COMPOSITE MEMBRANE BASED ON SULFONATED POLYSULFONE-NATURAL ZEOLITE-TITANIUM DIOXIDE

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ABSTRACT

Composite membrane based on sulfonated polysulfone-natural zeolite-titanium dioxide has been performed. The composite membrane is carried out by mixing the sulfonated polysulfone with natural zeolite, with the mass ratio of sulfonated polysulfone: zeolite; 1: 0.5, 1: 1, and 1: 2. In each variation has been added titanium dioxide with of 10% (w/v) to the polymer solution. The next step is the casting on the glass plate by pouring the mixture. Subsequent evaporation of the solvent slowly to form a membrane. From FT-IR analysis obtained the small bands observed at about 1223 cm^{-1} corresponding to the asymmetry stretching the external vibrational bands of SiO_4 or AlO_4 . On the other hand, bands around 792 cm^{-1} and 600 cm^{-1} are due to the symmetrical stretching of SiO_4 or AlO_4 and the vibrations of the double rings respectively. The small bands observed at about 600 cm^{-1} represent a bending mode for Si-O-Si. The interaction between sulfonated polysulfone and TiO_2 has shown from the widening band of O-H bond uptake. Ti-O bonds have shown in the absorption of wave numbers 539.58 - 516.32 cm^{-1} . Optimum ion exchange analysis obtained 1.003 meq/g for PSf 0.5 zeolite 10% TiO_2 membrane, the degree of swelling obtained the optimum on the membrane PSf 1.5 zeolite 10% TiO_2 of 0.09%, and methanol permeability was obtained on the membrane PSf 1.0 zeolite 10% TiO_2 of 6.9×10^{-9} S/cm. The result of optimum proton conductivity for zeolite addition of 1.5 gram at temperature 70 °C equal to 1.185×10^{-2} S/cm.

Keywords: Composite membrane, sulfonated polysulfone, polysulfone, zeolite, titanium dioxide.

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INTRODUCTION

Techniques in the manufacture of proton conducting membranes can be carried out in several ways, such as modifying an already available membrane in the market, among others, a naphthalized/polyvinyl fluorinesul fonated membrane, sulfonated hydrocarbon polymer, adding a non-solvent or a low volatile solvent, mixing an oxide hygroscopic, and may also add an inorganic compound¹.

Therefore it is done to improve the existing performance, looking for other alternatives that are cheaper. In an effort to improve membrane performance, one of the ways is to synthesize or manufacture membranes by adding other materials, so membrane performance depends not only on the water content present in the membrane, but also circumstances the protons transport existence can be maintained, Then when methanol is used as a feed, the presence of CO tolerance by the existing platinum catalyst in the electrode, further implies ions will increase mass transport and increase reaction kinetics².

One polymer having good thermal stability, where the degradation temperature of up to 500°C is polysulfone (PSU). With high degradation temperatures, this allows the membrane performance spectrum to be very wide namely it can work at low temperature to temperatures above 100 °C. Previous research has been reported that sulfonated polysulfone has been used in ultrafiltration membrane on ion bonding process through diffusion phenomena or dialysis process of metal ions³.

Previous studies have been carried out by sulfonated of polysulfone (SPSU)-added of benzotriazole with proton conductivity up from 3.44×10^{-4} to 3.6×10^{-3} S/cm at 150°C⁴⁻⁵.

Another attempt to improve the performance of proton conducting membranes of sulfonated polysulfone is to add activated carbon, as has been reported⁶ with proton conductivity of 8.8×10^{-4} S/cm at 40°C. A recent research report in which polysulfone was added with natural zeolite, its proton conductivity still

ranges from 7.15×10^{-4} S/cm at 40°C ⁷. The next attempt to improve membrane performance is by adding natural zeolite and titanium dioxide.

In this report discussed is the synthesis and characterization of the composite membranes, the sulfonated polysulfone has been synthesized using the preceding method^{4,5,6,7}. Sulfonated polysulfone is further composited with a natural zeolite which is impregnated with titanium dioxide. The composite membrane was evaluated, i.e functional group analysis using FT-IR, ion exchange capacity analysis, the degree of the swelling membrane, methanol permeability, and proton conductivity.

EXPERIMENTAL

Materials

Polysulfone (PSU), trimethylsilylchlorosulfonate (TMSCS) and methanol, dimethylformamide and 1, 2-dichloroethane, titanium dioxide and natural zeolite. Materials used are the same as previous research reports⁷, except titanium dioxide.

Preparation

The procedure used is the same as the previous research report⁷, except for the addition of titanium dioxide: sulfonated polysulfone and composite membrane were prepared according to literature^{4,5,6,7}. The composite membrane was made by mixing sulfonated polysulfone with natural zeolite as was done in the previous procedure⁷, with the mass ratio of sulfonated polysulfone: zeolite; 1: 0.5, 1: 1, and 1: 2 previously sulfonated polysulfone have been dissolved using dimethyl formamide solvent. The mixture is stirred for 12 hours, at room temperature. In each variation will be added titanium dioxide with a percentage of 10% of the polymer solution in the previous step. The next step is the casting on the glass plate by pouring the mixture. The solvent was evaporated slowly at 50°C for 24 hours then the membrane was transferred into the oven at 65°C for 24 hours to evaporate residual solvents still contained in the composite membranes.

Characterization

FT-IR spectra were recorded on a Bruker Alpha-P (Wismar, Germany) in the range of $4000\text{--}400\text{ cm}^{-1}$. Analysis of ion exchange capacity by titration method, the degree of membrane swelling by the gravimetric method, and methanol permeability by gravimetric method. The conductivity of the membrane was measured by IM 3590 Chemical Impedance Analyzer HIOKI in frequency 1 KHz, 0.05 Volt.

RESULTS AND DISCUSSION

Figure-1 shows the spectra of composite membranes PSF-0,5 ZEOLIT 10% TiO_2 , PSF-1,0 ZEOLIT 10% TiO_2 , PSF-1,5 ZEOLIT 10% TiO_2 . From spectra showed for composite membranes that have been added zeolites and TiO_2 , exhibit almost similar pattern spectra. The character of wave numbers for composite membranes is on the broad band in an area of about 1091 cm^{-1} , most prominent in the infrared spectrum, according to the asymmetrical internal stretch of the vibration band SiO_4 or AlO_4 . While the small bands observed around 1223 cm^{-1} are for asymmetric external vibration bands of SiO_4 or AlO_4 .

The band area around 792 cm^{-1} and 600 cm^{-1} caused by symmetrical stretches of SiO_4 or AlO_4 and vibrations of each double ring. The small bands observed at about 600 cm^{-1} represent a bending mode for Si-O-Si. The interaction between sulfonated polysulfone and TiO_2 is shown from the widening band of O-H bond uptake. Ti-O bonds are shown in the absorption of wave numbers $539.58\text{--}516.32\text{ cm}^{-1}$. The previous study on infrared titania sol-gel reported that an infrared band around 805 cm^{-1} related (Ti-O) vibration mode⁸.

Figure-2 showed ion exchange capacity of composite membranes PSF-0,5 ZEOLIT 10% TiO_2 , PSF-1,0 ZEOLIT 10% TiO_2 , PSF-1,5 ZEOLIT 10% TiO_2 . The ion exchange capacity analysis aims to determine the ability of the composite membrane in exchange for the ion bonded to the sulfonate group with other ions given to the system. As an alternative polymer material for making electrolytic membranes, sulfonated polysulfone must have the ability to exchange ions properly to improve the performance of fuel cells. The more the number of ions that can be exchanged the greater the electrical energy generated. Increased ion exchange capacity is proportional to the high degree of sulfonation in a polymer. The number of sulfonate

groups entering the polymer chain, the more interchangeable H^+ . The ion exchange capacity shows an amount equivalent to ions per gram of dry polymer weight. In the following curves are shown membrane ion exchange capacity. In Figure-2 showed that the ion exchange capacity obtained in this study is similar to the ion exchange capacity of Nafion 117 (0.91 meq/g) membrane ion⁹, the previous study have also reported that membrane ion exchange capacity Nafion 115 which is 0.89 meq/g¹⁰.

Fig.-1: Spectra of Composite Membranes PSF-0,5 ZEOLIT 10% TiO_2 , PSF-1,0 ZEOLIT 10% TiO_2 , PSF-1,5 ZEOLIT 10% TiO_2 .

Fig.-2: Ion Exchange Capacity of Composite Membranes PSF-0,5 ZEOLIT 10% TiO_2 , PSF-1,0 ZEOLIT 10% TiO_2 , PSF-1,5 ZEOLIT 10% TiO_2

Figure-3 showed degree of swelling composite membranes PSF-0,5 ZEOLIT 10% tio_2 , PSF-1,0 ZEOLIT 10% tio_2 , PSF-1,5 ZEOLIT 10% tio_2 . The degree of swelling analysis was performed to determine the extent of membrane swelling due to the influence of water absorption. A membrane capable of absorbing water well will affect the resulting proton conductivity value to be greater. This is because the water content of the membrane serves to facilitate the transfer of protons. The greater water content in the membrane causes proton transport to be easier. But the water content is too excessive to cause methanol diffuses through the membrane (methanol crossover) which leads to a decrease in the efficiency of methanol fuel and the efficiency of the cell voltage. Membranes containing many sulfonate groups can improve water absorption capacity with high conductivity, since hydrophilic groups can facilitate proton conductivity at low temperatures.¹¹ Methanol permeability analysis aims to determine whether or not methanol can pass through the membrane. As a DMFC electrolyte polymer membrane candidate should

avoid high permeability of methanol as it may lead to methanol crossover which will decrease overall DMFC performance. The results of the methanol permeability analysis of the composite membrane are shown in the following Fig.-4.

Fig.-3: Degree of Swelling of Composite Membranes PSF-0,5 ZEOLIT 10% TiO₂, PSF-1,0 ZEOLIT 10% TiO₂, PSF-1,5 ZEOLIT 10% TiO₂.

Fig.-4: Methanol Permeability of Composite Membranes PSF-0,5 ZEOLIT 10% TiO₂, PSF-1,0 ZEOLIT 10% TiO₂, PSF-1,5 ZEOLIT 10% TiO₂.

Figure-5 showed The Conductivity of composite membranes PSF-0,5 ZEOLIT 10% tio₂, PSF-1,0 ZEOLIT 10% tio₂, PSF-1,5 ZEOLIT 10% tio₂. The measurements of proton conductivity were carried out at temperatures of 30, 50, 70 and 90 °C. Measurements made by increasing the temperature aims to determine the ability of the membrane performance at what temperature the resulting membrane is and see if this composite membrane can work at temperatures close to 100°C. The objective of the test at temperatures up to 90 °C to see the effect of impregnants added, whether added important may contribute to the existence of the transport of protons. From the measurements, it is seen that both zeolites and TiO₂ added to sulfonated polysulfone are synergistic in increasing the conductivity of the protons, although both still have hydrophilic properties. At high temperatures, the reduced water content decreases the conductivity of the proton. Because generally at low temperatures, the proton conductivity is mostly facilitated by the water content contained or contained in the membrane. At high temperatures that play a role in facilitating the movement of protons is expected to come from impregnants added. Theoretically, the membrane performance at high temperature, the water content has started to evaporate so that the

proton movement facilitator no longer exists. Therefore with the impregnant, in this case, zeolite and TiO_2 can facilitate the movement of protons. The interaction between sulfonated polysulfone to the impregnant zeolite and TiO_2 through weak bonds makes it possible for the formation of protonated sites due to impregnant and sulphonated polysulfone relationships.

Fig-5: The Conductivity of Composite Membranes PSF-0,5 ZEOLIT 10% TiO_2 , PSF-1,0 ZEOLIT 10% TiO_2 , PSF-1,5 ZEOLIT 10% TiO_2

The weak bonds that occur are non-permanent, allegedly through the process of formation and the breaking of weak bonds leads to proton jumps from one protonated site to the next protonated site. The result of the research shows that the optimum proton conductivity for TiO_2 10% occurs with the addition of zeolite 1.5 gram (PSf 1.5 zeolite 10% TiO_2) at temperature 70 °C equal to 1.185×10^{-2} S/cm, Figure-6 showed a surface section of membrane. For comparison, the proton conductivity of Nafion 117 membrane measured at 60 °C is 6.7×10^{-2} S/cm at a relative humidity of 95%¹².

Fig-6: Morphology of Psf 1.5 g Zeolite 10% TiO_2 .

CONCLUSION

Efforts to improve membrane performance as fuel cell membranes have been conducted. The effort is to combine sulfonated polysulfone with inorganic materials such as natural zeolite and added titanium

dioxide. The addition of titanium dioxide greatly affects the performance of the obtained conductivity. From the ion exchange, the degree of swelling and methanol permeability showed that the membrane has been produced, close to the category of membranes that have been meticulously or patented as Nafion. Though there are still many shortcomings that need to be improved. From the proton conductivity analysis, it was found that the optimum proton conductivity was obtained from the addition of 1.5-gram zeolite i.e. for composite membrane Psf 1.5 g zeolite 10% TiO₂ at temperature 70 °C equal to 1.185×10^{-2} S/cm.

ACKNOWLEDGMENT

This work is supported through the Ministry of Research, Technology and Higher Education fund of the Republic of Indonesia with contract number 904 / UN30.15 / LT / 2017.

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[RJC-5010/2018]