



## Synthesis and characterization of hybrid zeolite, a chitosan sulfonated membrane for proton exchange membrane fuel cell (PEMFC)

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### ABSTRACT

Proton Exchange Membrane Fuel Cell (PEMFC) is fuel cells that utilize membrane as the electrolyte. The electrolyte membrane was synthesized utilizing the natural polymer chitosan modified into hybrid zeolite A chitosan sulfonated membrane. The objective of the research are to synthesize hybrid zeolite A chitosan sulfonated membrane for PEMFC with a variations of zeolite concentration range 0, 40, 50, 60, 70, 80% (w/w) and to determine the ability of a polymer electrolyte membrane for PEMFC. Preparation of the membrane initially by blending chitosan solution with zeolite then immersed with  $H_2SO_4$  0.36 N. Morphological of zeolite A was characterized by XRD and performance of the membrane was characterized by FTIR and SEM. The diffractogram of zeolite A synthesized appeared  $2\theta$  13.98; 24.05; 32.59; 35.79; 38.03; 43.58° and the FTIR spectra of synthesized hybrid zeolite A chitosan sulfonated membrane showed at  $3448.49\text{ cm}^{-1}$  for hydroxyl functional group,  $1648\text{ cm}^{-1}$  and  $1565\text{ cm}^{-1}$  for amide I dan amide II which is directly decrease with the addition of zeolite concentration. Hydrogen bonds between the Si-O from zeolite A – chitosan bonding showed at  $1040\text{ cm}^{-1}$  and  $455.14\text{ cm}^{-1}$ . The S-O bonding from sulfonate functional group showed at  $619.12\text{ cm}^{-1}$ . The ability of the membrane as the electrolyte membrane showed the high mechanical properties Modulus Young  $5.07 \times 10^7\text{ N/m}^2$ , water swelling test 61.38%, ion exchange capacity test with acid-base titration method is obtained IEC (Ion Exchange Capacity)  $1.0107\text{ meq/g}$ , proton conductivity test with EIS (Electrochemical Impedance Spectroscopy) method is  $2.2 \times 10^{-4}\text{ S/cm}$ , and the methanol permeability test with dead-end method  $1.26\text{ kg/m}^2\text{hour}$ . This characteristic showed that the hybrid zeolite A chitosan sulfonated membrane potential as proton exchange membrane to be applied to the PEMFC.

**Keywords:** chitosan, hybrid zeolite A, sulfonated, PEMFC

### INTRODUCTION

Fuel cells are electrochemical devices that convert chemical energy into electrical energy without combustion [1]. The principle of the fuel cell is electrolysis to occur cation  $H^+$  release events, thus forming electrons that can be converted into electrical energy and heat. In detail can be explained that the fuel cell, the electrons gather at the anode to form a pile of electrons that produces a difference potential and forces electrons flowing in a circuit currents and some electrons toward to the cathode and followed the flow of  $H^+$  from the anode to the cathode through the electrolyte membrane fuel cell which will meet the oxygen and electrons at the cathode to form  $H_2O$  residue [2].

Proton Exchange Membrane (PEM) is an important component to obtain electrical energy and heat and has a role as a proton transport. During this time, PEM was made by Nafion from the copolymerization of vinyl ether sulfonate comonomer perfluorination with tetrafluoroethylen (TFE) [3]. Nafion is widely used as a fuel cell membrane

because it has a hydrophilic and hydrophobic properties, a high ion exchange capacity that  $0.9 \text{ meqg}^{-1}$ , a high proton conductivity  $0.1 \text{ S cm}^{-1}$ , water swelling 33 % [4]. However, Nafion has disadvantages such as difficult degraded, can be damaged at temperatures above  $100^\circ \text{C}$  and very dependent on water for conduction process [5]. So, this research will be create a membrane capable degraded by environmental and economic value as PEM. Economical electrolyte membrane can be obtained from natural polymers such as chitosan. However, chitosan polymer has the weakness when used as a fuel cell membrane, because the proton conductivity less than  $0.1 \text{ Scm}^{-1}$ , high water swelling up to 55.2 % and poor thermal stability [6]. Therefore, to improve the performance of chitosan as a PEM (Proton Exchange Membrane), this research will be synthesized of hybrid zeolite A membranes sulfonated with a variations of zeolite concentration range 0, 40, 50, 60, 70, 80% (w/w). The structure of the membrane will be characterized using Scanning Electron Membrane (SEM) and Fourier Transformed Infra Red (FTIR), the mechanical properties of the membrane using tensile test, and the performance of the membrane as proton exchange membrane by proton conductivity test using EIS (Electrochemical Impedance Spectroscopy), proton exchange capacity test by acid-base titration method, water swelling test and methanol permeability test by dead-end filtration method.

## EXPERIMENTAL SECTION

### 2.1 Materials and instruments

The materials used is pro analysis (pa) ie TEOS (tetraethyl orthosilicate; Sigma Aldrich; 99%), sodium aluminate ( $\text{NaAlO}_2$ ; Sigma Aldrich, 50%), hydrochloric acid (HCl; Merck; 37%), sodium hydroxide (NaOH; Merck; 99%), glacial acetic acid ( $\text{CH}_3\text{COOH}$ ; Merck; 100%), sulfuric acid ( $\text{H}_2\text{SO}_4$ ; Merck; 98%), distilled water, demineralized water, phenolphthalein indicator, methanol ( $\text{CH}_3\text{OH}$ ; Sigma Aldrich; 99 , 8%). The instruments of the research were glassware, the tensile test equipment AG-1S 50 KN Autograph, JEOL JSM-8360LA SEM, FTIR Shymidzu 8400 s type, and the type of XRD Philips X'Pert MPD, HIOKI EIS (Electrochemical Impedance Spectroscopy), and instrument dead-end.

### 2.2 Synthesis of zeolite A

Zeolite A was synthesized by hydrothermal methods. The first, aging process begins by mixing 32.8 g  $\text{NaAlO}_2$  with 469 mL aquadem then drop wise with 22 mL of TEOS and stirred. The second, hydrothermal proces was done at  $100^\circ \text{C}$  for 44 hours. The mixture then filtered to obtain a residue and washed with distilled water, then dried. After drying, the mixture was calcined at  $450^\circ \text{C}$  for 4 hours.

### 2.3 Characterization of chitosan

Chitosan was characterized using 2% acetic acid for solubility test, FTIR absorption in the region  $400\text{-}4000 \text{ cm}^{-1}$  and deacetylation degree of chitosan was measured by the baseline method from FTIR spectrum. The molecular weight of chitosan was also determined using the Mark Houwink Sakurada equations.

### 2.4 Synthesis of hybrid zeolite A chitosan membrane with variation concentration of zeolite

Membrane was synthesized by dissolving 1.5 g of chitosan in 80 mL of acetic acid 2% (w/w). Zeolites 40% (w/w) of the total weight of chitosan was added to the chitosan solution and stirring for 2 hours at room temperature. Then the solution was poured on a slide and dried by heating on a hot plate at  $45^\circ \text{C}$ . The same procedure was done for variation of the concentration of zeolite from 50 to 80% (w/w). The membrane was soaked with a solution of NaOH 4% (w/v), then washed with distilled water and dried at  $40^\circ \text{C}$ .

### 2.5 Synthesis of hybrid zeolite A chitosan sulfonated membrane

Hybrid zeolite A chitosan sulfonated membrane was formed by soaked the membranes for 2 hours in 0.36 N  $\text{H}_2\text{SO}_4$  at room temperature. Then neutralized with washed using demineralize water, and then dried. The dried membranes was characterized using FTIR, ion exchange capacity test, the morphology using Scanning Electrone Microscopy (SEM), mechanical properties test and water swelling test.

### 2.6 Performance of hybrid zeolite A chitosan sulfonated membrane as proton exchange membrane

Performance of the membrane as proton exchange membrane determine by proton conductivity test using EIS (Electrochemical Impedance Spectroscopy), proton exchange capacity test by acid-base titration method, water swelling test and methanol permeability test by dead- end filtration method.

### 2.6.1 Methanol permeability test

Methanol permeability of the membranes was characterized accordance with research of Saim and Hassan [7] using dead-end filtration. The membranes strirring with 5 mL methanol for 6 hours without using pressure. Methanol permeability is calculated by equation :

$$J = \frac{L \cdot \rho}{A \cdot t}$$

Where the J, L, A, and t is a permeat flux rate, volume, area of the membrane, and for the last time is the density.

### 2.6.2 Proton conductivity determination of the membranes

Proton conductivity determined using EIS (Electrochemical Impedance Spectroscopy). Frequencies used in this study is 1 Hz up to 1x106 Hz with voltage of 20 mV. Conductivity measurements conducted on the condition of the membrane has been soaked with 0.2 M H<sub>2</sub>SO<sub>4</sub> at room temperature for 24 hours [8]. The measurement uses equation:

$$\rho = \frac{A \cdot R}{\ell}$$

$$\sigma = \frac{1}{\rho}$$

With  $\sigma$ ,  $\ell$ , A, R, is a proton conductivity (S/cm), length (cm) area of the membrane, the membrane area (cm<sup>2</sup>), resistance (ohm), a type of resistance (ohm m.)

## RESULTS AND DISCUSSION

### 3.1 Characterization of zeolite A

The obtained zeolite A have been characterized using X-ray diffraction and shown in Figure 1. The result shown intense peak at 13,98; 24,05; 35,79; 38,03; and 43,58 degrees and appropriate with Treacy and Higgins [9].

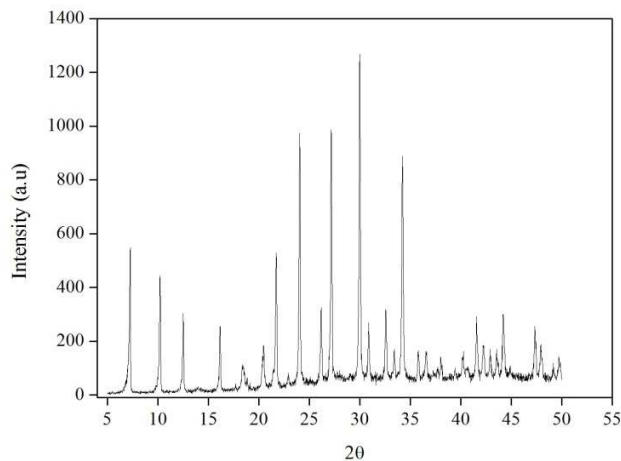


Figure 1. Diffractogram of zeolite A

### 3.2 Characterization of chitosan

The obtained chitosan are soluble in acetic acid 2 % and from FTIR baseline method was obtained Deacetylation Degree (DD) is 70, 72 % with molecular weighth 234.826, 26 g/mol. The result is appropriate with Khor [10] that molecular weight chitosan range is 190.000-700.000 g/mol with Deacetylation Degree more than 70 %.

### 3.3 Characterization of hybrid zeolite A chitosan sulfonated membrane

The Hybrid zeolite A chitosan sulfonated membrane was characterized using FTIR and the mechanical properties of the membrane was determined using autograph instrument. The FTIR spectra of Hybrid zeolite A chitosan sulfonated membrane shown in Figure 2.

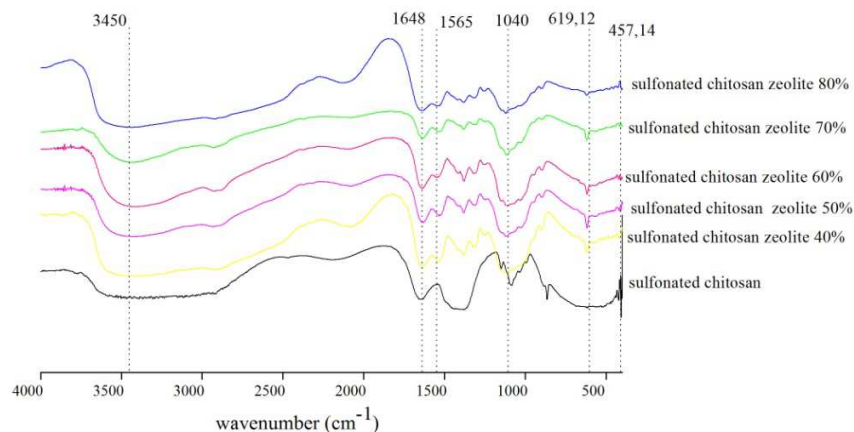


Figure 2. Spectra FTIR of hybrid zeolite A chitosan sulfonated membrane

The spectra shown that hydroxyl functional group at 3448,49  $\text{cm}^{-1}$  and amide I and amide II functional group at 1648  $\text{cm}^{-1}$  and 1565  $\text{cm}^{-1}$ . Hydrogen bonding between zeolite and chitosan was shown in Si-O bond at 1040  $\text{cm}^{-1}$  [12] and 455,14  $\text{cm}^{-1}$  [16]. Ionic bonding between sulfonated functional group with chitosan shown in S-O bond at 619,12  $\text{cm}^{-1}$  [16].

The mechanical properties of hybrid zeolite A chitosan sulfonated membrane shown in Figure 3.

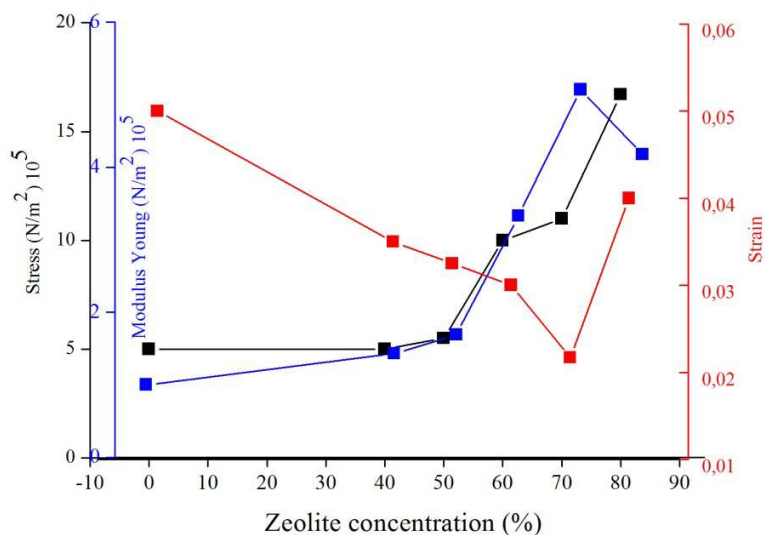


Figure 3. Mechanical properties of hybrid zeolite A chitosan sulfonated membrane

The increasing zeolite concentration made the stress and Modulus Young's of hybrid zeolite A chitosan sulfonated membrane increase and the strain decrease relatively. But the concentration of zeolite 80% shown the difference that is the decreasing of Modulus Young's and the increasing of strain. The increasing of stress was caused presence of zeolite A structure bonding to amide and hydroxyl groups on chitosan but in opposite the highest of zeolite concentration made the membrane weak because of the large space on the bonding of chitosan and zeolite A [11]. The decreasing of strain was caused the formation of plastis ties between membrane and amorphous zeolite A. But

the increasing of strain in highest zeolite concentration was caused the hydrogen bonding between zeolite and chitosan not on long bonds. The optimum mechanical membranes shown in zeolite concentration 70%. This membranes have a balanced composition of chitosan and zeolite and appropriate as membrane fuel cell that is stiff, strong with low elasticity [12].

The membranes was characterized by ion exchanger capacity test and swelling water test and shown in Figure 4. Figure 4 shown that the increasing of zeolite concentration, the increasing of water swelling percentage and the ion exchange capacity. The increasing of zeolite concentration, the increasing of water swelling because the affinity of zeolite from zeolite pore to water [13]. The increasing of ion exchange capacity was caused by the increasing negative charge from zeolite acts as an ion exchanger and from sulfonate cluster in membranes [12]. The optimum membranes (zeolite concentration 70 %) shown high ion exchange capacity i.e 1,0107 meq/g and water swelling i.e 61,38%.

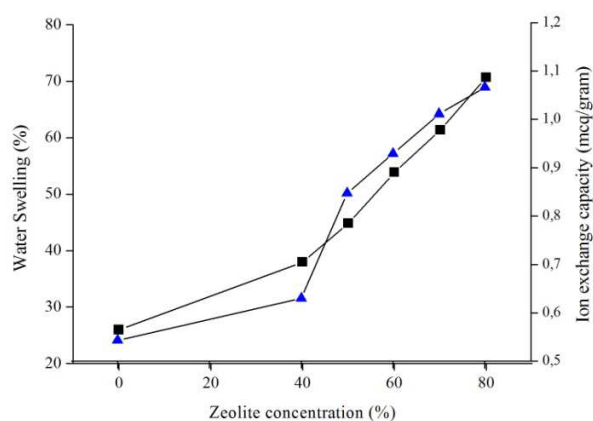
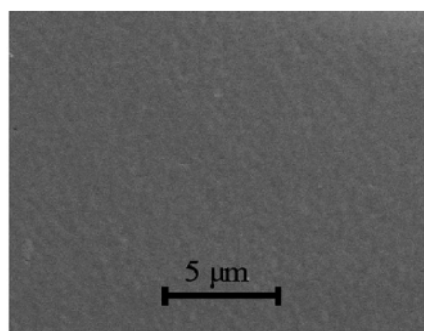


Figure 4. Water swelling and ion exchange capacity of membranes

The morphology of the optimum membranes was characterized using SEM and shown in Figure 5. The hybrid zeolite A chitosan sulfonated membrane shown more porous than pure chitosan. So can be said that modification chitosan membranes is appropriate to applied as membranes fuel cell because more porous.



a) The optimum hybrid zeolite A(70%) chitosan sulfonated membrane



b) pure chitosan

### 3.4 Performance of hybrid zeolite A chitosan sulfonated membrane as proton exchange membrane

Performance of hybrid zeolite A chitosan sulfonated membrane as proton exchange membrane shown in methanol permeability test and proton conductivity test. The result of methanol permeability test shown that flux rate obtained 1.26 kg/m<sup>2</sup>h with driving force is the variation concentration of methanol. This result is better than nafion i.e 1.30 kg/m<sup>2</sup>h. The flux rate membrane is less than nafion because presence crosslink between membranes and sulfonate reduce the methanol permeability. Its caused the London force membrane to againts methanol is reduce.

The proton conductivity test shown that proton conductivity of membranes is  $2.2 \times 10^{-4}$  S/cm. This result far away from the proton conductivity of Nafion i.e. 0,1 S/cm. But at least improved than a proton conductivity chitosan of  $3.16 \times 10^{-7}$  S/cm. Small proton conductivity of hybrid zeolite A chitosan sulfonated membrane is influenced of the addition of zeolite A and the crosslink of sulfonate-chitosan is too tiny. Its because the concentration of sulphate acid too tiny and time for sulfonated too fast. It is indeed not be demonstrated quantitatively crosslink theoretically according Ma and Sahai [15] that the number of functional groups that are bound to cross-influenced the three processes i.e concentration of reagent, time to crosslink, and temperature to crosslink.

### CONCLUSION

Hybrid zeolite A chitosan sulfonated membrane was synthesized by mixing of chitosan with zeolite A and the sulfonation membranes through immersion the membranes using  $\text{H}_2\text{SO}_4$  0.36 N at room temperature. The greater concentration of zeolite, the greater mechanical properties of the hybrid membranes. The optimum mechanical properties of hybrid zeolite A chitosan sulfonated membrane occurs on the addition of 70% (w/w) zeolite that has high Modulus was  $5.07 \times 10^9$  N/m<sup>2</sup>, ion exchanger capacity in excess of nafion 1,0107 meq/g, and the swelling water of 61,38%. The optimum mechanical properties of hybrid zeolite A chitosan sulfonated membrane showed the methanol permeability 1.26 kg/m<sup>2</sup>h with proton conductivity of  $2.2 \times 10^{-4}$  S/cm. This characteristic showed that the hybrid zeolite A chitosan sulfonated membrane potential used as Proton Exchange Membrane.

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