Synthesis and Characterization of Chitosan-Polyvinyl Alcohol-Fe2O3 Composite Membrane for DMFC Application

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Synthesis and Characterization of Chitosan-Polyvinyl Alcohol-Fe₂O₃ Composite Membrane for DMFC Application

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Abstract

This study investigates the utilization of different compositions of Fe₂O₃ and polyvinyl alcohol (PVA) to modify chitosan in order to prepare a composite membrane. The membranes were synthesized using the phase inversion method and extensively characterized by Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), mechanical properties analysis, and water uptake analysis, whereby SEM was used to confirm the morphology of the composite membranes. Different electrochemical properties such as ion exchange capacity, proton conductivity, and methanol permeability of these membranes were also measured. The results showed that increasing the PVA mass improved the water uptake, ion exchange capacity (IEC), and proton conductivity because the PVA addition increased the hydrophilicity of the membrane; thus, the pore surface on the membrane was more open, which also caused higher membrane permeability. However, the methanol permeability values of all composite membranes were lower than that of Nafion. The highest IEC and proton conductivity were obtained for the CS-PVA-H3070 membrane, with values of 4.300 meq/g and 6.71 × 10⁻² S·cm⁻¹, respectively. The mechanical strength of these membranes showed that the PVA addition increased the elongation break and decreased the tensile strength of the membrane. The results imply that the chitosan membrane modified with PVA and Fe₂O₃ has a potential for DMFC applications.

Keywords: chitosan, DMFC, Fe₂O₃, membrane, PVA

Introduction

Increasing the rate of population growth over time causes a continuous increase in energy needs. A population growth rate that is not balanced with sufficient energy availability will result in energy crisis in the future. Fuel cells have become one of the alternative energy sources to overcome the energy crisis because of their high energy efficiency and environmental friendliness [1].

Fuel cells are electrochemical cells that can convert chemical energy into electrical energy through electrochemical reactions. Fuel cells with polymer membranes as electrolytes (PEMFC) have bright prospects to be developed in Indonesia. These types of fuel cells include hydrogen fuel cell/polymer electrolyte fuel cell and direct methanol fuel cell (DMFC) [2]. Some of the requirements that must be met by electrolyte materials related to their application as PEMFC membranes include high proton conductivity, good mechanical resistance, good thermal resistance, and good and inexpensive reactant insulation [3].

A commonly used proton exchange membrane is Nafion, which is a perfluoro sulfonic acid polymer. The use of Nafion is based on its good thermal and chemical stability [4] and high ionic conductivity (~10⁻² S·cm⁻¹) at temperatures below 100 °C [2]. However, the membrane has several disadvantages, such as high cost; high methanol crossover, which makes it incompatible for application in a methanol fuel cell; and environmental unfriendliness, as wastes are generated in its synthesis process [5]. One solution to overcome this problem is to develop new materials for proton delivery membranes as an alternative to Nafion [6].

Natural polymers such as chitosan (CS) can be developed as an alternative, considering that CS is a
polymer that is abundant in nature and has the properties of biodegradability, biocompatibility, and nontoxicity [7]. In addition, the two main functional groups possessed by CS in the form of amine groups and hydroxyl groups make it easy to modify and provide high hydrophilicity and good resistance to chemicals, mechanical stress, and thermal stress [8].

Chitosan in normal conditions has a low ionic conductivity because it does not have ions that can be immobilized under the influence of an electric field to produce proton conductors [9]. Meanwhile, it has been found that CS dissolved in acetic acid can be a polyelectrolyte through protonation by NH$_2$ groups. The H$^+$, H$_2$O$_2^-$, or CH$_3$COO$^-$ ion in the CS layer will be dispersed in the CS solvent, and these ions can be immobilized under the influence of the electric field. If the H$^+$ or H$_2$O$_2^-$ ions are more mobile than CH$_3$COO$, the CS layer will be a proton conductor [10]. Studies of CS membranes with high molecular weight and certain degrees of deacetylation show proton conductivity values around 10 S cm$^{-1}$. These values are low compared with Naftion proton conductivity, which is in the range of 10$^{-1}$ S cm$^{-1}$. The conductivity of CS membranes is still relatively low for practical purposes, although it shows good methanol barrier properties [11]. Because of this, CS polymer is usually modified either with organic or inorganic salts. It is also usually combined with other substances to generate ion exchange sites. As a result, this action significantly enhances the ionic conductivity of the mixed matrix membranes and also increases the mechanical, hydrolytic, and thermal stabilities [12].

Many researchers have reported polyvinyl alcohol (PVA) to be a potential blend polymer of CS for the amelioration of the mechanical, chemical, and electrochemical properties of CS ion exchange membranes [13], [14]. To increase the conductivity and mechanical properties of composite membranes, PVA has been mixed with CS to form a strong hydrogen bond between the hydroxyl groups of PVA and the amino and hydroxyl groups of CS [15]. Polyvinyl alcohol is widely used as a mixture because of its low cost, chemical stability, and good mechanical properties [16]. Several modifications of CS/PVA composite membrane have been reported, such as those involving the incorporation of phosphoric acid group [17], calcium oxide [18], graphene oxide [19], montmorillonite [20], graphene [16], and anionic resins (anionic ionomers) [21].

In addition to the modification of CS with PVA, hematite material has recently been developed as a candidate electrolyte for fuel cells due to its considerable ion conductivity [22]. To the best of our knowledge, hematite has been used in a polyelectrolyte membrane as a source of an active anode material, as reported by Hikmah and co-worker [23]. El Sayed and co-worker [24] reported using hematite as an electrolyte material in the synthesis of CS with polyvinylpyrrolidone for medical and technological applications. The authors synthesized a composite membrane using different polymers, methods, and applications. Based on their description, in the present work, CS, PVA, and hematite composite membranes are synthesized and characterized as proton delivery membranes.

**Methods**

**Materials.** Chitosan with a deacetylation degree of 81% was obtained from a previous research team by Ahmad [25]. Iron sand was obtained from sub-district Tapung Gaeya, Konawe Utara. Analytical grade reagents used in this study were PVA, acetic acid, sodium hydroxide, sulfuric acid, chloride acid, ethanol, and methanol, and they were purchased from Emsure Merck, Jakarta. De-ionized water was used in all experiments.

**Separation of iron sand.** The process of separating iron oxide in the sample was carried out using a magnet. The permanent magnet stem with strength of about 38.9 kJ/m$^2$, which has been coated with plastic paper with a thickness of 0.1 mm. Magnets were placed around all parts of the sand, at a distance of about 1.5 cm from the sand, until all the iron sand was lifted. The iron sand was placed in another container. The separation was carried out repeatedly against the raised iron sand by making a magnetic distance with a further sample until the iron sand was black.

**Leaching process.** The leaching process was carried out by heating 200 mL of 20% HCl at 100 °C. Subsequently, 2.5 g of iron sand was added to the solution and then heated for 3 h. The solution was filtered using filter paper no. 40, and it was left at room temperature [26]. Leachate of iron sand was obtained with yellow colors. Here FeCl$_3$ is assumed to be the source of Fe$_2$O$_3$.

**Synthesis of CS-PVA-Fe$_2$O$_3$ membrane.** Composite membranes were synthesized by the phase inversion method. A CS solution was made by dissolving CS in a 2% (v/v) acetic acid solution, and a PVA solution was made by dissolving PVA in distilled water. Subsequently, both CS and PVA solutions were mixed using a magnetic stirrer until homogeneity was achieved. The CS-PVA solutions were cast into a petri dish and dried at room temperature for 72 h. The compositions of CS and PVA in each sample are presented in Table 1. The composite membranes were dried at room temperature until they were peeled off. Subsequently, the composite membranes were soaked in 20 mL leachate of iron sand for 24 h, and then they were soaked in 2% NaOH solution. The composite membranes were annealed at 60 °C, and hematite was formed in situ in the CS-PVA membranes. The formed hematite in the membranes was characterized by X-ray diffraction (XRD).
Characterization of CS-PVA-Fe$_2$O$_3$ membranes. The CS-PVA-Fe$_2$O$_3$ membranes were characterized using XRD, Fourier-transform infrared (FTIR) spectroscopy, and scanning electron microscopy (SEM). Water uptake, mechanical properties, ion exchange capacity (IEC), methanol permeability, and proton conductivity were also measured. The membrane was used to analyze the incorporation of hematite into membrane using Cu-Kα radiation axis, with a wavelength of 1.54 Å in a 2θ range between 10° and 100°. Fourier-transform infrared spectroscopy was used to analyze the functional groups in the composite membranes. All FTIR spectra were measured over a wave number range of 4000–500 cm$^{-1}$ in the transmittance mode. Scanning electron microscopy (Jeol JSM-6360) was used to confirm the morphology of all composite membranes. Water uptake analysis was used to determine the amount of water absorbed by the membrane. Tensile testing was carried out by subjecting material samples of a certain size to a pull force until breaking point. The data were obtained in the form of stress and strain curves. The IEC was analyzed by titrating the soaked membranes using 0.01 M HCl with a phenolphthalein indicator. Methanol permeability was measured via a two-compartment glass diffusion cell. The concentrations of alcohol diffused from cells A and B across the membranes were examined with time using a density meter. Proton conductivity was measured using two-point-probe conductivity cells with two platinum wire electrodes as the working electrode. The electrical resistance data were obtained using an impedance analyzer (Agilent E4980A) and were recorded between 20 Hz and 2 MHz at a working voltage amplitude of 1 V.

Results and Discussion

FTIR Analysis. Figure 1 shows the structural changes of CS-PVA-Fe$_2$O$_3$ in all variations. Based on the FTIR spectra, the absorption peaks at 850–1463 cm$^{-1}$ showed similarities. As a reference, Fig. 1(a) shows the peak of CS-PVA without the addition of FeCl$_3$. The difference seen from the FTIR spectra is the presence of absorption peaks at wave number 543 cm$^{-1}$, which shows the presence of Fe-O functional groups, and changes in absorption peaks at wave numbers 1658 and 3450 cm$^{-1}$, which indicate the presence of electrostatic interactions between the -NH$_2$ groups from CS and the –OH group of PVA. This is in accordance with the research of [27], which shows that the spectrum at wave number 543 cm$^{-1}$ is a characteristic of the Fe-O function group, and [28] states that the addition of PVA in a CS solution causes a long shift waves on the stretches of −OH and −NH groups, which are thought to be caused by electrostatic interactions.

XRD Analysis. Figure 2 shows the result of XRD testing of the obtained CS-PVA-Fe$_2$O$_3$ membrane. The main XRD peak was formed at 2θ of 24.149°, 33.159°, 35.633°, 40.863°, 49.463°, 62.437°, 64.235°, and 79.156°. The XRD pattern of the composite membrane is similar to the standard hematite diffraction pattern of reference JCPDS (Joint Committee on Powder Diffraction Standards) 96-501-5504. This means that hematite was well attached to the membrane composite.

Mechanical Properties. Figure 3 shows the profile of the mechanical properties of CS-PVA-Fe$_2$O$_3$ composite membranes. It can be seen that the highest elongation break was obtained for CS-PVA-H3070, with the elongation value of 52.2%, and the highest tensile strength was obtained for CS-PVA-H4060, with the stress value of 3.363 MPa. As more PVA was added to the membrane, the elongation break tended to increase. This is due to the nature of PVA, which contains a lot of hydrophilic groups. Therefore, it has a high flexibility, which results in the elastic and non-rigid membranes [29].
Figure 1. Fourier Transform Infrared Spectra of Membrane for (a) CS-PVA, (b) CS-PVA-H20:80, (c) CS-PVA-H30:70, (d) CS-PVA-H40:60, (e) CS-PVA-H50:50, (f) CS-PVA-H60:40, (g) CS-PVA-H70:30, (h) CS-PVA-H80:20, and (i) CS-PVA-H90:10

Figure 2. (a) The Obtained Membrane of CS-PVA-Fe$_2$O$_3$ and (b) Reference Pattern from the Crystallography Open Database Entry, 96-501-5504

Figure 3. Mechanical Properties of CS-PVA-Fe$_2$O$_3$ Membranes
Meanwhile, membranes with a composition of more CS increased the stress because CS has high mechanical properties. However, the CS-PVA membrane with mass fraction 80:20 to 90:10 showed a lower stress value compared to membranes with a variation of CS-PVA 60:40. This is possible in the process of mixing PVA with less homogeneous CS; thus, the interaction of active groups on PVA with active groups on CS is not optimal. Therefore, it can be concluded that the membrane with a high CS composition shows a low tensile test result especially in the strain. Adding PVA to CS produces a membrane that has better mechanical properties.

**SEM Analysis.** SEM analysis was used to confirm the morphology of all membranes. As seen from Figures 4a and 4b, CS and CS-PVA-H90:10 membranes displayed a smooth and homogenous surface. More addition of PVA to composite membranes (Figures 4c to 4h) led to an increase in the size of the pore in the membrane. However, pores were clearly observed in CS-PVA-H50:50.

**Water Uptake.** Water uptake analysis was carried out to determine the water absorption ability of a polymer matrix. The ability of an electrolyte membrane to absorb water depends on its hydrophilic nature. Membranes that have hydrophilic properties will have a higher water absorption rate than hydrophobic polymers. The profile of membrane water absorption is shown in Figure 5.

![SEM images of the Surfaces of (a) CS, (b) CS-PVA-H90:10, (c) CS-PVA-H80:20, (d) CS-PVA-H70:30, (e) CS-PVA-H60:40, (f) CS-PVA-H50:50, (g) CS-PVA-H40:60, (h) CS-PVA-H30:70, and (i) CS-PVA-H20:80](image)

![Figure 4. SEM images of the Surfaces of (a) CS, (b) CS-PVA-H90:10, (c) CS-PVA-H80:20, (d) CS-PVA-H70:30, (e) CS-PVA-H60:40, (f) CS-PVA-H50:50, (g) CS-PVA-H40:60, (h) CS-PVA-H30:70, and (i) CS-PVA-H20:80](image)

![Figure 5. Water Uptake of CS-PVA-FeO₃ Composite Membrane (at Room Temperature)](image)
Based on the water absorption profile in Figure 5, it can be seen that the higher the CS mass fraction, the smaller the water absorption rate. This occurs due to the presence of a strong hydrogen bond between the amine group (-NH$_2$) and the hydroxyl group (-OH) in CS [31]. Conversely, the water absorption on the composite membrane is improved with increasing mass fraction of PVA. This is due to the hydroxyl group in PVA, which can hold water molecules through hydrogen bonds. Polyvinyl alcohol membrane is also hydrophilic and is known to absorb water almost equal to its own weight.

**Methanol Permeability.** The slope of the straight line in Figure 6 was used to obtain the values of methanol permeability for all the membranes. It was found that the methanol permeability ($P$) values of all composite membranes were 0.12–5.84 × 10$^{-7}$ cm$^2$ s$^{-1}$, respectively, as listed in Table 2. As seen, the CS-PVA-H4060 membrane exhibited the highest methanol permeability; however, it had a lower methanol permeability than Nafion (10 × 10$^{-6}$ cm$^2$ s$^{-1}$) [32]. The methanol permeability was increased because of the increase in the pores amount due to the hematite not being dispersed well in the CS-PVA matrix. This result is related to the SEM image in Fig. 3; the hematite particulates cause the membrane to tend to be porous, and thus, methanol travels through the pores.

**Ion Exchange Capacity.** IEC reveals the number of groups randomly distributed in the polymer chain that can exchange the protons in solution [33]. The IEC is determined by the amine and hydroxyl groups that are bound to the material. Composite membranes are made, and the groups expected to support the activity of proton exchange are amine and hydroxyl groups on the CS and hydroxyl groups on PVA. Adding the hydroxyl group to the polymer chain of CS can make the CS more polar. This result is related to the water uptake properties of the composite membranes. The IECs of CS-PVA-Fe$_2$O$_3$ composite membranes range between 0.687 and 4.300 meq.g$^{-1}$.

![Figure 6. The Methanol Concentration vs. Time Curve for the CS-PVA-Fe$_2$O$_3$ Composite Membranes](image)

![Table 2. Ion Exchange Capacities, Proton Conductivity and Methanol Permeability of CS-PVA-Fe$_2$O$_3$ Composite Membranes](table)

| Membrane  | IEC (meq/g) | Proton Conductiviy (x10$^{-2}$ S.cm$^{-1}$) | $P$ (x10$^{-7}$ cm$^2$ s$^{-1}$) |
|-----------|-------------|------------------------------------------|----------------------------------|
| CS-PVA-H 9010 | 0.791        | 0.62                                    | 1.08                             |
| CS-PVA-H 8020 | 0.741        | 0.63                                    | 2.46                             |
| CS-PVA-H 7030 | 0.687        | 1.32                                    | 0.12                             |
| CS-PVA-H 6040 | 1.145        | 1.47                                    | 4.85                             |
| CS-PVA-H 5050 | 1.360        | 2.44                                    | 1.09                             |
| CS-PVA-H 4060 | 1.475        | 3.91                                    | 5.84                             |
| CS-PVA-H 3070 | 4.300        | 6.71                                    | 4.54                             |
| CS-PVA-H 2080 | 2.600        | 3.21                                    | 4.95                             |
The results of the IEC of CS-PVA-Fe$_2$O$_3$ composite membranes are presented in Table 2. It can be seen that the highest IEC was obtained for CS-PVA-H3070, with the IEC value of 4.300 meq.g$^{-1}$, and the lowest IEC was obtained for CS-PVA-H7030, with the IEC value of 0.687 meq.g$^{-1}$. Generally, the IEC of CS-PVA-Fe$_2$O$_3$ composite membranes increased; this is because the membrane becomes more hydrophilic due to the addition of the PVA hydroxyl group. However, a high-IEC membrane means the membrane can better pass protons from the anode to the cathode [34].

Proton Conductivity. The analysis results of the proton conductivity of CS-PVA-Fe$_2$O$_3$ composite membranes are also presented in Table 2. The results show that the proton conductivity of CS-PVA-Fe$_2$O$_3$ composite membranes significantly increased within the range of 0.62 × 10$^{-2}$ to 6.71 × 10$^{-2}$ S cm$^{-1}$. The optimum proton conductivity was obtained for CS-PVA-H3070, with a proton conductivity of 6.71 × 10$^{-2}$ S cm$^{-1}$. Generally, increasing the PVA composition led to an increase in the proton conductivity. This result is attributed to three possible reasons: One is that increasing the PVA composition resulted in the addition of acid properties (from the membrane with PVA hydroxyl group) to the membrane structure. The second reason is the increase in the interaction between the amine group from CS and the hydroxyl group from PVA to form a complex polyelectrolyte. The third reason is the hematite material contributed to increasing the proton conductivity of the composite membrane. Xia et al. [35] reported that the addition of hematite material contributes to increasing the proton conductivity because hematite has a high ion conductivity.

Figure 7 shows the proposed interaction in polyelectrolyte CS-PVA-Fe$_2$O$_3$ composite membrane. In the polymer chain, protons move by jumping through functional groups or negatively charged atoms. In this case, PVA acts as a proton conductor. In the Grotthus mechanism, hopping protons move through the membrane as if drawn by functional groups or negatively charged atoms, so that the number of functional groups contained in the polymer chain greatly determines the number of protons that can be passed through the membrane [36].

Proton conductivity in polyelectrolyte membranes must have a high value. Thus, the optimal process of transferring protons from the anode to the cathode could be achieved. The value of proton conductivity was still lower than that of Nafion 117 of 4.76 × 10$^{-1}$ S cm$^{-1}$. However, the conductivity value approached that of a polyelectrolyte membrane; therefore, the CS-PVA-Fe$_2$O$_3$ composite has the potential to be a polyelectrolyte membrane.

![Figure 7. Proposed interaction in polyelectrolyte complexes of CS-PVA-Fe$_2$O$_3$](image-url)
Conclusion

The in situ preparation of CS-PVA-Fe₃O₅ composite for a proton-conducting matrix membrane was successfully realized. The favorable characteristics of the composite membrane are not only in terms of high conductivity but also in terms of other properties such as water uptake (20% – 40%), mechanical properties, and morphology. The results show that the methanol permeability values of all the composite membranes were lower than that of Nafion. The addition of PVA and Fe₃O₅ improves the IEC and also the mechanical properties of composite membranes. However, the proton conductivity of the composite membrane was lower than that of Nafion, but it approached the conductivity value required to consider the composite as a polyelectrolyte membrane.

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References

[1] Kim, Y.S., Kim, D.S., Guiver, M.D., Pivovar, B.S., 2011. Interpretation of direct methanol fuel cell electrolyte properties using non-traditional length-scale parameters. J. Membr. Sci. 374(1): 49–58, https://doi.org/10.1016/j.memsci.2011.03.004.
[2] Kim, D.J., Jo, M.J., Nam, S.Y., 2014. A review of polymer–nanocomposite electrolyte membranes for fuel cell application. J. Ind. Eng. Chem. 21: 36–52, https://doi.org/10.1016/j.jiec.2014.04.030.
[3] Díaz, M., Ortiz, A., Ortiz, I., 2014. Progress in the use of ionic liquids as electrolyte membranes in fuel cells. J. Membr. Sci. 469: 379–396, https://doi.org/10.1016/j.memsci.2014.06.033.
[4] Ahmad, F. and Sheha, E., 2013. Preparation and physical properties of (PVA)x0.5(NaBr)y0.5(H3PO4)zM solid acid membrane for phosphoric acid–Fuel cells. J. Adv. Res. 4(2): 155–161, https://doi.org/10.1016/j.jare.2012.05.001.
[5] Wu, H., Zheng, B., Zheng, X., Wang, J., Yuan, W., Jiang, Z., 2007. Surface-modified Y zeolite-filled chitosan membrane for direct methanol fuel cell. J. Power Sources. 173(2): 842–852, https://doi.org/10.1016/j.jpowsour.2007.08.020.
[6] Ma, J., Sahai, Y., 2013. Chitosan biopolymer for fuel cell applications. Carbohydr. Polym. 92(2): 955–975, https://doi.org/10.1016/j.carbpol.2012.10.015.
[7] Vaghar, H., Jafarizadeh-Malmiri, H., Berenjian, A., Anarjan, N., 2013. Recent advances in application of chitosan in fuel cells. Sustain. Chem. Process. 1(1):16, https://doi.org/10.1186/2043-7129-1-16.
[8] Permana, D., Purwanto, M., Ramadhan, L.O.A.N., Atmaja, L., 2015. Synthesis and Characterization of Chitosan/Phosphotungstic Acid-Montmorillonite Modified by Silane for DMFC Membrane. Indones. J. Chem. 15(3): 218–225, https://doi.org/10.22146/ijc.21188.
[9] Ramirez-Salgado, J., 2007. Study of basic biopolymer as proton membrane for fuel cell systems. Electrochimica Acta. 52(11): 3766–3778, https://doi.org/10.1016/j.electacta.2006.10.051.
[10] Mohamed, N.S., Subban, R.H.Y., Arof, A.K., 1995. Polymer batteries fabricated from lithium complexed acetylated chitosan. J. Power Sources. 56(2): 153–156, https://doi.org/10.1016/0378-7753(95)80027-E.
[11] Mukoma, P., Jooste, B.R., Vosloo, H.C.M., 2004. Synthesis and characterization of cross-linked chitosan membranes for application as alternative proton exchange membrane materials in fuel cells. J. Power Sources. 136(1): 16–23, https://doi.org/10.1016/j.jpowsour.2004.05.027.
[12] Merle, G., Wessling, M., Nijmeejer, D.C., 2011. Anion exchange membranes for alkaline fuel cells: A review. J. Membr. Sci. 377(1–2): 1–35, https://doi.org/10.1016/j.memsci.2011.04.043.
[13] Maiti, J., Kakati, N., Lee, S.H., Jee, S.H., Viswanathan, B., Yoon, Y.S., 2012. Where do poly(vinyl alcohol) based membranes stand in relation to Nafion® for direct methanol fuel cell applications? J. Power Sources. 216: 48–66, https://doi.org/10.1016/j.jpowsour.2012.05.057.
[14] Xiong, Y., Liu, Q.L., Zhang, Q.G., Zhu, A.M., 2008. Synthesis and characterization of cross-linked quaternized poly(vinyl alcohol)/chitosan composite anion exchange membranes for fuel cells. J. Power Sources. 183(2): 447–453, https://doi.org/10.1016/j.jpowsour.2008.06.004.
[15] Buraidah M.H., Arof, A.K., 2011. Characterization of chitosan/PVA blended electrolyte doped with NHI. J. Non-Cryst. Solids. 357(16): 3261–3266, https://doi.org/10.1016/j.jnoncrysol.2011.05.021.
[16] Yang, J.M., Wang, S.A., 2015. Preparation of graphene-based poly(vinyl alcohol)/chitosan nanocomposites membrane for alkaline solid electrolyte membrane. J. Membr. Sci. 477: 49–57, https://doi.org/10.1016/j.memsci.2014.12.028.
[17] Binsu, V.V., Nagarale, R.K., Shahi, V.K., Ghosh, P.K., 2006. Studies on N-methylene phosphonic chitosan/poly(vinyl alcohol) composite proton-exchange membrane. React. Funct. Polym. 66(12): 1619–1629, https://doi.org/10.1016/j.reactfunctpoly.m.2006.06.003.
[18] Mat N.C., Liong, A., 2009. Chitosan-poly (vinyl alcohol) and calcium oxide composite membrane for Direct Methanol Fuel Cell Applications. Eng. Let. 17(4): 4-14.
[19] Feng, X., Wang, X., Xing, W., Yu, B., Song, L., Hu, Y., 2013. Simultaneous reduction and surface
Functionalization of Graphene Oxide by Chitosan and Their Synergistic Reinforcing Effects in PVA Films. Ind. Eng. Chem. Res. 52(36): 12906–12914, https://doi.org/10.1021/ie402073x.

[20] Palani, P.B., Abidin, K.S., Kannan, R., Sivakumar, M., Wang, F.M., Rajashabala, S., Velraj, G. 2014. Improvement of proton conductivity in nanocomposite polyvinyl alcohol (PVA)/chitosan (CS) blend membranes. RSC Adv. 4(106): 61781–61789, https://doi.org/10.1039/C4RA10788H.

[21] Garcia-Cruz, L., Casado-Coterillo, C., Iniesta, J., Montiel, V., Iribien, A. 2016 Chitosan-poly(vinyl alcohol) composite alkaline membrane incorporating organic ionomers and layered silicate materials into a PEM electrochemical reactor. J. Membr. Sci. 498: 395–407, https://doi.org/10.1016/j.memsci.2015.08.040.

[22] Xia, C., Cai, Y., Ma, Y., Wang, B., Zhang, W. 2016. Natural Mineral-Based Solid Oxide Fuel Cell with Heterogeneous Nanocomposite Derived from Hematite and Rare-Earth Minerals. ACS Appl. Mater. Interfaces. 8(32): 20748–20755, https://doi.org/10.1021/acsami.6b05694.

[23] Hikmah, A.M., More, E., Ramadhan, L.O.A.N., Atmaja, L., Subhan, A. 2018. Southeast Celebes iron sand as source of active anode material with chitosan-PVA binder on lithium-ion battery. AIP Conf. Proc. 2049(1): 020059, https://doi.org/10.1063/1.5082464.

[24] El-Sayed, A.M., Mohamad, M.D.A. 2018. Synthesis, structural, thermal, optical and dielectric properties of chitosan biopolymer; influence of PVP and α-Fe₂O₃ Nanorods. J. Poly. Res. 25(125): 1–14, https://doi.org/10.1007/s10965-018-1571-x.

[25] Permana, L.O.A.D., Wahab, S.I., Sedjaran, L.O.A.N., Rianse, U. 2015. Improved chitosan production from tiger shrimp shell waste (Peneaus monodon) by multistage deacetylation method and effect of bleaching. Advances in Environmental and Geological Science and Engineering, 373–378.

[26] Yarkadas, G., Toplan, H.Ö., Yıldız, K. 2009. Effect of Mechanical Activation and Iron Powder Addition on Acidic Leaching of Pseudosulfa. SAÜ. Fen Bilimleri Dergisi. 13(1): 18–21.

[27] Zhu, Y., Xia, S., Liu, G., Jin, W. 2010. Preparation of ceramic-supported poly (vinyl alcohol)–chitosan composite membranes and their applications in pervaporation dehydration of organic/water mixtures. J. Membr. Sci. 349(1): 341–348, https://doi.org/10.1016/j.memsci.2009.11.065.

[28] Zheng, H., Yu, D., Yu, J., Huang, R., Zhang, L. 2001. Preparation and characterization of chitosan/poly (vinyl alcohol) blend fibers. J. Appl. Polym. Sci. 80(13): 2558–2565, https://doi.org/10.1002/app.1365.

[29] Maksum, S.M.M. 2015. Pengaruh komposisi terhadap perilaku membran komposit pva/kitosan /grafin oksida yang terikat silang asam sulfat. Jurnal Sains Dan Seni ITS. 4(2), https://doi.org/10.12962/j23373520.v5i1.15932.

[30] Danwanichakul, P., Sirikajornnam, P. 2013. An Investigation of Chitosan-Grafted-Poly (vinyl alcohol) as an Electrolyte Membrane. J. Chem. Engine. doi:dx/doi.org/10.1155/2013/642871.

[31] Svang-Ariyaskul, A., Huang, R.Y.M., Douglas, P.L., Pal, R., Feng, X., Chen, P., Liu L. 2006. Blended chitosan and polyvinyl alcohol membranes for the pervaporation dehydration of isopropanol. J. Membr. Sci. 280(1): 815–823, https://doi.org/10.1016/j.memsci.2006.03.001.

[32] Li, T., Yang, Y. 2009. A novel inorganic/organic composite membrane tailored by various organic silane coupling agents for use in direct methanol fuel cells. J. Power Sources. 187(2): 332–340, https://doi.org/10.1016/j.jpowsour.2008.11.035.

[33] Septiawan, M., Permana, D., Sabarwati, S.H., Ahmad, L.O., Ramadhan, L.O.A.N. 2018. Functionalization of chitosan with maleic anhydride for proton exchange membrane. Indones. J. Chem. 18(2): 313–320, https://doi.org/10.22146/ijc.33141.

[34] Smitha, B., Sridhar, S., Khan, A.A. 2005. Chitosan–sodium alginate polymer complexes as fuel cell membranes. Eur. Polym. J. 41(8): 1859–1866, https://doi.org/10.1016/j.eurpolymj.2005.02.018.

[35] Xia, C., Cai, Y., Wang, B., Afzal, M., Zhang, W., Soltaninazarlou, A., Zhu, B. 2017. Strategy towards cost-effective low-temperature solid oxide fuel cells: A mixed-conductive membrane comprised of natural minerals and perovskite oxide. J. Power Sources. 342: 779–786, https://doi.org/10.1016/j.jpowsour.2016.12.120.

[36] De Luca, N.W., El abd, Y.A. 2006. Polymer electrolyte membranes for the direct methanol fuel cell: A review. J. Polym. Sci. Part B Polym. Phys. 44: 2201–2225, https://doi.org/10.1002/polb.20861.