

# Performance evaluation of a Nafion/silicon oxide hybrid membrane for direct methanol fuel cell

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## Abstract

Nafion/silicon oxide composite membranes were produced via the in situ acid-catalyzed sol–gel reaction of tetraethylorthosilicate (TEOS) in Nafion perfluorosulfonic acid films. The TEOS uptake content of a composite membrane was varied according to the sol–gel reaction time. The physicochemical properties of the composite membranes were investigated by FT-IR. The water uptake contents and the thermal properties of the composite membrane were analyzed by DSC–TGA. The performance of a membrane–electrode assembly (MEA) using the composite membrane was evaluated by single cell test and methanol permeability was measured by gas chromatography (GC). The results show that the performance of a MEA using the composite membrane was higher than that of a commercial membrane at high temperature.

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## 1. Introduction

Direct methanol fuel cells (DMFCs) using polymer electrolyte membranes are promising candidates for the application of portable power sources, electric vehicle and transport applications because they do not require any fuel processing equipment and can be operated at low temperature of 25–130 °C [1]. However, commercialization of the DMFC is inhibited by two major technical problems. One is the slow methanol oxidation kinetics of the anode catalyst. The second is methanol diffusion from the anode to the cathode side, across the polymer electrolyte membrane. This causes loss of fuel, reduced fuel efficiency, reduced cathode voltage, and excess thermal load in the cell. Recently, perfluorosulfonate ionomer membranes such as Nafion<sup>®</sup> 115 (DuPont), Flemion<sup>®</sup> (Asahi Glass Co.), Aciplex<sup>®</sup> (Asahi Chem.), and Dow XUS (Dow Chemical) have been used as polymer electrolyte membranes for the DMFC [2]. These membranes do not sustain prolonged operation at temperatures higher than 130 °C due to dehydration phenomena occurring at high temperature, with consequent lower conductivity and performance losses [3].

In this paper, we describe a Nafion/silicon oxide hybrid membrane with various contents of silicon oxide incorporated

via in situ sol–gel reaction of tetraethylorthosilicate (TEOS) [4]. The composite membrane was characterized with FT-IR and DSC–TGA. The effect of impregnated silicon oxide on methanol permeability and conductivity was examined by gas chromatography (GC) and an impedance analyzer, respectively. The single cell performance of this composite membrane in a DMFC was evaluated, and the results are discussed.

## 2. Experimental

### 2.1. Preparation of composite membrane

The Nafion membrane (Nafion<sup>®</sup> 115) used in this work had 1100 eq. weight and 150 μm thickness. The membrane was pre-treated in 5 wt.% aqueous H<sub>2</sub>O<sub>2</sub> solution for 60 min at 90 °C, and washed repeatedly with deionized water. To obtain a membrane in the H<sup>+</sup> form, the membrane was boiled in 0.5 M H<sub>2</sub>SO<sub>4</sub> at 90 °C for 60 min, and finally, rinsed repeatedly with deionized water. The washed membrane in the H<sup>+</sup> form was dried in vacuum oven for 1 day at 80 °C. All pre-treated membranes were equilibrated in stirred 2:1 methanol:water (v/v) solutions for 3 h at 20–22 °C. The absorbed water, serving to initiate TEOS hydrolysis, was introduced such that the ratio of H<sub>2</sub>O:TEOS was 4:1 (mol/mol). A solution of 1:5 TEOS:methanol (v/v) was then added to the flasks that already contained the acid-form

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membranes in equilibrium with the above methanol:water solutions. These flasks were stopped after the liquids were added.

The membranes were removed from these solutions after exposure to TEOS for various impregnation times. After removal of the membrane from the solutions, the membranes were dried in a vacuum oven for 24 h at 80 °C. Finally, the membranes were dried for 2 h at 110 °C to remove trapped volatiles and promote further silicon oxide network condensation.

## 2.2. Water uptake properties of a composite membrane

To investigate the dehydration properties of the composite membrane, the composite membranes with various TEOS contents were analyzed by DSC–TGA (SETARAM, TG–DSC 92). The thermal analyzer system was programmed to heat the samples from 20–140 °C at the heating rate of 2 °C/min.

## 2.3. Methanol permeability measurement

The methanol permeability of the membranes was performed in the permeation measuring device. The polymer membrane (16 cm<sup>2</sup>) was inserted between vessels 1 and 2. Sixty milliliter methanol solution (2 M) and 60 ml deionized water was placed in each vessels 1 and 2, respectively. After a fixed period of time, the amount of methanol that crossed through the membrane and diffused to the other side of the vessel (vessel 2) was determined by GC (GC17A, Shimadzu). The gas chromatograph was equipped with a capillary column (14% cyano propyl phenyl methyl poly siloxane, 30 m × 0.25 mm × 1.0 μm) and a flame ionization detector (FID).

## 2.4. IR spectroscopy

To investigate the bonding states of the silicon oxide in the ion-clusters of the composite membrane, membranes with various TEOS contents were analyzed by FT-IR spectrometer (MAGNA 560, Nicolet Co.). The ATR cell was set at 45° with a ZnSe ATR prism on FT-IR spectrometer. The penetration depth of an IR beam in ATR mode is considerable (ca. 0.2–4 μm) in relation to the size of the ionic clusters in Nafion (ca. 30–50 Å) [5].

## 2.5. Proton conductivity measurement

The proton conductivity of the hybrid composite membranes was measured by using an impedance analyzer. The composite membrane was fixed in a four-point probe conductivity measuring cell. This cell consisted of two platinum wire outer current-carrying electrodes (distance 4 cm) and two platinum wire inner potential-sensing electrodes (distance 1 cm). The structure of the cell was fabricated from Telfon material.

The conductivity of the membrane was measured in the longitudinal direction, and was calculated using the following equation:

$$\rho = \frac{L}{RS}$$

where  $\rho$ ,  $L$ ,  $R$  and  $S$  denote the ionic conductivity, distance between reference electrodes, the resistance of the membrane and the cross-sectional area of the membrane, respectively.

The impedance measurements were carried out in the frequency region from 10 to 6 MHz and in the ac current amplitude of 0.01 mA using a frequency–response analyzer (Solatron SI 1260, impedance/gain-phase analyzer) and potentiostat (Solatron SI 1287, Electrochemical interface). The conductivity of the hybrid membrane was measured at room temperature.

## 2.6. Fabrication of the MEA, and measurement of single cell performance

Catalyst slurry was prepared by mixing Nafion solution (5%, DuPont), and 60% Pt/C for cathode ink and 60% PtRu/C for anode ink. For fabrication of the membrane–electrode assembly (MEA), the catalyst slurry was coated on carbon paper for the electrode substrate. The catalyst loadings were approximately 5 and 10 mg/cm<sup>2</sup> for anode and cathode, respectively. The effective electrode area of the single cell was 7.6 cm<sup>2</sup>.

The procedures for the cell assembly and the measurements of cell performance were described in detail in [6]. The fabricated composite membrane was used to manufacture a MEA. The MEA was fabricated by hot pressing at 135 °C and 81 kg/cm<sup>2</sup> for 10 min. A 2 M methanol:water solution and oxygen gas were supplied to the anode side and cathode side of the single cell respectively. The performances of the single cell were evaluated over the range of 60–125 °C at 1:1.6 atm (anode:cathode). An electronic load with a maximum capability of 0.1 kW (EL-1010D, Dae-Jin Instrument, South Korea) was used to evaluate the performance of the single cell.

## 3. Results and discussion

Thermal analysis was performed to investigate the patterns of dehydration. As shown in Fig. 1, the amounts of uptake water in Nafion/silicon oxide hybrid membrane were increased according to the increase of silicon oxide contents in the impregnated Nafion membrane. This result showed that the amount of water uptake in the membrane was controlled by the silicon oxide contents in the ion clusters of composite the Nafion membrane.

Fig. 2 shows the proton conductivity of the composite hybrid membrane with various contents of TEOS. This was obtained using the full hydrated hybrid membrane without heat treatment.

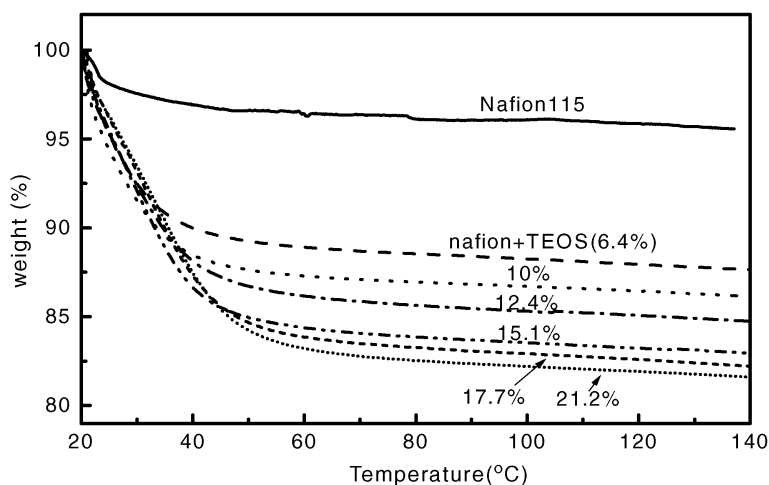


Fig. 1. TGA thermograms of Nafion/silicon oxide composite membrane.

The proton conductivities of the composite membrane decreased according to the increase of the silicon oxide content in the impregnated Nafion membrane. The proton conductivity of the membrane has been attributed to a “liquid-like” proton conductivity mechanism whereby protons are transported as free  $H^+$  ions through water-filled ionic pores and channels in the ionomer membrane [7]. It is considered that the conductivity of the Nafion/silicon oxide hybrid membrane decreased due to inhibition of the proton conduction in the membrane with increasing silicon oxide content.

Fig. 3 shows the IR spectra of the Nafion/silicon oxide hybrid membranes that were exposed to TEOS:MeOH solution for various times. Two prominent peaks are observed in the range of  $1000\text{--}1150\text{ cm}^{-1}$  [8–14]. Those spectra represent the Si–O–Si asymmetric stretching vibration,  $\nu_{\text{asym}}(\text{Si–O–Si})$ , being the signature of bridging oxygen. This band is known to split into two components arising from groups in linear and cyclic configurations respectively. Comparison of the intensities of the cyclic and linear components contributes to an understanding of the degree of molecular connectivity within the silicon oxide phase. As shown in Fig. 3, the cyclic peak is unchanged with respect to the content of silicon oxide in the membrane, whereas

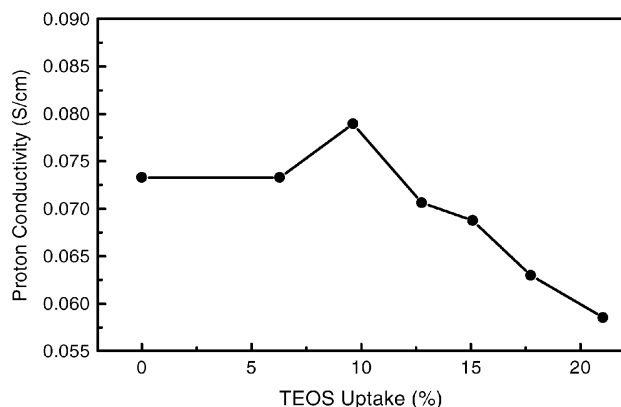


Fig. 2. Proton conductivity versus TEOS uptake (wt.%).

the linear peak is increased with increasing silicon oxide content. The cyclic:linear component absorbance ratio decreases with increasing percent of silicon oxide. This is interpreted in terms of an increasing degree of molecular linearity within the silicon oxide phase. This means that the molecular connectivity of the silicon oxide phase decreases with increasing silicon oxide impregnated into the Nafion. The considerable linearity of these systems is underlined by the large relative  $\nu(\text{Si–OH})$  absorbance for all samples.

The spectra of the Si–OH vibration,  $\nu(\text{Si–OH})$ , were also observed in the range of  $820\text{--}980\text{ cm}^{-1}$  (Fig. 3). The spectra of the Si–OH vibration increased with increasing content of silicon oxide in the membrane. Of primary importance in this analysis is the absorbance associated with the Si–OH vibration,  $\nu(\text{Si–OH})$ , which is a measure of the degree of hydrolysis, or number of uncondensed silanol groups [8–14].

Fig. 4 shows the measured methanol permeability of the composite membranes versus the TEOS uptake in the membrane. It was found that the methanol permeability

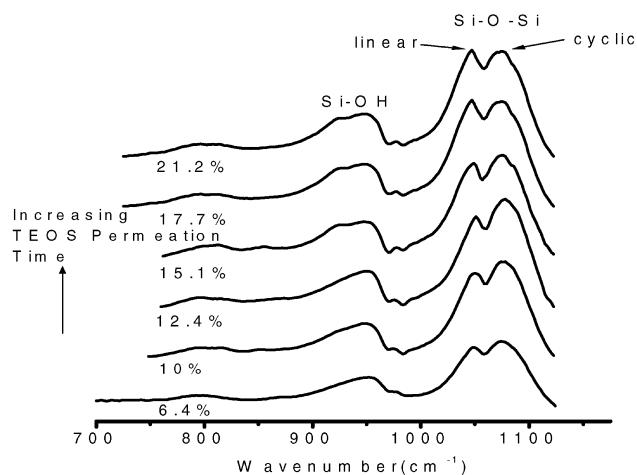


Fig. 3. FT-IR/ATR silicon oxide (difference) spectra for the sulfonate layer of the membrane, with inorganic contents and characteristic silicon oxide vibration bands indicated.

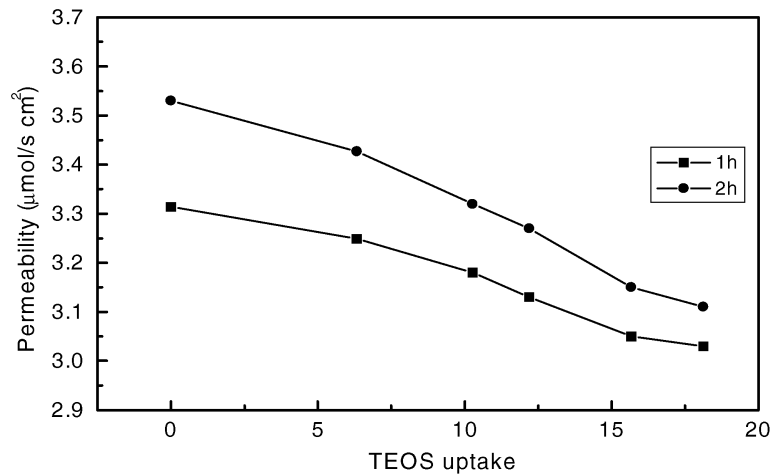


Fig. 4. Methanol crossover rate measured from gas chromatography data obtained under open-circuit condition.

decreased with increasing silicon oxide content in the membrane. Thus, the methanol permeability of the Nafion/silicon oxide composite membrane was effectively reduced the comparison to the pure Nafion membrane.

Fig. 5 shows the  $I$ - $V$  characteristics of the single cell ( $7.6 \text{ cm}^2$ ) using the Nafion/silicon oxide composite membrane, with different silicon oxide contents. The performance of the single cell was measured at various cell temperature (60, 90, 110, 125 °C). Each data set represents a typical steady state voltage that was taken. As shown in Fig. 5, the performance of the single cell improved with increasing silicon oxide content up to 12.4%. With increasing the content of silicon oxide more than 12.4%, the performance of the single cell was decreased. It can be seen

that the highest cell current density using the composite membrane with 12.4% silicon oxide at a constant cell voltage of 0.5 V was  $650 \text{ mA/cm}^2$  at 125 °C. On the other hand, the highest cell current densities of the single cell using the composite membrane with 17.7 and 6.4% silicon oxide content at a constant cell voltage 0.5 V were of 578 and  $551 \text{ mA/cm}^2$  respectively.

It is clearly indicated that silicon oxide impregnated into Nafion<sup>®</sup> 115 decreased the rate of methanol crossover in these membrane, as shown in Fig. 4. However, the performance of the single cell decreased with increasing silicon oxide content more than 12.4%. It is considered that higher silicon oxide contents in the composite membrane decreased the proton conductivity of the composite membrane.

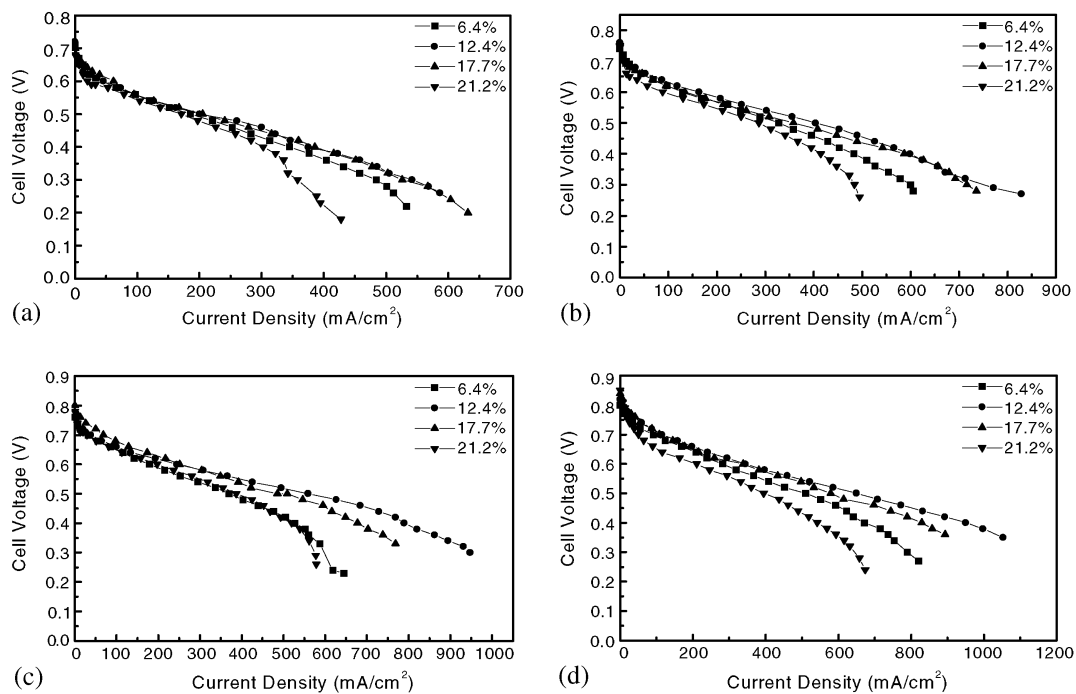


Fig. 5. Cell voltage-current density relations of the single cell using Nafion/silicon oxide composite membrane at (a) 60 °C, (b) 90 °C, (c) 110 °C (d) 125 °C (d).

#### 4. Conclusion

Nafion/silicon oxide hybrid membranes with various silicon oxide contents were prepared by incorporation via in situ sol–gel reaction of TEOS. The performance of the Nafion/silicon oxide hybrid membrane for the DMFC was evaluated.

The rate of methanol crossover was reduced by impregnation of silicon oxide into the Nafion membrane, due to the impregnation of silicon oxide into the ion clusters of the Nafion membrane. Enhancing of the water uptake of the composite membrane, the highest performance of the single cell was evaluated at a cell temperature of 125 °C. At higher silicon oxide content than 12.4% in the Nafion/silicon oxide hybrid membrane, the performance of the single for DMFC was reduced due to the decrease of proton conductivity of the membrane. The highest current density achieved using a composite membrane of 12.4% silicon oxide was 650 mA/cm<sup>2</sup> at 0.5 V (125 °C).

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