ALKIMIA : Jurnal Ilmu Kimia dan Terapan

ARTICLES

View Article Online
View Journal | View Issue

OPEN ACCESS

Sulfonated Nano-bentonite as Doping Material in Chitosan/PVA Membran in Fuel cell Application

Nina Ariesta[a]*, Nurlela[a], Regita Rachmalia[a]

Abstract. Electrolyte membrane of fuel cell is the main component that plays a role in separating the reactants and being a means of transporting hydrogen ions produced by the anode reaction to the cathode so that the reaction at the cathode produces electrical energy. Chitosan/PVA/ Nanobentonite based membrane was made of natural bentonite form Karang Tengah, Bogor. The study was conducted to know the effect of particle size of doping materials added to chitosan/PVA membrane for fuel cell. The method used in the experiment was casting method with variation of concentration of sulfonated bentonite. Then, membranes were namely C/PVA/n-ben 0.3, 0.6 and 0.9. The membrane that had been synthesized was identified by swelling test, proton conductivity test and cation exchange capacity test then characterized by FTIR and SEM. The result of the experiment showed the best swelling test was presented on the membrane with concentration of 0.9% sulfonated bentonite by 62.79% and the best proton conductivity test was shown on a membrane with a concentration of 0.6% sulfonated bentonite which was 2.24 x 10^{-6} S/cm, supported by the result of the cation exchange capacity data.

Keywords : bentonite, fuel cell, membrane, proton conductivity

[a] *Program Studi Kimia, Universitas Nusa Bangsa, Jl. Kh Sholeh Iskandar Km.4, Tanah Sareal, Bogor, Indonesia*
Correspondence and requests for materials should be addressed to Nina Ariesta
(email : ariestanina14@gmail.com)

Introduction

A fuel cell is a device that generates electricity directly through an electrochemical process using hydrogen gas (H_2) as fuel and oxygen as an oxidizing agent. The use of fuel cells is expected to reduce people's dependence on fuel oil and will reduce the damage to the atmosphere due to emissions [1]. In fuel cells, the electrolyte membrane is the main component that plays a role in separating reactants and being a means of transporting hydrogen ions produced by the anode reaction to the cathode so that the reaction at the cathode produces electrical energy [2]. This membrane is namely the Proton Exchange Membrane, or Proton Electrolyte Membrane (PEM) [3]. The main property of this membrane is its ability to exchange ions. In fuel cell applications, electrolyte membranes must have high cation exchange capacity and thermal stability [4].

There were two types of Proton Exchange Membrane Fuel Cell (PEMFC) namely Hydrogen Fuel Cell and Direct Methanol Fuel Cell (DMFC), both of which utilize PEM for proton transfer [5]. In this research, PEM for PEMFC will be synthesized based on its characteristics. The PEMFC that is usually used was Nafion. Nafion was a commercial membrane that was widely used but had an expensive price, and there were still some limitations to the use of Nafion, namely in terms of usage (life time), such as degradation, corrosiveness and operating temperature. Application of Nafion limited to a temperature not exceeding 80 °C because use above that temperature caused the membrane to expand as a result of the absorption of excessive moisture, thereby reducing the performance of the membrane [6]. Chitosan had a potential as a fuel cell membrane synthesis material because of its several advantages. The chitosan as raw materials was abundant and had high thermal stability, but modifications to the chitosan was needed to be made in order to produce a charged material so that it could be used as an electrolyte polymer membrane. Chitosan had an amino group and a hydroxyl group that allows it to be modified [4].

Previous research had been carried out the use of bentonite in the synthesis of chitosan/PVA membranes, but the bentonite particle size that was not yet optimal results in a membrane with a less homogeneous distribution of bentonite spread in membrane. The particle size and unhomogenized filling in membrane yielded membrane with the proton conductivity value was only about 10^{-8} S/cm [7]. The goals of research were synthesizing membranes using chitosan/PVA and nanobentonite, and characterizing the membrane to examine whether it would be appropriate as a fuel cell membrane.

Experimental

The research was carried out using an experimental method, which was sulfonated nanobentonite in various proportions as filler in chitosan/PVA membrane. Bentonite was collected from Ciburial Village, Karang Tengah District, Bogor. The samples were ground to nano size using ball mill . The obtained nanoparticles were tested for their functional groups. Nanoparticles were filled into chitosan-PVA as membrane synthesis. The characteristics of the membrane identified in the research were functional group of membrane, proton conductivity, water swelling test and cation exchange capacity.

Sulfonated Nano-bentonite preparation

Natural bentonite (from Ciburial Village, Karang Tengah, Babakan Madang District, Bogor Regency) was rinsed and filtered obtain colloidal bentonite. The colloid was allowed to stand overnight until two layers were formed. The paste (bottom layer) was dried at 150 °C. Bentonite samples were calcined using a kiln at 650 °C for 2 hours, then stored in a desiccator. Dry bentonite was ground using ball mill to get nanoparticle size. The milled samples were tested using Particle Size Analyzer to ensure particle size. Nanobentonite was sulfonated using sulfuric acid in methanol with a volume of 10 mL, 1:10 (m/v) stirred at room temperature for 12 hours, then dried at 70 °C. Then, sulfonated nano-bentonite, examined using PSA to know the distribution of particle size, was leveraged as filler of the membrane.

Membrane synthesize

Synthesis of chitosan/PVA composite membranes were carried out with a composition of 60:40. Chitosan was dissolved in dilute acetic acid, then PVA was added to the solution. It stirred for 6 hours at room temperature. The mixture was dried for 30 minutes at 60 °C to dissolve the remaining PVA. Sulfonated nano bentonite 0.3, 0.6, and 0.9% (w/w) was used in membrane. The solution was casted on a petri dish and dried at 60 °C for 6 hours. Then, membranes were namely C/PVA/n-ben 0.3, 0,6 and 0.9. The membrane were characterized using FT-IR (Agilent Cary 630) to confirm synthesize process and SEM (Carl Zeiss-Bruker EVO MA10) to know the homogenity of filler on membrane.

Membrane Properties as a Fuel cell Membrane

Water swelling*.* The synthesized membrane was cut with a weight of ±0.01 gram, each replicated 3 times at a random location. The membrane was first dried in an oven at a temperature of 125 °C for 5 hours and then the dry weight (D) was weighed. Furthermore, the membrane was immersed in distilled water for 6 hours, then the water was removed (wiped with a tissue) then weighed and the wet weight (W) was obtained. Water swelling is equal to percentage of dry weight per wet weight.

Proton Conductivty. The proton conductivity (σ) was measured using an LCR-meter. The thickness of the membrane (L) was first measured and cut to a size of 1x4 cm. The frequency used in this study was 100 kHz with a voltage of 20 mV. Before measuring the membrane, it was soaked in distilled water for 24 hours. The wet membrane was clamped between two electrodes which are then connected to the positive and negative poles on the LCR-meter Autolab (PGSTAT128N) so that the conductivity value of the membrane was measured. The membrane cross-sectional area (A) is the effective membrane area connected to the electrode.

Cation Exchange Capacity. The membrane with a size of 2x2 cm was weighed and the weight was recorded. The membrane was put in an Erlenmeyer and added 50 mL of H_2O, then they were dried at a temperature of 60 °C for an hour. 50 mL of 1 M NaCl solution was added to the Erlenmeyer and allowed to stand overnight. Then 10 mL of the solution was taken and titrated with 0.005 M NaOH solution.

Result and Discussion

Sulfonated Nano-bentonite Chitosan-PVA Membrane

Before milling process, bentonite were calcined at 600 °C for 2 hours. The purpose of heating at high temperatures was to remove water molecules and other impurities. The surface area increases with increasing temperature caused by the loss of adsorbed and hydrated water molecules and volatile organic compounds bound to the natural bentonite surface [8]. The diameter of milled nano-bentonit was 431,8 nm.

The size of the diameter was related to the ability of the pores to absorb a gas or fluid. Particles would be smaller with increasing milling time used [9]. In this study, the milling time used was 6 hours. Nano-bentonite was improved the capability as fuel cell filler by sulfonation process.

The colour of membrane (Figure 1) was affected by the amount of sulfonated nano-bentonite added in the membrane. The membrane with 0.3% addition had the lightest brown color, and the highest elasticity. In contrast, for the 0.6% addition of sulfonated nano-bentonite, the membrane had a darker color because the composition of nano-bentonite was much than the first type, and the elasticity was stiffer than the 0.3% membrane. The last membrane was 0.9% composition, this membrane had the darkest color and was the stiffest.

FT-IR Spectra Analysis

Infrared spectroscopy was used to identify the functional groups of membrane and their composed materials, as a confirmation of membrane synthesize process. Spectra (Figure 2 and b) compared functional groups of unsulfonated and sulfonated nano-bentonite. The figure showed that

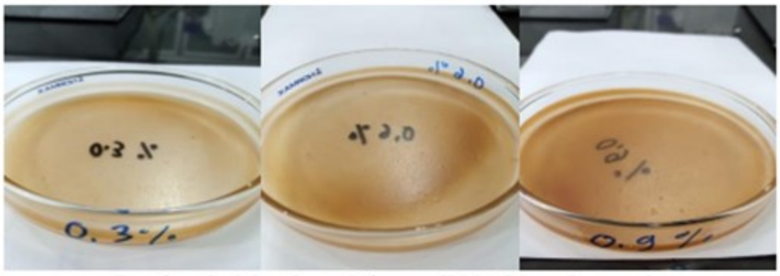

Figure 1. Membrane Physical Appearance

there were specific peaks at wave number 3384.14 cm^{-1} which indicated symmetric OH strain and 1035.95 cm^{-1} which indicated Si-O strain [10]. Then after sulfonation, There was a peak at wave number 596.66 cm^{-1} which indicated a symmetrical strain of S-O, 1023.71 cm^{-1} for the Si-O strain, 1632,19 cm^{-1} which indicated the water molecular strain and 3212.47 cm^{-1} which indicated the O-H strain [6]. At the time before and after sulfonation shown the difference where there was a peak at wave numbers 596.66 and 1632.19 cm^{-1}. The peak that appeared at wave number 599.66 cm^{-1} indicated that S-O bonds occur so that it confirmed that the sulfonation process has been successful. The success of the sulfonation process was also indicated by the formation of a peak at wave number 1632.19 cm^{-1} which indicated the stretch of water molecules where in the sulfonation reaction there will be a by-product of H_2O molecules. The H_2O molecule formed was also seen at the intensity in the wave number 3200 – 3500 cm^{-1} which was getting bigger due to the O-H band.

The sulfonated nano-bentonite was then added to the mixture to cast membranes with a concentration variation of 0.3; 0.6 and 0.9% were then measured by FTIR.

In this research, cotton was extracted by microwave assisted and sulfuric acid as hydrolysis agent. The optimum conditions were reached at 55% of sulfuric acid (the effect of concentration), 30°C (the effect of temperature) and in all reaction time (the effect of reaction time). In addition, the refinement of XRD data using Rietica software with Le Bail method indicated that the crystal structure of extraction product were in the monoclinic system.

IR spectra of membranes with a sulfonated clay concentration of 0.3; 0.6 and 0.9% are shown in Figure 2. (c), Figure 2. (d) and Figure 2. (e) respectively. In these three membrane spectra, it was shown that there are pencaks at relatively the same wave numbers, namely 650, 1019, 1150, 1408, 1537, 1622, 2900 and 3225 cm^{-1}. At wave number 650 cm^{-1} was sulfonic acid strain, 1019 cm^{-1} was S-O strain, 1150 cm^{-1} was asymmetric S=O strain, 1408 cm^{-1} was alkane strain, 1537 cm^{-1} was aromatic C=C strain, 1622 cm^{-1} was the C=O strain of the amide, 2900 cm^{-1} was the symmetrical and asymmetrical C-H strain then 3225 cm^{-1} showed the O-H strain. In the three spectra there were only differences in intensity where the membrane in Figure 2. (c) had a smaller peak size than the membrane in Figure 2. (d) and Figure 2. (e). So it can be said that the greater the concentration of sulfonated clay mixed, the greater the peak intensity produced.

Morphologhy of Electrolyte Membranes

The morphological structure of Chitosan/ PVA/Nanobentonite membranes was analyzed

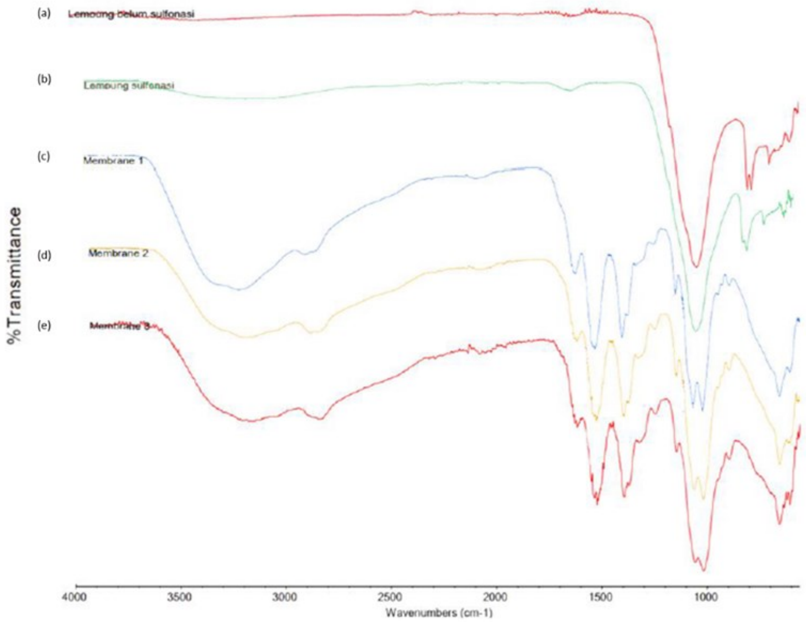

Figure 2. Overlay of FT-IR Spectra

with Scanning Electron Microscopy (SEM). Mass gain sulfonated nanobentonite containing silica, resulting information of pores with a small size and form a structure mesh in the form of cavities on the membrane surface. Group negative charge OH- of chitosan reacts with silica to form very dense cavities, a large amount of sulfonated nanobentonite contains silica, resulting in a tighter membrane morphology (Figure 3). When viewed from the homogeneity, nanobentonite sulfonated to produce a less homogeneous composite membrane. This matter because the less fine nanobentonite particles cause bentonite not to tightly fills the space between the membranes, so that when the solution is print on glass plate media, nanobentonite in distributed solution is not equally. Based on the morphology, a white circle is formed on the membrane surface due to the limited solubility of the chitosan polymer or PVA. The spots are chitosan that has not completely dissolved with the solvent is 2% acetic acid which causes the homogeneity of the solution not perfect, so it is still in the form of lumps.The bubbles distributed among the constituent materials were caused by the rapid when stirring process [7].

Proton Conductivity

The membrane conductivity was measured using an LCR-Meter with measure the impedance of the membrane. Prior to the test, the membrane must be fully hydrated or completely wet with a relative humidity of 98%, because ionic conduction would only occur when the membrane was [11]. Conductivity indicated the ability of a membrane to conduct protons, the greater the value, The better the membrane was used in the fuel system [12].

The proton conductivity increase equal to the composition nanobentonite added to the membrane. The addition of silica into the polymer matrix affected the magnitude of the proton conductivity [13]. In addition, other factors such as the number of ionic groups and the rate of hydration also affected the performance of the membrane [14]. It can be seen that the proton conductivity increased equal to the composition of nanobentonite from a concentration of 0.3% - 0.6%. This showed that nano-bentonite that filled the polymer matrix was a proton conductor. Membrane performance depended on the number of ionic groups and the rate of hydration [14]. There were two types of proton conduction in PEM, namely the vehicle-type mechanism and the Grotthuss-type (hopping) mechanism. As described in Figure 4. In the vehicle mechanism pro-

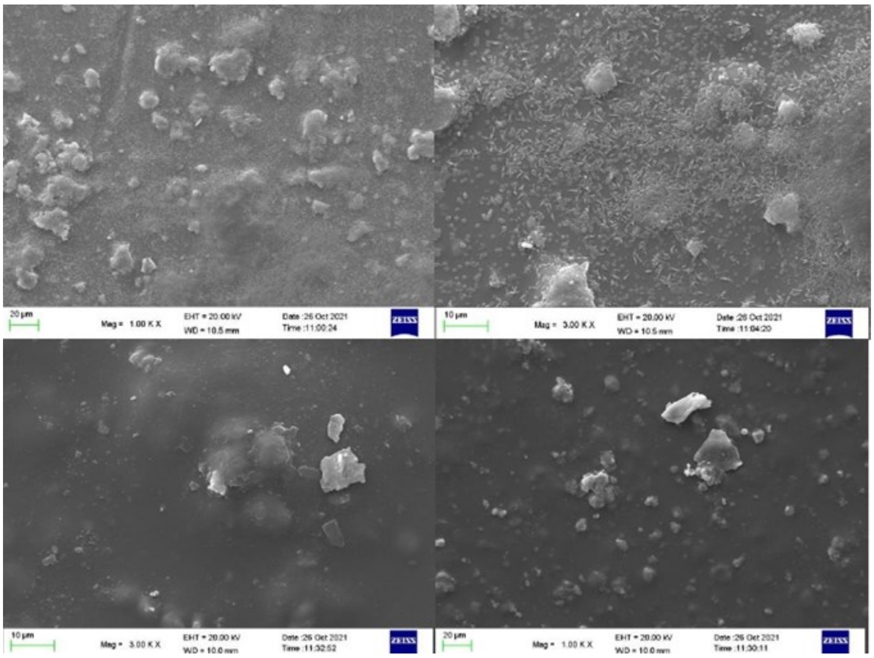

Figure 3. Morphology of Electrolyte Membranes (top: C/PVA/n-ben0.6 bottom: C/PVA/n-ben0.9)

tons moved due to the help of carriers such as water (H_3O^+) and solvent. The overall proton conductivity was determined by the vehicle diffusion coefficient. Whereas in the Grotthuss mechanism, proton conduction occured through hydrogen bonds (proton hopping). The transfer of protons through the solvent was not required, but a reorganization of the proton environment consisting of the reorientation of one or more hydrogen bonds was required to establish an unbroken pathway for proton transfer [13].

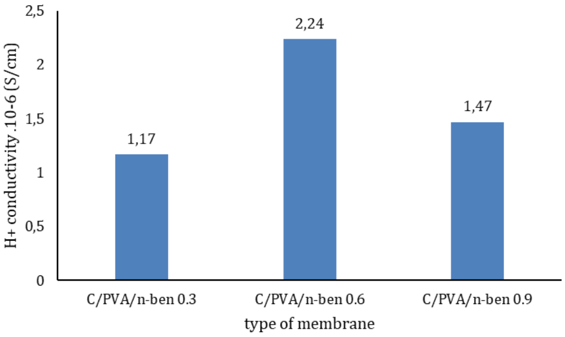

Figure 4. Proton Conductivity Membrane

The higher the nanobentonite composition, the higher the proton conductivity also higher because it was influenced by the presence of the Si-OH group of nanobentonite which could facilitate proton conduction, but there was a decrease in the membrane composition of 0.9%. The decrease in conductivity could be caused by the addition of excess nanobentonite which causes the formation of silicic acid from the silica contained. The more concentrated the acid formed, the less dissociated H^+ ions so that the proton conductivity declined [2].

Water Swelling

Water swelling test was needed to test the ability of water absorption by the membrane, as a measure of how strongly water could be absorbed by the membrane. Water trapped in the fuel cell membrane could act as a proton transport medium for H^+ at a certain level, which was related to proton conductivity, so it could be used to estimate the performance of the membrane, when the membrane changes from its initial state. Water absorbed in the composite membrane indeed functions as a proton transfer medium, but if the membrane is too high in swelling percent, the membrane will tend to be brittle [16].

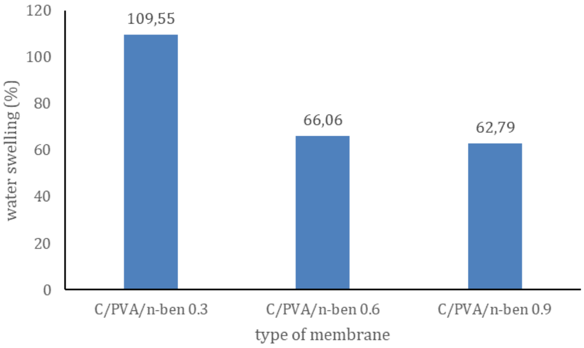

Figure 5. Water Swelling Membrane

The data obtained showed that the increasing the percentage of clay from 0.3% - 0.9% caused the swelling percentage of the membrane lower, because the addition of clay with a higher percentage affected the membrane capacity already optimum in dispersing water [7]. The addition of clay was expected to increase the ionic conductivity of the membrane, although up to the addition of a certain percentage, the clay has hygroscopic properties that could bind additional water [16].

The U.S. Department of Energy had determined that the swelling water on the membrane for the conduction target was a maximum absorption degree of 50%. If the water absorption was high, it caused increasing of water swelling. The circumtance was possible to lengthen the distance of proton conductvity, thus it could decreased the proton conductivity. The high of water swelling caused the membrane did not need more humidification [17]. Based on the results of the % swelling water test, the composite membrane was potential as fuel cell membrane.

Cation Exchange Capacity

The cation exchange capacity indicated the number of ionic groups in the polymer matrix which was indirectly related to the proton conductivity of a polymer. Figure 6. showed the value of the cation exchange capacity of the membrane with a composition of 0.3, 0.6 and 0.9% nanobentonite. In the 0.3-0.6% membrane there was an increase in the value of CEC with the addition of sulfonated nanobentonite. This is due to the presence of the -SO3H group that helped the exchange of H+ [18]. The results show the 0.6% composition has the highest CEC value high that is 0.0317 meq/gr, and with the addition of 0.9% there was a decrease in the value of CEC, it was possible that the material distribution was uneven compared to the addition of 0.6%.

Conclusion

Nanobentonite was successfully sulfonated in the presence of H_2O IR spectra, which H_2O was a by-product of the sulfonation reaction. The more mass of nanobentonite added to the membrane, the larger the bands formed. Nanobentonite seen from the XRD test results contained the dominant SiO_2, this was indicated by the highest intensity value. For the swelling water test, the 0.9% membrane had the best percentage of results, namely 62.79% because the results were close to the value of 50%. The result of the highest proton conductivity was the membrane with composition 0.6% at 2.24 x 10^{-6} S/cm, this was not in accordance with the PEM membrane requirements, namely >10^{-5}. This was the same as the CEC results, which the best value is 0.6% for the membrane.

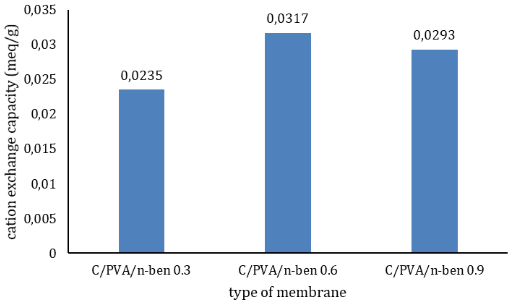

Figure 6. Cation Exchange Capacity of Membrane

Acknowledgements

This research had been funded by the National Competitive Research program through the Beginner Lecturer Research Scheme for the 2021 implementation year by the Ministry of Research, Technology and Higher Education of the Republic of Indonesia.

Author Contributions

Nina Ariesta carried out the physical chemistry studies of membrane, participated in the conducting research in laboratory, sequence alignment and drafted manuscript. Nurlela carried out organic chemistry, participated in the sequence alignment. Regita Rachmalia participated in research conducting in laboratory and helped to reference draft.

References

[1] Kim, D. S., Yun, T. Il, Seo, M. Y., Cho, H. Il, Lee, Y. M., Nam, S. Y., and Rhim, J. W., "Preparation of ion-exchange membranes for fuel cell based on crosslinked PVA/PSSA_MA/silica hybrid," *Desalination*, vol. 200, no. 1–3, pp. 634–635, 2006, DOI: 10.1016/j.desal.2006.03.456.

[2] Suka, I. G., Simanjuntak, W., & Dewi, E. L., "Pembuatan Membran Polimer Elektrolit Berbasis Polistiren Akrilonitril (SAN) untuk Aplikasi Direct Methanol Fuel Cell," *Jurnal Natur Indonesia*, vol. 13, no. 1, pp. 1-6, 2012, DOI: 10.31258/jnat.13.1.1-6.

[3] Im, M., "Membran Peek Silika / Clay Untuk Aplikasi Direct Methanol Fuel Cell.," *In Thesis* (2011), URL:http://eprints.undip.ac.id/36551/1Tesis_S2_Marita_Im.pdf

[4] Pramono, E., Purnawan, C., Hidayat, Y., Wulansari, J., & Wahyuningsih, S., "Composite of Chitosan Vanilin / Sulfonated Polystyrene As Polymer Electrolyte Membranes : Cationic Exchange Capacity, Swelling Degree and Thermal Properties," *ALCHEMY Jurnal Penelitian Kimia*, vol. 10, no. 2, pp. 116-29, 2016, DOI: 10.20961/alchemy.10.2.55.116-129.

[5] Nugraeni, C. D., Hayati, N., Santoso, M., Kusumawati, Y., & Atmaja, L., "Preparation of proton exchange membrane based on

chitosan phthaloyl and chitosan blend for direct methanol fuel cell application," *AIP Conference Proceedings*, vol. 2049, pp. 020077-1— 020077-6, 2018, DOI: 10.1063/1.5082482.

[6] Jesuraj, K., & Manimuthu, R. P., "Preparation and characterization of hybrid Chitosan/PEO–silica membrane doped with phosphotungstic acid for PEM fuel cell application," *Polymer-Plastics Technology and Engineering*, vol. 58, no. 1, pp. 14–30, 2018, DOI: 10.1080/03602559.2018.1455862.

[7] Kharisma, T., Ariesta, N., & Arrisujaya, D., "Characteristics of Clay Modified/Chitosan/PVA Based Composite Membranes From Babakan Madang Bogor," *Jurnal Sains Natural*, vol. 10, no. 1, pp. 33-42, 2020, DOI: 10.31938/jsn.v10i1.276.

[8] Purkait, M. K., Maiti, A., DasGupta, S., & De, S, "Removal of congo red using activated carbon and its regeneration," *Journal of Hazardous Materials*, vol. 145, no. 1–2, pp. 287–295, 2007, DOI: 10.1016/J.JHAZMAT.2006.11.021.

[9] Widjanarko, S.B., and Suwasito, T.S., "Pengaruh Lama Penggilingan dengan Metode Ball Mill Terhadap Rendemen dan Kemampuan Hidrasi Tepung Porang (Amorphophalus muelleri blume)," *Jurnal Pangan dan Argoindustri*, vol. 2, no. 1, pp. 79-85, 2014, URL: https://jpa.ub.ac.id/index.php/jpa/article/view/24.

[10] Banik, N., Jahan, S., Mostofa, S., Kabir, H., Sharmin, N., Rahman, M., & Ahmed, S., "Synthesis and characterization of organoclay modified with cetylpyridinium chloride," *Bangladesh Journal of Scientific and Industrial Research*, vol. 50, no. 1, pp. 65–70, 2015, DOI: 10.3329/bjsir.v50i1.23812.

[11] Zulfikar, M., Hidayati, N., Majiburrahman, M., Purnama, H., "Karakteristik Membran sPEEK-Kitosan dengan Bahan Pengisi Silika-carbon nanotube untuk Sel Bahan Bakar Metanol," *Proceeding of The 10th University Research Colloqium*, 2019, URL: http://repository.urecol.org/index.php/proceeding/article/view/784.

[12] Putro, A. S., "Membran Komposit Kitosan-Zeolit untuk Aplikasi Direct Methanol Fuel Cell," 2013, URL:http://repository.ipb.ac.id/handle/123456789/61466.

[13] XiaoJin Li, ChangChun Ke, S. Q., & Jin Li, Z. S. and B. Y., "High Temperature PEM Fuel Cells Based on Nafion®/SiO_2 Composite Membrane, *Energy Storage in the Emerging Era of Smart Grids*, Prof. Rosario Carbone (Ed.)., 2009, DOI: 10.5772/19029.

[14] Pereira, F., Vallé, K., Belleville, P., Morin, A., Lamberts, S., & Sanchez, C., "Advanced mesostructured hybrid silica-nafion membranes for high-performance PEM fuel cell," *Chemistry of Materials*, vol. 20, no. 5, 2008, DOI: 10.1021/cm070929j.

[15] Hande, V. R., Rath, S. K., Rao, S., & Patri, M., "Cross-linked sulfonated poly (ether ether ketone) (SPEEK)/reactive organoclay nanocomposite proton exchange membranes (PEM)," *Journal of Membrane Science*, vol. 372, no. 1–2, pp. 40–48, 2011, DOI: 10.1016/j.memsci.2011.01.042.

[16] Pulungan, A. N., "Preparasi dan Karaterisasi Alternatif Membran Fuel Cell dari Lateks Karet Alam dan Polistirena Tersulfonasi (SPs)," *Doctoral Thesis*, 2020, URL: http://repositori.usu.ac.idhandle/123456789/27244

[17] Dewi, S. Pengurangan Kadar Oksalat Pada Umbi Talas Dengan Penambahan Arang Aktif Pada Metode Pengukusan. *Jurnal Aplikasi Teknologi Pangan*, vol. 6, no. 2, pp. 2–5, 2017, DOI: 10.17728/jatp.191.