

# Preparation and Characterization of Nafion/Microporous Titanosilicate Composite Membranes as Ion-Conducting Materials

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## ABSTRACT

Microporous ETS-4 particles were synthesized by the hydrothermal method and characterized by XRD and FE-SEM/EDX. Nafion/ETS-4 composite membranes were prepared by mixing 5 wt% Nafion solution with microporous titanosilicate ETS-4. The water uptake increased with an increase in the ETS-4 content. However, the IEC decreased with an increase in the ETS-4 content due to the addition of ETS-4 with no reactive sites ( $-\text{SO}_3\text{H}$ ). From the FE-SEM/EDX images, it was confirmed that Nafion/ETS-4 composite membranes had homogenous distribution over the surface. The methanol permeability of composite membranes decreased with an increase in ETS-4 content up to 15 wt% of ETS-4 and increased with further addition. The proton conductivity decreased with an increase in the ETS-4 content. From methanol permeability and proton conductivity results, it was confirmed that the selectivity parameter of the NE10 composite membrane containing 10 wt% ETS-4 was the highest value.

**Keywords:** Nafion, ETS-4, methanol permeability, proton conductivity, fuel cell

## 1 INTRODUCTION

One of the most severe environmental issues is nowadays the pollution level due to internal combustion motor devices [1]. Fuel cells, characterized by near-zero emission levels, represent a promising alternative for on-board power generation [2]. Among the different types of such systems, direct methanol fuel cells (DMFCs) are suited for portable devices or transportation applications owing to their high energy density at low operating temperature and the ease of handling a liquid fuel. However, they have a major drawback such as slow oxidation kinetics of methanol at low temperature below 100 °C and high methanol crossover from anode to cathode. In particular, methanol crossover through the membrane as a result of electro-osmotic drag and the concentration gradient decreases the performance of the fuel cell because of the resulting mixed potential.

There have been many attempts to reduce the methanol permeability through the polymer electrolyte membranes: (1) to modify the surface of the membranes to block the methanol transport, (2) to control the size of the proton

transport channels using different block copolymers and cross linkages, (3) to introduce a winding pathway (also called tortuous pathway) for a methanol molecule by making a composite with inorganic materials, and (4) to develop new types of electrolyte polymers. Among these attempts, Nafion has recently been modified with a variety of organic/inorganic materials, yielding Nafion-based composite membranes.

We chose the microporous Engelhard titanosilicate-4 (ETS-4) particles as an inorganic particle because of their regular pore size selective separations based on molecular size and shape. ETS-4 can also separate components based on preferential adsorption, in which the strong adsorption of one components [3,4]. Thus ETS-4 will effectively block the methanol molecules by tortuous pathway effect while maintaining the transport of the water molecules because it plays a role as size-selective adsorbent. That is, opening pore size (0.3 – 0.4 nm) of ETS-4 has smaller than that of methanol and bigger than that of water. However, membranes made of pure ETS-4 are plagued by defects such as cracks or gaps and exhibit poor mechanical properties such as brittleness and fragility. Therefore, Nafion/ETS-4 composite membranes represents a compromise between the non-selective polymeric films (against methanol/water mixture) and the brittle ETS-4 films. The objective of this study is to prepare and characterize the Nafion/ETS-4 composite membranes with various ETS-4 contents.

## 2 EXPERIMENTAL

### 2.1 Materials

The ETS-4 was synthesized by the hydrothermal method using gels of the following molar compositions;  $5\text{H}_2\text{O}_2:0.5\text{TiO}_2:10\text{SiO}_2:18\text{NaOH}:675\text{H}_2\text{O}$ . Titanium(III) chloride and sodium silicate solution were used as titanium and silicon sources, respectively. The synthesis was carried out in Teflon-lined stainless steel autoclave at 200 °C for 3 days. The as-synthesized ETS-4 particles were ground using a mortar. Ground ETS-4 particle/water solution was sonicated for 30 min in a water-bath sonicator (Branson 3510, Branson Ultrasonic Corp.) and then filtered through a 0.45  $\mu\text{m}$  pore size membrane filter (cellulose acetate, DISMIC-25cs, Toyo Roshi Kaisyu Corp.). Nafion perfluorinated ion-exchange resin (5 wt% solution in a

mixture of lower aliphatic alcohols and water) was purchased from Aldrich Chemicals and used as the membrane material; it has an equivalent weight (EW) of 1100 g for each sulfonic acid group.

## 2.2 Fabrication of Composite Membranes

The composite membranes were prepared by the solution casting method. The desired amount of ETS-4 was added into 5 wt% Nafion solution, and then stirred at room temperature and degassed by ultrasonication. The ETS-4 content of the mixture was 5, 10, 15, and 20 wt% with respect to Nafion. The resulting mixture was slowly poured into a glass dish in an amount that would produce a formed membrane thickness of approximately 80  $\mu\text{m}$ . The filled glass dish was evaporated at 40  $^{\circ}\text{C}$  for 2 days and then annealed at 120  $^{\circ}\text{C}$  in a convection oven for 2 h. After cooling, the membrane was peeled off the glass dish by the addition of water. The membranes were stored in deionized water so that they were water-saturated. In this study, NEx denotes a Nafion/ETS-4 composite membrane containing  $x$  wt% of ETS-4.

## 2.3 Characterization

X-ray diffraction (XRD) was used to identify the phase of the ETS-4 by using a MAC Science MXP 18A-HF X-ray diffractometer with  $\text{CuK}\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ), which was generated at a voltage of 40 kV and a current of 40 mA. The diffraction angle was scanned at a  $2^{\circ} \text{ min}^{-1}$  from 5 to 40 $^{\circ}$ . Field emission scanning electron microscopy (FE-SEM, JEOL, JSM-6330F) equipped with energy dispersive X-ray (EDX) detector was used to observe the morphology of the ETS-4 crystals. The swelling characteristics of the membranes were determined with water uptake measurements. The samples were completely dried under vacuum for 3 days at 30  $^{\circ}\text{C}$  and then weighed. They were then placed in deionized water for a week at 25  $^{\circ}\text{C}$ . Water on the surfaces of the wet samples was removed with filter paper, and then the samples were immediately transferred to a weighing dish and weighed. The water uptake was calculated according to the equation

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

where  $W_{\text{wet}}$  and  $W_{\text{dry}}$  are the weights of the wet and dried membranes, respectively.

The ion exchange capacity (IEC) indicates the number of milliequivalents of ions in 1 g of the dry polymer. The samples of similar weight were soaked in 50 mL of 0.1 N NaCl solution for 24 h at 25  $^{\circ}\text{C}$  in order to achieve complete  $\text{H}^+$  to  $\text{Na}^+$  ion exchange. 10 mL of the released  $\text{H}^+$  was then titrated with 0.1 N NaOH solution. The IEC was calculated from the titration data with the following equation:

$$\text{IEC (mequiv/g)} = \frac{V_{\text{NaOH}} \times N_{\text{NaOH}} \times 5}{W_{\text{dry}}} \quad (2)$$

where  $V_{\text{NaOH}}$  is the amount of NaOH required to neutralize a blank sample,  $N_{\text{NaOH}}$  is the normality of the NaOH solution, 5 is the ratio of the amount of NaOH required to dissolve the sample to the amount used for titration, and  $W_{\text{dry}}$  is the weight of the dried sample.

Methanol permeability measurements were carried out using a home-made, glass, diffusion cell that consisted of two cylindrical glass compartments (A for feed and B for permeate) separated by a composite membrane with an effective area of 3.8  $\text{cm}^2$ . In order to determine the methanol permeability of each membrane, liquid samples of 1 mL were taken from the feed and the permeate using a syringe at prescribed time intervals (20, 40, 60, 80, 100, and 120 min). The liquid samples extracted from permeate were analyzed with a calibrated gas chromatograph (HP 5980, Hewlett-Packard, USA) equipped with a capillary column (14% cyano propyl phenyl methyl polysiloxane, 30 m  $\times$  0.25 mm  $\times$  1.0  $\mu\text{m}$ ) and a flame ionization detection (FID). The uncertainty of the obtained values was less than 2%.

The proton conductivity measurements on fully hydrated membrane samples were carried out with the cell immersed in liquid water. The installed cell was placed in a chamber with controlled temperature. The impedance measurements were carried out in the frequency region from 1 Hz to  $10^5$  Hz and in the ac current amplitude of 1 mA using a Solartron 1255 electrochemical impedance analyzer with ZPLOT software.

## 3 RESULTS AND DISCUSSION

### 3.1 General Characterization of ETS-4

Figure 1 shows the X-ray diffraction peaks of the ETS-4 sample, synthesized by the procedures mentioned in the experimental section. Based on the two contributions by Kuznicki [3] and Chapman and Roe [4], this product was identified as pure ETS-4. As shown in Figure 1 (inset image), the ETS-4 produced intergrowth polycrystalline spherulitic particles composed of two semispheres, each with a shape that resembles a maple leaf. In addition, each semisphere was consisted of many needle-like crystals.

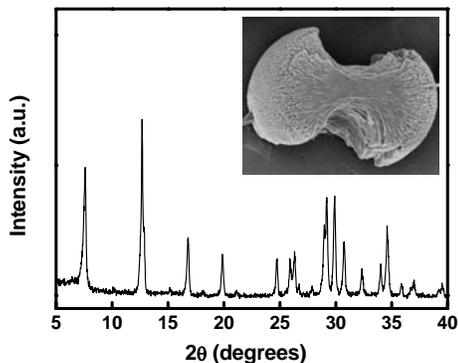


Figure 1: XRD patterns of the ETS-4 particles. The FE-SEM image in the inset shows the ETS-4 morphology.

The Si/Ti ratio in the ETS-4 particles is characterized by Si and Ti mapping images employing  $K\alpha$  peak of Si and Ti with FE-SEM/EDX. ETS-4 particles were found to have a Si/Ti ratio value of ca. 2.51. It was reported [5] that Si/Ti ratio of as-synthesized ETS-4 was 2.7, which is in relatively good agreement with our result. The ETS-4 crystals reported so far were large aggregations of highly intergrowth plates. Neither small ETS-4 crystals in the nanometer scale for the use as as-synthesized particles were reported, nor synthesis conditions for the crystallization of large, uniform crystals, were available. Therefore, grind procedures of ETS-4 particles were needed prior to the preparation of Nafion/ETS-4 composite membranes. The as-synthesized ETS-4 particles were ground using a mortar and filtered through a 0.45  $\mu\text{m}$  pore size membrane filter. From the DLS measurements, it was confirmed that one narrow peak of the ETS-4 particle size distribution was observed and its average size was found to be ca. 217 nm. This narrow size is due to selectively permeative characteristic of a 0.45  $\mu\text{m}$  pore size membrane filter.

### 3.2 General Characterization of Composite Membranes

Figure 2 shows the equilibrium percentage sorption of water, obtained by soaking the membranes in water at 25  $^{\circ}\text{C}$ . The water uptake of the membranes was found to increase from 21.4 for NE0 to 32.2% for NE20 with an increase in the ETS-4 content. This result shows that the water uptake of the membranes can be controlled by varying their ETS-4 content.

The ion exchange capacity (IEC) provides an indication of the number of ion-exchangeable groups present in an ion-conducting polymer membrane; these groups are responsible for the conduction of protons and thus the IEC is a reliable measure of the proton conductivity. The IEC of each membrane was determined by using the acid-base titration method. The results are shown in Figure 2 and demonstrate that the IECs of the membranes decrease from 0.89 to 0.72 mequiv/g with an increase in the water uptake. Thus the introduction of ETS-4 with no reactive sulfonic acid sites into the membranes contributes to a decrease in the IEC.

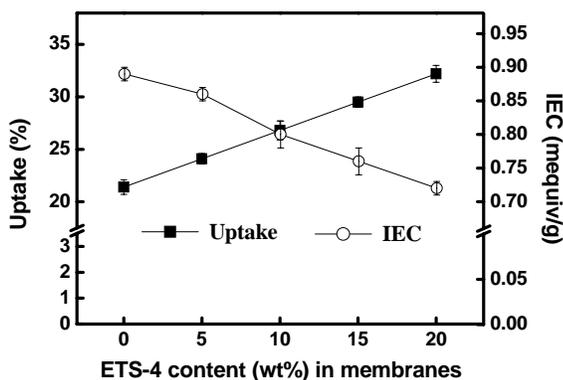


Figure 2: Water uptake and IEC for the composite membranes as a function of ETS-4 content.

The FE-SEM/EDX surface mapping images of silicon for the Nafion/ETS-4 composite membranes are shown in Figure 3. From FE-SEM results, it was demonstrated that Nafion/ETS-4 composite membranes had homogenous distribution of ETS-4 particles over the surface. These results are evidence that the ground ETS-4 particles are well dispersed in Nafion membranes by solution casting method.

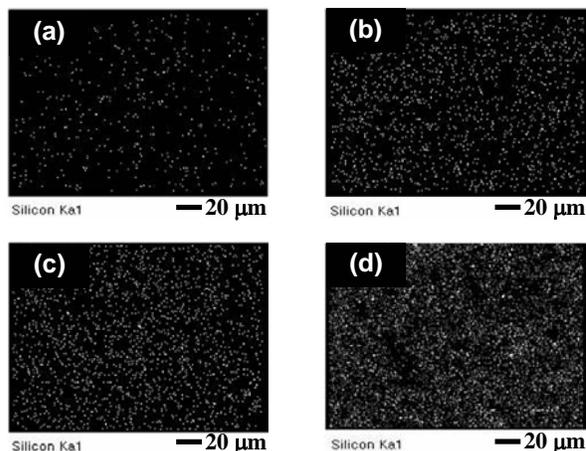


Figure 3: FE-SEM/EDX surface images of silicon for (a) NE5, (b) NE10, (c) NE15, (d) NE20 membranes.

### 3.3 Methanol Permeability

High methanol crossover is an enormous obstacle for membranes in fuel cell applications such as DMFC. Therefore, methanol permeability of the membranes needs to be reduced, while maintaining proton conductivity. The methanol permeability of NE series composite membranes decreased with an increase in ETS-4 content up to 15 wt% of ETS-4 and increased with further addition of ETS-4 as shown in Figure 4. The decrease in the methanol permeability can be explained in terms of internal changes in the Nafion structures depending on the ETS-4 content. That is, methanol molecules have a more tortuous path around the ETS-4 particles. Similar trends have been reported for other composite membranes, such as Nafion/montmorillonite composite membranes [6] and polyvinylalcohol (PVA)/zeolite composite membranes [7]. However, inspection of the NE20 containing the 20 wt% ETS-4 shows a slight drop in methanol permeability. One can assume that at high loading i.e. higher than 20 wt%, methanol can easily diffuse through the composite membranes due to ETS-4 particle's aggregate, while at low loading the crossover is hindered by the ETS-4 particles which are still finely subdivided in the Nafion matrix. From these results, it was demonstrated the critical role of ETS-4 loading in controlling the methanol crossover phenomena.

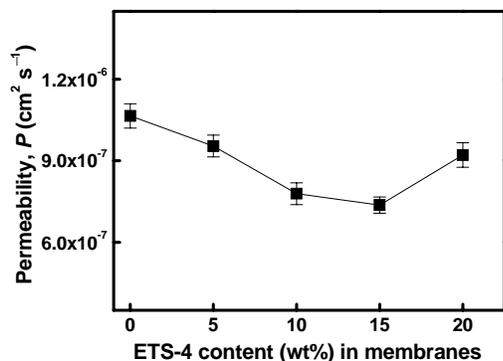


Figure 4: Methanol permeability of NE series composite membranes according to ETS-4 content in membranes.

### 3.4 Proton Conductivity and Selectivity

The proton conductivity of the composite membranes was measured using an ac impedance analyzer at various temperatures. Protons travel through ionic channels formed inside the Nafion matrix as well as through the matrix itself, provided the matrix possesses ionic sites. The proton conductivity of composite membranes showed behavior similar to that observed for their IEC. That is, as shown in Figure 5, the proton conductivity decreased with an increase in ETS-4 content at all different temperatures. In addition, all of the composite membranes exhibited a marked increase in proton conductivity with increasing temperature, indicating that temperature played a main role in the kinetics of proton motion in the polymer membrane and mobility of polymer chains. It was tentatively concluded that pristine Nafion membrane could be the highest level in the composite membrane for DMFC.

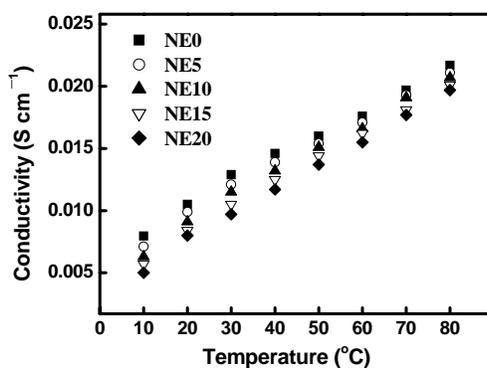


Figure 5: Proton conductivity of composite membranes fabricated with different ETS-4 content.

One of the methods used to elucidate membrane performance is the selectivity parameter,  $\Phi$  ( $S s cm^{-3}$ ), calculated using,  $\Phi = \sigma/P_{\text{methanol}}$ , where  $\sigma$  is the proton conductivity ( $S cm^{-1}$ ) and  $P_{\text{methanol}}$  ( $cm^2 s^{-1}$ ) is the methanol permeability through the membrane. Table 1 lists the selectivity parameters of NE series composite membranes

as a function of ETS-4 content for methanol permeability and proton conductivity measured at 20 °C. The maximum selectivity was found at 10 wt ETS-4 content, i.e., NE10 membrane, implying the optimum membrane.

Membrane	Methanol permeability ( $cm^2 s^{-1}$ )	Proton conductivity ( $S cm^{-1}$ )	Selectivity parameter ( $S s cm^{-3}$ )
NE0	$1.065 \times 10^{-6}$	$1.05 \times 10^{-2}$	$0.986 \times 10^4$
NE5	$0.954 \times 10^{-6}$	$0.99 \times 10^{-2}$	$1.037 \times 10^4$
NE10	$0.779 \times 10^{-6}$	$0.91 \times 10^{-2}$	$1.168 \times 10^4$
NE15	$0.737 \times 10^{-6}$	$0.84 \times 10^{-2}$	$1.132 \times 10^4$
NE20	$0.921 \times 10^{-6}$	$0.80 \times 10^{-2}$	$0.869 \times 10^4$

Table 1: Experimental parameters of composite membranes.

## 4 CONCLUSIONS

The ETS-4 was successfully synthesized by the hydrothermal method using gels of the following molar compositions; 5  $H_2O_2$  : 0.5  $TiO_2$  : 10  $SiO_2$  : 18  $NaOH$  : 675  $H_2O$ . Nafion/ETS-4 composite membranes were prepared with the solution casting method. The water uptake values were found to increase with an increase in the ETS-4 content. The acid-base titration results show that the IECs of the membranes decrease from 0.89 to 0.72 mequiv/g with an increase in the ETS-4 content. From the FE-SEM/EDX measurement, it was demonstrated that Nafion/ETS-4 composite membranes had homogenous distribution of ETS-4 particles over the surface. The methanol permeability of composite membranes decreased with an increase in ETS-4 content up to 15 wt% of ETS-4 and increased with further addition of ETS-4. The proton conductivity decreased with an increase in the ETS-4 content at all different temperatures due to the decrease of IEC values. From methanol permeability and proton conductivity results, it was confirmed that the selectivity parameter of the NE10 composite membrane is the highest value, implying the optimum membrane.

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