance of the membrane. Silanol groups of nanosilica increased the ability of membrane to absorb water thus it could easily transfer protons. The interaction of chitosan (NH₄)₂SO₄ membrane and nanosilica by Duncan test has a significant effect on the performance of the water absorption, methanol absorption, IEC, and ion conductivity membrane. Membrane with 0.1 M of ammonium sulfate and 3% of nanosilica had the highest performance with 40.75% of water absorption, 44.22% of methanol absorption, 0.66 meq/g of ion exchange capacity, and 6.48 x 10⁻⁴ S/cm of ion conductivity.

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