

Nafion/Analcime and Nafion/Faujasite Composite Membranes for High Temperature Operation of PEMFC

Paisan Kongkachuichay and Siraprapa Pimprom

Abstract—The Nafion/zeolite composite membranes were synthesized for polymer electrolyte fuel cells (PEMFCs) by adding zeolite in the matrix of Nafion polymer. Two kinds of zeolites, Analcime and Faujasite, were used. The physico-chemical properties of the composite membranes such as water uptake, ion-exchange capacity, hydrogen permeability, and proton conductivity were determined. The fabricated composite membranes show the significant improvement of all tested properties compared to that of pure Nafion membrane. The maximum proton conductivity of 0.4373 S/cm was obtained from Nafion/Analcime (15%) at 80 °C which is 6.8 times of pure Nafion (0.0642 S/cm at 80 °C). Conclusively, Analcime yielded higher improvement than Faujasite.

Index Terms—Composite membrane, Fuel Cell, Nafion, Zeolite

I. INTRODUCTION

Polymer electrolyte membrane fuel cell (PEMFC) is one of the most attractive power sources for a variety of applications. It has high efficiency and is environment friendly [1]–[6]. PEMFC requires a membrane to separate the chemical reaction at anode from cathode both chemically and electrically. The electrolyte membrane of PEMFC should keep good chemical, physical and thermal stabilities as well as high proton conductivity [7]. Perfluorinated sulfonic acid polymer, Nafion[®], has been the most commonly used membrane. One limitation of the current PEMFC is the CO in the hydrogen feed is enough to poison the Pt anode. The CO poisoning effect can be retarded by operating at an alleviated temperature above 100 °C [1] – [3], [8]. At higher temperature

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Paisan Kongkachuichay is with the Department of Chemical Engineering, Faculty of Engineering, Kasetsart University, Bangkok, 10900, Thailand (corresponding author: phone +6625792083; fax: +6625614621, e-mail: fengpsk@ku.ac.th).

Siraprapa Pimprom is with the Department of Chemical Engineering, Faculty of Engineering, Kasetsart University, Bangkok, 10900, Thailand

the reaction rates at the anode and cathode are increased. However, the proton conductivity of Nafion membrane strongly depends on humidity in the membrane. Therefore, Nafion membrane cannot operate at too high temperature because of the decreasing of water content inside the membrane. Thus, the concept of operating a cell at higher temperature to solve the CO poisoning problem is keeping the membrane hydrated to maintain its proton conductivity [5], [7], [8]–[11].

Several researchers have tried to prevent the loss of water from the ionic pores of the Nafion by the way of modifying membranes. One of the approaches is incorporating hydrophilic metal oxide particles (e.g., SiO₂, ZrO₂, TiO₂) to enhance the water retention property [3], [10]–[13]. Other hybrid membranes were also fabricated by adding phosphotungstic acid [10], cesium sulfate and zirconium phosphate [3], [11], and mordenite [14].

In this work, zeolite/Nafion composite membranes were fabricated. Zeolites are a well-defined class of crystalline naturally occurring aluminosilicate minerals. They have three-dimensional structures arising from framework of [SiO₄]⁴⁻ and [AlO₄]⁵⁻ coordination polyhedral linked by all corners. There are 39 naturally occurring zeolite species that have been recorded and more than 100 species are synthesized [15]. It is widely known that zeolites can be used as ion exchangers and they can be hydrated with high amount of water [16]. Therefore, they are expected to retain water and enhance proton conductivity of the composite membranes. Two kinds of zeolites, Analcime and Faujasite, were used in this work.

II. EXPERIMENTAL

A. Preparation of Composite Membranes.

Analcime (Na₁₆Si₃₂Al₁₆O₉₆·16H₂O, Zeolyst) and Faujasite (Na₅₆Si₁₃₆Al₅₆O₃₈₄·250H₂O, Zeolyst) were converted into H-form by exchanging Na ion with 1 M. NH₄NO₃ for 72 h followed by rinsing with deionized water and calcined at 400 °C for 8 h. Nafion[®] solution (5 % w/w, Ion power) was dried at 50 °C for 30 min. and diluted with dimethylacetamide (DMAc) (10 % w/w solution). An appropriate amount of zeolite powder (5, 10, 15, 25, and 35 % wt.) was added and dispersed in Nafion solution by a sonicator (Starsonic 35, LIARRE) and

a microscan ultrasonic probe. The membranes were casted on glass plates and dried at 50 °C for 2 h. Then they were compressed between a pair of Teflon plates and dried at 160 °C for 30 min.

B. Morphology Analysis

The surface of the Nafion/zeolite composite membranes were inspected by a scanning electron microscope (SEM, Phillips XL30). The distribution of added zeolite particles in the Nafion matrix was assessed by an energy dispersive X-ray spectrophotometer (EDS, Phillips XL30).

C. Water Uptake Measurement

The membrane was immersed in deionized water at room temperature for 24 h. Then the water uptake was determined by (1). The sample was kept in an oven at 50 °C for 6 h.

$$\% \text{ water uptake} = \frac{(W_{wet} - W_{dry})(100)}{W_{wet}} \quad (1)$$

W_{wet} = weight of fully wetted membrane

W_{dry} = weight of dried membrane (dried at 50 °C for 6 h)

D. Ion-exchange Capacity Measurement

The ion exchange capacity (IEC) of the membrane was determined by an acid-base titration. The dried membrane was immersed in 0.01 M NaOH solution for 24 h and then, the solution was sampled and titrated with 0.005 M HCl solution. Subsequently, the IEC was obtained using the following equation:

$$IEC = \frac{(N_1V_1 - (N_2V_1V_2/V_3))}{m} \quad (2)$$

N_1 = concentration of NaOH (M)

N_2 = concentration of HCl (M)

V_1 = total volume of NaOH (ml)

V_2 = volume of HCl (ml)

V_3 = titrated volume of NaOH (ml)

m = mass of membrane (g)

E. Hydrogen Permeability Measurement

Practically, a good membrane must allow less hydrogen molecules diffusing through its matrix. Otherwise, the PEMFC will loss the hydrogen supplied before it is dissociated to protons. The hydrogen permeability (P) through the fabricated membrane was measured under constant input pressure. The flow rate of hydrogen passing through the membrane was detected and the permeability was determined according to the following equation:

$$P = \frac{QL}{\Delta PA} \quad (3)$$

Q = hydrogen flow rate through the membrane (cm³/s)

L = thickness of membrane (cm)

ΔP = pressure drop across the membrane (cm Hg)

A = area of membrane (cm²)

F. Proton Conductivity Measurement

The proton conductivity of the membrane was determined by a four-probe method. The membrane (1 cm x 4 cm) was assembled in the cell contacting with two platinum electrodes. The hydrogen having different relative humidity was filled into the cell and the temperature was controlled isothermally. The resistance between two probes was measured by a milliohm meter (Hewlett Packard 4338A). The conductivity (σ) was then determined by the following equation:

$$\sigma = \frac{L}{(R)(A)} \quad (4)$$

L = distance between the Pt electrodes (cm)

R = resistance (ohm)

A = cross section area of the sample (cm²)

III. RESULTS AND DISCUSSIONS

A. Morphology of the Composite Membrane

The typical surface morphology of Nafion/zeolite membranes is shown in Fig. 1. Fig. 1(a) and (c) obtained from the SEM shows quite smooth surface of the membranes. Using the EDS mode the well distribution of Si that represents the added zeolite can be seen from Fig. 1 (b) and (d). The dimension of the prepared membrane is 5 cm x 5 cm x 30-70 μm.

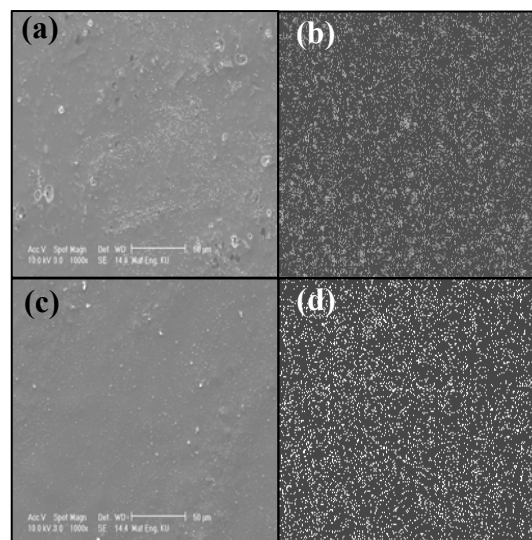


Fig. 1 SEM/EDS pictures of Nafion/zeolite (35 %) membranes (a) surface of Nafion/Analcime, (b) Si-mapping (as white dots) of Nafion/Analcime, (c) surface of Nafion/ Faujasite, (d) Si-mapping (as white dots) of Nafion/Faujasite

B. Water Uptake

The variations of the water uptake of the Nafion/zeolite membranes are shown in Fig. 2.

From the figure, it is clearly seen that the composite membrane can adsorb water much more than that of pure Nafion membrane (shown in Table 1), especially at high amounts of zeolites.

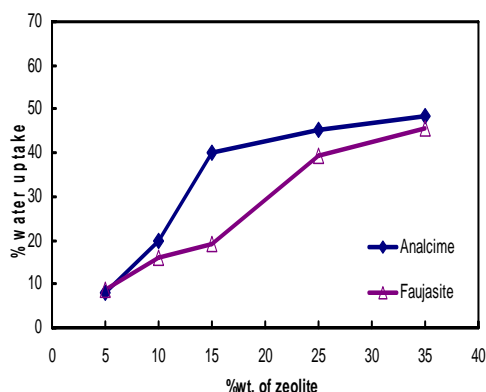


Fig. 2 Water uptake of Nafion/zeolite membranes at 25 °C

Table 1. Properties of Nafion membrane*

Water uptake (%)	6
IEC (meq/g)	2.50
H ₂ permeability at 25°C (Barrel)	590
Proton conductivity at 25°C (S/cm.)	0.031

* tested by this work

The water uptake of the composite membranes increase with increasing amount of added zeolites. Because zeolite structure consists of 3-D connected pores having strong polarity, it can adsorb water well. Comparing between Nafion/Analcime and Nafion/Faujasite, it is found that Nafion/Analcime membrane can adsorb higher water content than Nafion/Faujasite membrane. This difference may come from the stronger polarity of Analcime that has lower Si/Al than Faujasite (more $[AlO_4]^{-5}$ in the structure leads to more negative charges in the secondary building units of zeolite).

C. Ion-exchange Capacity (IEC)

The ion-exchange capacities (IEC) of the fabricated membranes are presented in Fig. 3. Similar to water uptake, the addition of zeolite into Nafion increases the IEC of the composite membrane to be much higher than that of pure Nafion membrane. The maximum IEC 8.07 meq/g that is 3.2 times of pure Nafion was obtained from the Nafion/Analcime (35%). Comparing between Analcime and Faujasite, the former has higher IEC than the latter (4.45 and 3.39 meq/g, respectively [17]). Accordingly, Nafion/Analcime performs better IEC than Nafion/Faujasite.

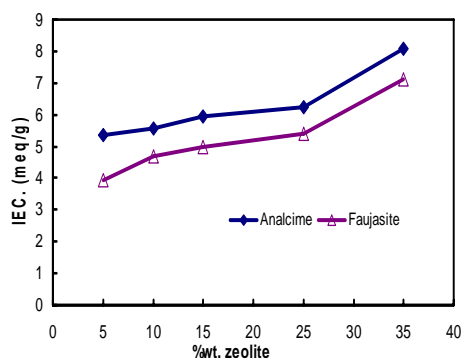


Fig. 3 Ion-exchange capacity of Nafion/zeolite membranes.

D. Hydrogen Permeability

The H₂ permeability was tested at varied temperatures (28 - 80 °C) and the results are shown in Fig. 4. It shows that hydrogen can diffuse through Nafion matrix easier than through zeolite particles because the solid particle has much higher density than the polymer matrix. Thus, the larger amount of zeolite added, the higher resistance to the hydrogen diffusion achieved. On the other hand, when temperature is increased, the hydrogen molecules move faster due to the higher energy supplied causing an increase in diffusion. In this work, Analcime used had average particle size larger than Faujasite (4 μm compared to 0.5 μm). Consequently, the Nafion/Analcime membranes have lower hydrogen permeability.

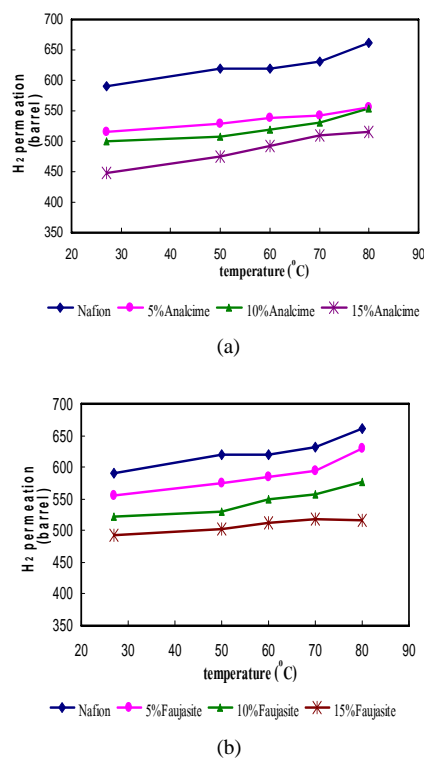


Fig. 4 H₂ permeability of Nafion/zeolite membranes (a) Nafion/Analcime (b) Nafion/ Faujasite

E. Proton Conductivity

Fig. 5 shows the proton conductivity of the Nafion/zeolite membrane under 99.9 %RH, 25°C. The addition of zeolite enhances the proton conductivity compared to pure Nafion membrane. However, above 15 % zeolite the conductivity declines with the added amount. When large amount of zeolite was dispersed inside the polymer matrix, it might reach the limitation of uniform dispersion and started to agglomerate creating some voids among the particles. These voids caused the increase of resistance to proton transfer. The maximum obtained conductivity at 25 °C is 0.3531 S/cm from Nafion/Analcime (15%) that is 11 times of pure Nafion (0.0316 S/cm). This improvement may come from the hydration inside the 3-D channels of zeolite. The hydrated water enhances the motion of proton or hydronium ion via the exchange of proton between hydronium ion and water molecule [5], [14]. Similar to previous properties, Nafion/ Analcime exhibits better proton conductivity than Nafion/Faujasite.

When the temperature is raised from room temperature, the proton conductivity increases for all tested membranes as shown in Fig. 6 and reaches the maximum point at 80 °C, before decreasing drastically. The maximum value of 0.4373 S/cm was obtained from Nafion/Analcime (15%) at 80 °C which is 6.8 and 1.6 times of pure Nafion (0.0642 S/cm at 80 °C) and Nafion/Faujasite (15%) (0.2803 S/cm at 90 °C), respectively. At high temperature the dissociation of hydrogen is promoted causing an increase of proton conductivity. However, at temperatures close to boiling point of water the membrane lost water rapidly and consequently, the conductivity decreased.

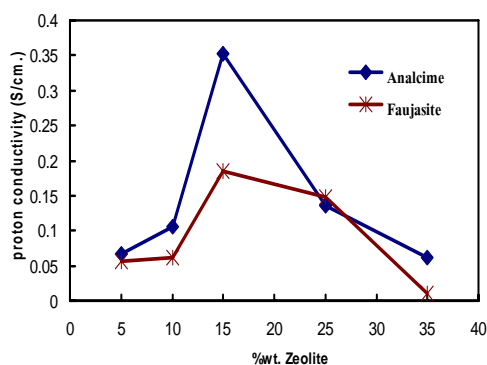


Fig. 5 Proton conductivity of Nafion/zeolite membranes at 25°C.

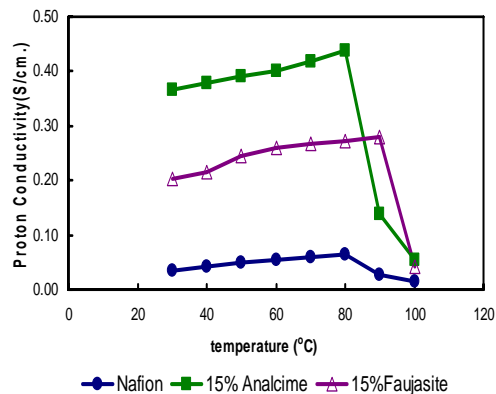


Fig. 6 Proton conductivity of Nafion/zeolites membranes compared with Nafion membrane at varied temperatures.

IV. CONCLUSIONS

The zeolites, Analcime and Faujasite, were added into Nafion to form composite membranes. The prepared Nafion/zeolite membranes yielded better tested properties than that of Nafion membrane. The proton conductivity of the Nafion/Analcime membrane can be improved 11 times at room temperature and 6.8 times at 80 °C, compared to Nafion membrane. However, there is a limitation of zeolite dispersion causing a reduction of conductivity.

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