

PHOSPHORYLATED ZEOLITE-A/CHITOSAN COMPOSITES AS
PROTON EXCHANGE MEMBRANE FUEL CELL*Siti Wafiroh^{1,*}, Abdulloh Abdulloh¹, Alfa Akustia Widati¹*<https://doi.org/10.23939/chcht12.02.229>

Abstract. Phosphorylated zeolite-A/chitosan composites were prepared and characterized as an alternative material for proton exchange membrane fuel cell (PEMFC). Their applicability was demonstrated by mechanical properties, swelling property, proton conductivity, methanol permeability, and thermal resistance. Chitosan was prepared from shrimp shell waste by deproteination, demineralization, and deacetylation. Chitosan was modified using zeolite A in the various concentrations. Chitosan membrane hybrid zeolite A was further modified using sodium triphosphate (STPP) as phosphorylation and glutaraldehyde as a cross linker. The SEM results showed that the membrane had rigid pores. Moreover, this research stated that phosphorylated zeolite-A/chitosan hybrid composite as an electrolyte membrane with modified natural polymers could be a solution of environmental and economical fuel cell.

Keywords: chitosan, hybrid, zeolite A, phosphorylated, PEMFC.

1. Introduction

In the future, the energy sector will face the economic, geopolitical, technological, and environmental challenges. The increasing of population growth in developing countries such as Indonesia will require large energy supply. At present, about 85 % of energy use is still based on fossil fuels. Based on this phenomenon, the solution of alternative energy that would be cheap, safe, and environmental friendly is needed. Fuel cell is one of novel energy conversion devices which is efficient, non-polluting, environmentally and economically advantageous. Fuel cell requires chemical reaction between hydrogen and oxygen to produce electricity and water as byproduct. One type of fuel cell is a polymer electrolyte membrane fuel cell, which can be called a proton exchange membrane fuel cell (PEMFC). Currently,

Nafion dominates the market of membrane fuel cell since the hydrophobic polytetrafluoroethylene (PTFE) backbone provides thermal and chemical stability and the hydrophilic sulfonic acid ($-\text{SO}_3\text{H}$) provides channels for proton conduction [1].

Nafion also exhibits the high ion exchange capacity equal to $0.9 \text{ mmol}\cdot\text{g}^{-1}$, high proton conductivity with the value of $0.1 \text{ S}\cdot\text{cm}^{-1}$, as well as water swelling by 33 % [2]. However, Nafion is difficult to degrade, expensive, can be damaged at above 353 K and its conductivity depends on water [3]. Many approaches have been developed to increase the cost efficiency and improve the performance of membrane fuel cell [4, 5].

Chitosan is one of the most common natural polymers used because of its abundance. Chitosan is a linear polymer with structural units (2-acetamido-2-deoxy- β -D-glucose), which is hydrophobic, inert, and able to degrade in the environment [6]. However, chitosan membrane exhibits the low proton conductivity (less than $0.1 \text{ S}\cdot\text{cm}^{-1}$), high water swelling up to 55.2 % and low thermal stability. Xiang *et al.* [7] reported that the performance of chitosan can be enhanced through modification using crosslinking agent. Cross link polymer is where the linear polymers are chemically joined by covalent linkage.

Modification of chitosan through cross link technique was used to reduce the water swelling by sulfonation, phosphorylation, and carboxylation. The previous research stated the phosphorilated group can increase the proton conductivity of membrane [8]. Xiang *et al.* [7] reported that while chitosan was crosslinked by sulfonation to form chitosan sulfate, the water swelling was up to 6 %, proton conductivity was increased up to $0.03 \text{ S}\cdot\text{cm}^{-1}$, and thermal stability increased to 523–593 K. Overall, the sulfonation of chitosan can enhance the performance of fuel cell membrane, but the conductivity proton must be improved in order to become competitive with Nafion technologies.

Hybrid inorganic is one of methods to improve the proton conductivity of electrolyte membrane. Commonly, this process uses zeolite, bentonite, and CaO to modify the PEMFC. Chitosan modified bentonite exhibited low

¹ Faculty of Science and Technology, Universitas Airlangga,
Campus C Mulyorejo, 60115 Surabaya, East Java, Indonesia
* sitiwafiroh@yahoo.com

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proton conductivity of $4.86 \cdot 10^{-3} \text{ S} \cdot \text{cm}^{-1}$. Hybrid inorganic containing CaO generated the proton conductivity of CaO-chitosan hybrid about $0.0023 \text{ S} \cdot \text{cm}^{-1}$ [9]. Interestingly, zeolite A have been used as hybrid inorganic and the observed membrane was rigid and produced greater exchange capacity than Nafion, of about $5.24 \pm 0.03 \text{ meq} \cdot \text{g}^{-1}$ [10]. Zeolites are hydrated aluminosilicate minerals that have a negative charge.

In this study, another approach has been developed to create the PEMFC membrane based on phosphorylated zeolite-A/chitosan hybrid composite. They were prepared using various concentrations of zeolite A. The synthesized membranes were phosphorylated by sodium triphosphate (STTP) and were crosslinked using glutaraldehyde. The chemical and physical properties were characterized using SEM and FTIR analyses, and mechanical test by tensile test. The performance of fuel cell membrane was evaluated by proton conductivity, capacity of proton exchange, water swelling, and methanol permeability test.

2. Experimental

2.1. Materials and Instruments

All chemicals were of analytical grade and used as received without further purification. Tetraethyl orthosilicate (TEOS), sodium aluminate (NaAlO_2), and methanol were purchased from Sigma-Aldrich. Hydrochloric acid, sodium hydroxide, glacial acetic acid, sulfuric acid, and andphenolphthalein indicator were obtained from Merck. The used instruments were the tensile test equipment AG-1S 50 KN Autograph, SEM JEOL JSM-8360LA, FTIR Shimadzu 8400S, JEOL JDX-3530, and Hand IOKI EIS (Electrochemical Impedance Spectroscopy).

2.2. Methods

2.2.1. Preparation of zeolite A

Zeolite A was synthesized based on the previous research with the molar composition of $3.9\text{Na}_2\text{O}:1\text{Al}_2\text{O}_3:1.8\text{SiO}_2:270\text{H}_2\text{O}$ [11]. NaAlO_2 was dissolved in water at room temperature. TEOS was added dropwise in the solution of NaAlO_2 . The mixture was aged under hydrothermal condition at 373 K for 44 h. The resulting solid was collected, washed and dried. After that the solid product was calcined at 723 K for 4 h and analyzed using XRD.

2.2.2. Preparation of chitosan

The production of chitosan from shrimp shells consists of 4 steps: deproteination, demineralization,

depigmentation and deacetylation. The shrimp shells were deproteinated with 3.5 % NaOH (w/v) with the ratio of shrimp shells and NaOH of 1:10 (w/v). This process resulted in crude chitin and it was demineralized with 2N HCl with the ratio of 1:15 (w/v). The depigmentation process was carried out *via* chitin soaking in acetone for 30 min. Then, the chitin was transformed to become chitosan *via* deacetylation process using 50 % NaOH with the ratio of chitin and NaOH 1:10 (w/v). The mixture was heated at 368 K for 2 h and the resulting material was called chitosan. Chitosan solubility was determined using 2 % acetic acid. The average molecular weight of the product was determined and it was analyzed using FTIR.

2.2.3. Preparation of phosphorylated zeolite A/chitosan membrane

1.5 g of chitosan were dissolved in 80 ml of 2 % acetic acid (w/w). Zeolite was dispersed in solution at different concentration (40; 60; 80; 100 % (w/w)). The mixture was stirred for 2 h at room temperature and resulted in the white viscous solution. The solution was then poured on a Petri dish and dried at 318 K. The dried membrane was soaked with 4 % NaOH solution (w/v), washed with distilled water, and dried. After that the membrane was replaced and washed until neutral.

The phosphorylated membrane was prepared by soaking of chitosan membrane hybrid zeolite A in 2N STTP solution for 1 h. Then the membrane was crosslinked using 0.05% glutaraldehyde for 1 h. The resulted solid was characterized using Fourier transform infra red (FTIR), ion exchange capacity test, tensile test, differential scanning calorimetry (DSC), and water swelling test. The methods to determine the ion exchange capacity and mechanical properties are described by Wilkinson *et al.* [12], Vijayaekshmi and Khastgir [13].

3. Results and Discussion

3.1. Synthesis and Characterization of Zeolite A

Zeolite A was prepared using NaAlO_2 as a source of alumina and sodium oxide, and tetraethyl orthosilicate (TEOS) as the silica source. Subsequently, the mixture was stirred for 1 h and heated at 373 K for hydrothermal process. The process of hydrothermal usually refers to growth of crystal in the presence of aqueous solvent under high temperature and pressure. The XRD patterns of zeolite A was shown in Fig. 1. The characteristic peaks at $2\theta = 7.16; 13.88; 21.63; 23.98; 27.08; 29.91; \text{ and } 34.15$ of diffractogram are in a good agreement with the database Collection of Simulated XRD Powder Patterns for Zeolites A.

3.2. Synthesis of Phosphorylated Zeolite-A/Chitosan Hybrid Composite

There are several stages in the preparation of chitosan. Firstly, the process of proteins removal in shrimp shells using high concentration of NaOH solution at high temperature. This process resulted in a change of solid colour from brownish yellow to reddish yellow. It indicated that there was termination of chemical bonds between chitin and proteins, therefore the solubility of the pigment of shrimp shells was increased. In this research, the yield of crude chitin obtained was 48.08 %. The second step was demineralization. This process aimed to remove such minerals as CaCO_3 and $\text{Ca}_3(\text{PO}_4)_2$. The obtained resulting solid from this process was 15.57 %. The third step was depigmentation used to remove the pigment. The yield observed was 14.22 %. The last stage was deacetylation, to break the bonds between acetyl and nitrogen group of chitin and generate the amine group (NH_2). This process was the structure transformation from chitin to chitosan [14].

In this research, the solubility test has been done as an initial test to ensure the formation of chitosan. If the solid dissolves in 2 % acetic acid, it means the solid is

chitosan. Since the resulted solid was soluble in 2% acetic acid, in this research we successfully synthesized chitosan.

FTIR spectra of chitin as well as synthesized and commercial chitosan are presented in Fig. 2. FTIR spectra were used to determine the degree of deacetylation (DD) of chitin and chitosan. Chitin has the absorption peak at 1656.74 and 3446.56 cm^{-1} . Table 1 shows peaks of the amide group at wavenumber of 1654.34 cm^{-1} and the hydroxyl group of about 3452.34 cm^{-1} . These results are in agreement with the previous studies [15]. While the spectra of chitin and chitosan were compared, the absorption peak of amide groups in chitosan spectra was decreased. Comparing with commercial chitosan spectra, the synthesized chitosan had similar pattern. It supported the results observed from solubility test.

In this study, DD of chitin and chitosan were 66.67 and 75.71 %, respectively. The DD of chitosan increased with increasing solubility in acetic acid dilution. According to the viscometry method, the average molecular weight of chitosan was 552598.9137 g/mol. Based on the literature, chitosan had the average molecular weight of about 190000–700000 g/mol [16].

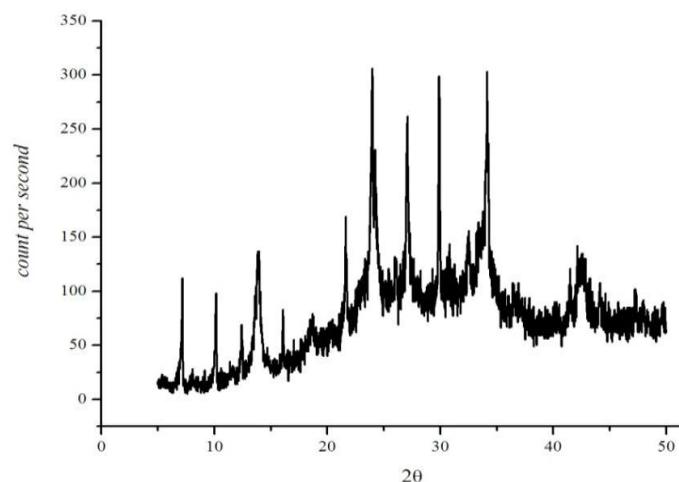


Fig. 1. The diffractogram of the synthesized zeolite A

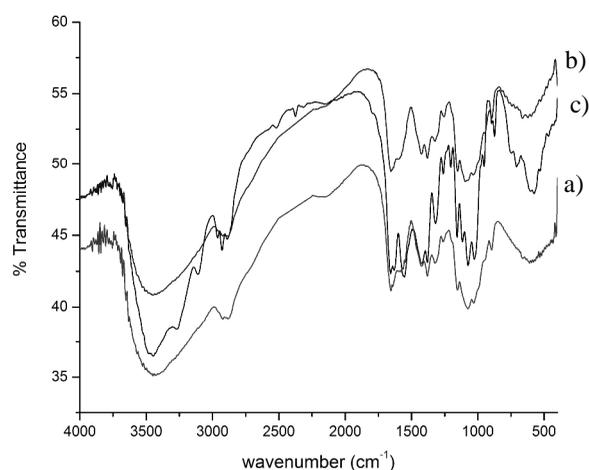


Fig. 2. FTIR spectra of chitin (a), chitosan (b) and commercial chitosan (c)

Table 1

Data on FTIR spectra of chitosan and synthesized chitosan

Type of vibration	Wavenumber, cm^{-1}	
	Synthesized chitosan	Commercial chitosan
OH stretching	3452.34	3425.34
CH ($-\text{CH}_2-$) stretching asymmetry	2883.38	2921.96
C=O ($-\text{NHCOCH}_3-$) stretching	1654.81	1658.67
NH ($\text{R}-\text{NH}_2$) bending	1596.95	1581.52
CN stretching	1153.35	1153.35
C-O ($-\text{C}-\text{O}-\text{C}-$) stretching asymmetry	1076.21	1074.28
C-O ($-\text{C}-\text{O}-\text{C}-$) stretching symmetry	1035.37	1031.85

The chitosan hybrid zeolite A phosphorylated membrane was synthesized by mixing a dope solution of chitosan, STTP as a phosphorylation agent, and glutaraldehyde as a crosslinker. As demonstrated in Fig 3, there was a difference between chitosan and phosphorylated zeolite-A/chitosan hybrid membrane. FTIR spectra of phosphorylated zeolite-A/chitosan hybrid membrane were revealed at about 472, 892, 1211, 1565, 1648, and 3448 cm^{-1} . The presence of hydroxyl group, amide I and amide II were confirmed by characteristic bands at 3448, 1565 and 1648 cm^{-1} . The intensity of absorption bands decreased because of the zeolite addition. Those bands increased with the increase in zeolite concentration. On the other hand, the absorption bands at 472 and 1080 cm^{-1} were typical of tetrahedral building unit (TO_4) of zeolite. The increase in zeolite concentration decreased the intensity of absorption bands. This result is in agreement with the literature data [17]. A peak at 1211 cm^{-1} indicated the presence of vibration of P–O from TPP. The absence of peak at 1380 cm^{-1} indicated the crosslink interaction between glutaraldehyde and chitosan [18].

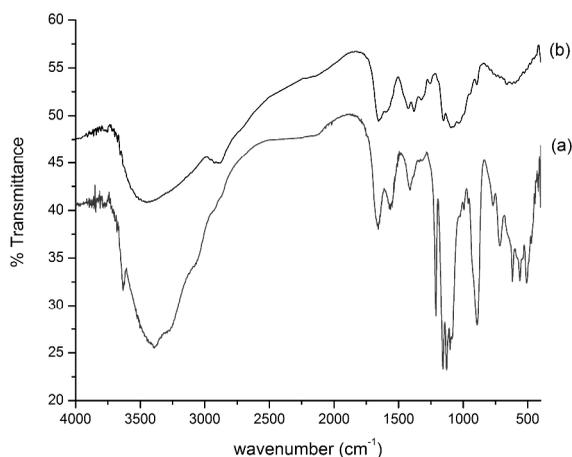


Fig. 3. FTIR spectra of chitosan (a) and phosphorylated zeolite-A/chitosan hybrid composite (b)

FTIR data of phosphorylated zeolite-A/chitosan hybrid membrane also showed the decreasing of peak intensity at 3367, 1664, 1564 cm^{-1} because there was an increasing of hydrogen bond between hydroxyl and amine group of chitosan toward the hydroxyl surface of zeolite. Ma and Sahai [19] reported that the functional group of phosphorous acts as a crosslinker and increases the acidity of zeolite; therefore they can enhance the hydrogen bond in chitosan molecule. The interaction of crosslinked chitosan-zeolite with glutaraldehyde-STTP can be described by interaction between silanol group of zeolite and C6 of chitosan. It resulted in chitosan-zeolite. After that, the protonation of acid towards amide of chitosan produced an ionic bond between phosphor as anion and protonated amide of chitosan ($-\text{NH}_3^+$) as cation [15]. The

interaction of crosslinked chitosan-zeolite with glutaraldehyde-STTP is shown in Fig. 4.

Fig. 5 demonstrates the experimental results concerning stress, strain, and Young's modulus of the synthesized phosphorylated zeolite-A/chitosan hybrid membrane. The data show that zeolite A concentration of about 40–80 % is able to improve the stress properties of membrane due to the rigid framework structure of zeolite. The similar pattern was found for the Young's modulus value. Decrement of Young's modulus strength of membrane with 100 % of zeolite A is due to formation of spaces in membrane which lead to rupture of its structure. Strain of composite decreased by the increase in zeolite amount. High crystallinity and zeolite dense-packed structure makes phosphorylated zeolite-A/chitosan hybrid membrane more rigid. However, the increase of zeolite content up to 80 % lead to higher strain. Probably zeolite does not bind chitosan by C6 atom *via* hydrogen bonding which makes the bond longer. Plasticity of membrane disappears due to formation of strong bond between zeolite and chitosan. This feature is beneficial especially on application of composite as fuel cell membrane. So, using 80 % concentration of zeolite A, the membrane was rigid, strong, with low elasticity. It is in agreement with previously reported data [10].

The capacity of ion exchange was examined using acid base titration. The capacity of ion exchange increased with increasing amount of zeolite. It was found that the negative charge of zeolite and negative phosphorous group of chitosan acted as ion exchange agent. The negative charge developed high affinity of water possessing high ion exchange capacity and proton conductivity. The properties of water swelling are shown in Fig. 6. The high concentration of zeolite decreased the water swelling properties due to the adsorbent properties of zeolite. These results are better than those for nafion.

The SEM analysis showed that phosphorylated zeolite-A/chitosan hybrid membrane had the rigid pores and hollow cross section (Fig. 7). The methanol permeability of the synthesized membrane was better than that of nafion. It had the rate flux of about 0.0007505 $\text{kg/m}^2/\text{h}$ while nafion – about 1.30 $\text{kg/m}^2/\text{h}$. The methanol permeability decreased because London dispersive force of membrane decreased toward methanol and crosslinking of glutaraldehyde is able to reject the flow of methanol. Unfortunately, this membrane disables achieving the high proton conductivity like nafion. This membrane only generated the proton conductivity of about $3.2 \cdot 10^{-4} \text{ S/cm}$. Based on DTA analysis, the boiling point of chitosan and phosphorylated zeolite-A/chitosan hybrid as PEMFC membrane were 400.6 and 415 K, respectively. The length of chain of chitosan influenced its boiling point. The boiling point of PEMFC increased because the contribution of hybrid zeolite could improve the membrane's crystallinity.

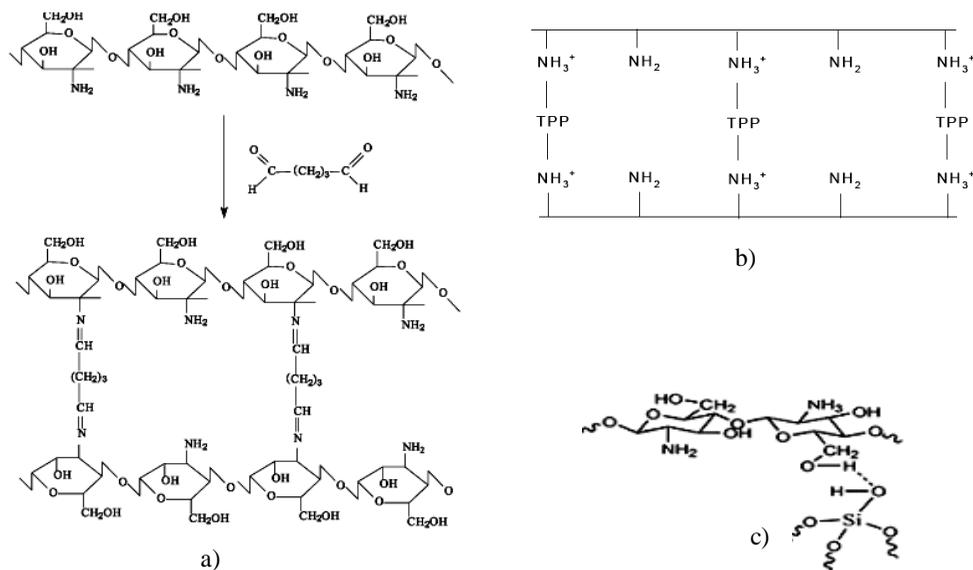


Fig. 4. The crosslinked interactions between chitosan and glutaraldehyde (a) [18], chitosan and TPP (b) [21], chitosan and zeolite (c) [22]

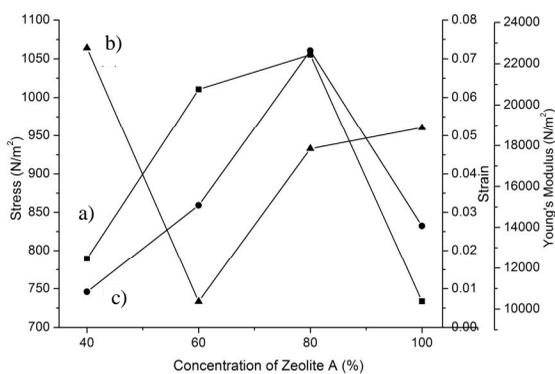


Fig. 5. The influence of zeolite A concentration on stress (a), strain (b), and Young's modulus (c) of phosphorylated zeolite-A/chitosan hybrid membrane

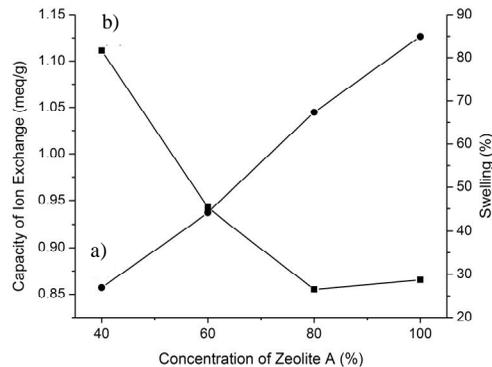


Fig. 6. The influence of zeolite A concentration on the capacity of ion exchange (a) and swelling properties (b) of phosphorylated zeolite-A/chitosan hybrid membrane

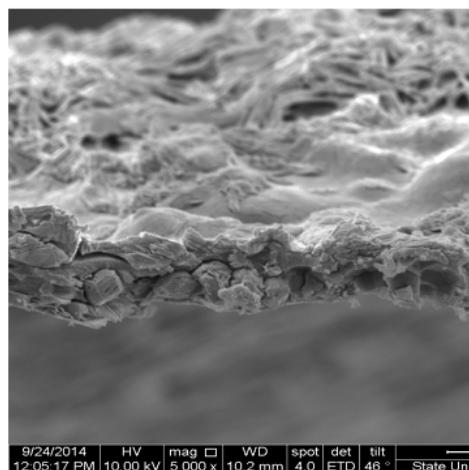
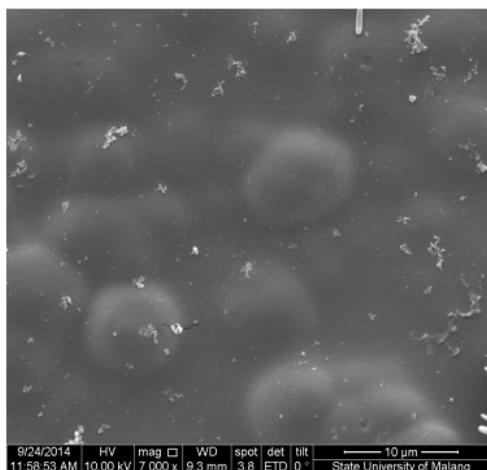


Fig. 7. A view of morphological surface (a) and the cross section (b) of phosphorylated zeolite-A/chitosan hybrid membrane

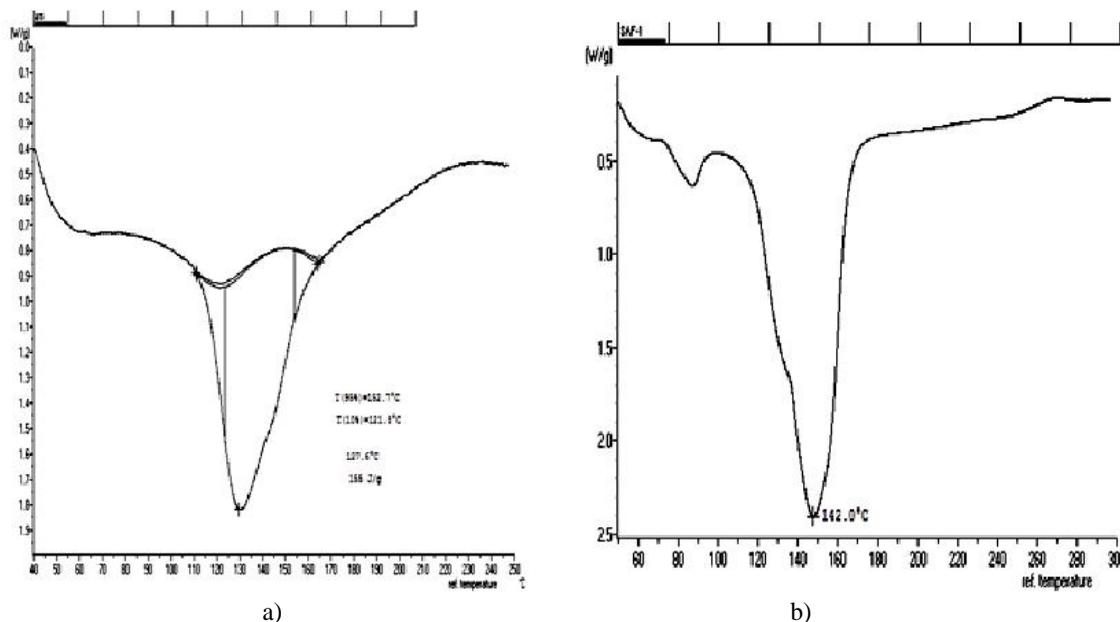


Fig. 8. DTA plots of chitosan (a) and phosphorylated zeolite-A/chitosan hybrid membrane (b)

4. Conclusions

In this study, the preparation and characterization of phosphorylated zeolite-A/chitosan hybrid for PEMFC were accomplished. The optimum performance was conducted by mixing chitosan dope solution with 80 % of zeolite A, by 0.5N STTP as phosphorylation agent and 0.05 % glutaraldehyde as crosslinker. The presence of zeolite improves the mechanical properties of phosphorylated zeolite-A/chitosan hybrid composite membrane (stress of 1055.3 N/m^2 , strains of 0.0466 and Young modulus of 22633.78 N/m^2).

Upon the performance, this membrane exhibited the swelling properties of about 26.5 %, proton conductivity of $3.2 \cdot 10^{-4} \text{ S/cm}$, methanol permeability of about $0.0075005 \text{ kg/m}^2\text{h}$, capacity of cation exchange of 1.0449 meq/g, thermal resistance of about 415 K, and rigid pore. Interestingly, the resulting PEMFC exhibited low methanol permeability and high ion exchange capacity exceeding nafion and proton conductivity of the membrane. Therefore, the phosphorylated zeolite-A/chitosan hybrid composite membrane has potential to be used as an environmental friendly and effective proton exchange membrane.

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ФОСФОРИЛЬОВАНІ ЦЕОЛІТ-А/ХІТОЗАНОВІ КОМПОЗИТИ ЯК ПРОТОНООБМІННІ МЕМБРАННІ ПАЛИВНІ ЕЛЕМЕНТИ

Анотація. Виготовлено фосфорильовані цеоліт-А/хітозанові композити та показано можливість їх викорис-

тання як альтернативного матеріалу для протонобмінних мембранних паливних елементів (ПОМПЕ). Таку можливість продемонстровано механічними властивостями, властивістю до набухання, протонною провідністю, метанольною проникністю та термічною стійкістю. Депротонуванням, демінералізацією та деацетилюванням одержано хітозан з відходів ракоподібних креветок. Проведено його модифікування з використанням цеоліту А в різних концентраціях. Додаткове модифікування проведено з використанням трифосфату натрію (ТФН) як фосфорилуючого агенту та глутаральдегіду як зшивачого агенту. За результатами скануючої електронної мікроскопії встановлено, що мембрана має жорсткі пори. Показано, що фосфорильований цеоліт-А/хітозан гібридний композит як електролітна мембрана з модифікованими природними полімерами може стати рішенням екологічного та економічного паливного елемента.

Ключові слова: хітозан, гібрид, цеоліт А, фосфорильований, ПОМПЕ.