



# Effect of silane hydrophilicity on membrane transport properties of *in-situ* hybrid Nafion/organically modified silicate proton conductors for DMFC applications

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## ABSTRACT

In order to build a better understanding of *in-situ* hybrid Nafion/ORMOSIL (Organically MODified SILicates) membranes for DMFC (direct methanol fuel cells) applications, we investigate the effect of silane hydrophilicity on membrane transport properties of the hybrid proton conductors in terms of water-channel structure and state of water. The following three contrast silanes are introduced in the decreasing order of hydrophilicity: tetraethoxy silane (TEOS), methyl triethoxy silane (MTES), and diethoxy dimethyl silane (DEDMS). To focus exclusively on the silane hydrophilicity, a pre-requisite condition assuring that the same concentration of silanes should be immersed into Nafion115 is fulfilled by examining the silane diffusion behavior. As the silane hydrophilicity increases, the water-channel size and water uptake of the hybrid membranes become larger but the number of freezable water molecules decreases. Meanwhile, the hybrid membranes prepared from the hydrophobic silanes show the higher proton conductivity, leading to the superior selectivity. This interesting transport behavior is explained by considering the morphological change and state of water in the hybrid membranes.

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## 1. Introduction

As portable power sources continue to demand high-energy density, the importance of direct methanol fuel cells (DMFC) as a promising candidate is rapidly growing [1–3]. Nafion, a perfluorinated sulfonic acid ionomer, has been commonly used as a promising DMFC membrane due to the high proton conductivity and long-term durability. However, its high methanol crossover from anode to cathode has caused severe problems that bring out poor fuel efficiency, voltage drop and excess thermal load in the cells [4,5]. Among the various approaches to overcome the drawbacks of Nafion, *in-situ* hybrid organic/inorganic membranes [6–11] have drawn great attention, due to their unique phase structure and preparation simplicity. A Nafion/ORMOSIL (Organically MODified SILicates) hybrid is a representative example, where Nafion is used as a reaction template and sol–gel reaction of silanes proceeds in water channels of Nafion. The silicates synthesized in the water channels of Nafion are believed to effectively act as a barrier to methanol transport. Meanwhile, considering the fact that protons in water-swollen membranes move forward via water channels, the management of water molecules is considered to be crucial in determining DMFC membrane properties such as proton conductivity, methanol permeability, and selectivity. Therefore, a fundamental understanding of

water-channel structure and state of water must be essential in designing advanced *in-situ* hybrid organic/inorganic membranes for DMFC applications.

A major objective of this study is to quantitatively identify the effect of silane hydrophilicity on the water-channel structure and state of water in *in-situ* hybrid Nafion/ORMOSIL membranes and also to investigate its relationship with the DMFC membrane properties. In order to achieve this goal, the following three contrast silanes were introduced in decreasing order of hydrophilicity: tetraethoxy silane (TEOS), methyl triethoxy silane (MTES), and diethoxy dimethyl silane (DEDMS). An accurate comparison between the silanes having different silane hydrophilicity necessitates a pre-requisite condition assuring that the same concentration of silanes should be immersed into Nafion. To fulfill this condition, an investigation on silane diffusion behavior with soaking time was preceded.

The proton conductivity of water-swollen membranes is closely related to the water molecules' mobility that is heavily influenced by electrostatic interaction with ionic groups in polymer chains [11–19]. If the interaction is stronger, the mobility of water molecules in membranes would be suppressed, resulting in sluggish proton movement. This behavior can be quantitatively analyzed by examining the state of water. The state of water in hydrated membranes can be broadly classified into two groups that are freezable water (i.e., free and slightly bound water) and non-freezable water (i.e., strongly bound water), depending on the interaction between water molecules and ionic groups in polymer chains [12–18]. These two states of water exhibit different calorimetric behaviors and can be detected with DSC

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measurements. Previous studies [14–18] on the proton transport mechanism reported that freezable water acts as an effective proton-carrying medium following the vehicle mechanism, as freezable water is not strongly bound to ionic groups of polymer chains. Meanwhile, non-freezable water is considered to help the Grotthuss mechanism by establishing hydrogen bonds between captured water molecules. In this study, in terms of not only the water-channel structure but also the state of water, the influence of silane hydrophilicity on DFMC membrane properties concerning proton conductivity, methanol permeability, and selectivity is discussed.

## 2. Experimental

### 2.1. Preparation of hybrid membranes

TEOS ( $\text{Si}(\text{OCH}_2\text{CH}_3)_4$ ), MTES ( $(\text{CH}_3)_2\text{Si}(\text{OCH}_2\text{CH}_3)_3$ ), and DEDMS ( $(\text{CH}_3)_2\text{Si}(\text{OCH}_2\text{CH}_3)_2$ ) were purchased from Aldrich and used as received. A Nafion115 membrane was employed as a membrane matrix and pretreated by 10 wt.% hydrogen peroxide solution, 1 N sulfuric acid solution, and water, consecutively. The membrane was then dried in a vacuum oven at 100 °C for 24 h. To examine the silane diffusion behavior with soaking time, as a first step, silane solutions were prepared using methanol as a solvent, where silane concentration was fixed at 1.5 M and water concentration (mole-based) was determined to be identical to the alkoxy content of silanes. The pretreated Nafion115 membranes were first soaked in methanol solution for 24 h. Then, the methanol-swollen Nafion115 membranes were immersed in the silane solutions under sonication at room temperature, where the amount of silane uptake ( $= (1000 \times \text{weight of silane uptake}) / (\text{molecular weight of silane} \times \text{weight of dry Nafion membrane})$ ,  $\text{mmol g}^{-1}$ ) was determined by varying the soaking time from 0.5 min to 11 min. The amount of silane uptake was measured after removing the silane-immersed Nafion115 membranes from the silane solutions and subsequently washing them in methanol. The control of soaking time based on this silane diffusion behavior allowed the same molar content of silanes to be incorporated in Nafion115 membranes (Fig. 1). The silane-immersed Nafion115 membranes were then dried in a vacuum oven at 100 °C for 36 h to remove the remaining solvent and complete the *in-situ* sol–gel reaction of silanes.

### 2.2. Characterization

The water-channel structure of fully hydrated hybrid membranes was measured by using a tapping-mode AFM (Digital Instrument Dimension 3000), where the water-channel size was quantitatively examined by an image analyzer (LEICA Qwin Standard). The water

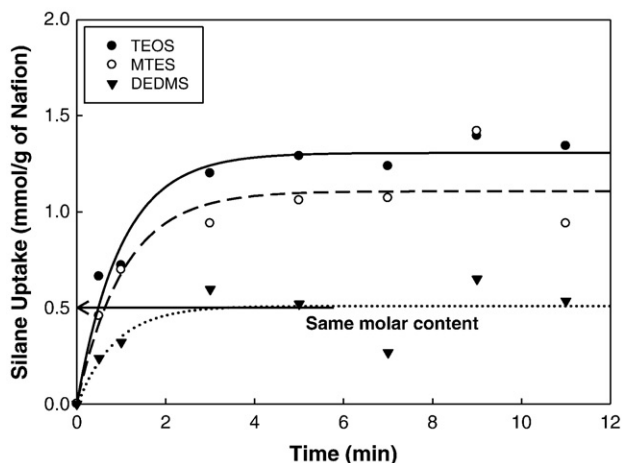


Fig. 1. Silane diffusion behavior into Nafion115 membranes as a function of silane hydrophilicity.

uptake was determined by measuring the weight difference between the dry state and the wet-swollen state at 25 °C. To distinguish the state of water in hybrid membranes, the thermal characterization by DSC (TA instrument Q100) was carried out, where a high-pressure pan was employed to prevent water loss during this measurement [14–18]. DSC samples were held at  $-50$  °C for 0.5 h and then heated to 50 °C at a heating rate of  $10$  °C  $\text{min}^{-1}$ . The fraction of freezable water was quantified by comparing the experimental melting enthalpy of hybrid membranes at around 0 °C with the theoretical melting enthalpy ( $334.0$   $\text{J g}^{-1}$ ) of pure water [12–18]. The amount of non-freezable water was calculated by subtracting the freezable water content from the total water uptake. The two probe, in-plane proton conductivity was measured by an impedance analyzer (Solartron 1255) over a frequency range of  $0.1$ – $10^6$  Hz at a voltage of 10 mV, where samples were equilibrated at 100% relative humidity and 25 °C. The proton conductivity was calculated from  $(\sigma[S/\text{cm}] = l/(R w d))$ , where  $\sigma$  is proton conductivity,  $l$  is the distance between the platinum electrodes,  $d$  is the thickness of sample,  $w$  is width of the membrane, and  $R$  is the measured impedance. The methanol permeability was measured in an isothermal bath at 25 °C using a two chamber-diffusion cell method with a 10 M methanol solution [17,19].

## 3. Results and discussion

As a first step, in order to focus exclusively on the effect of silane hydrophilicity, a pre-requisite condition assuring that the same concentration of silanes should be immersed into Nafion115 was fulfilled by examining the silane diffusion behavior. Fig. 1 apparently shows that the hydrophilic silanes exhibited not only the faster diffusion but also the larger silane uptake compared to the hydrophobic ones. Hydrophilic silanes are known to exhibit good miscibility with water, which leads to their facile diffusion into hydrophilic channels of Nafion115. The control of soaking time based on this diffusion behavior allows us to incorporate the same molar content of silanes into Nafion115 (0.5 mmol per 1.0 g of dry Nafion115) for all the hybrid membranes.

Fig. 2 demonstrates the effect of silane hydrophilicity on the water-channel structure (cross-sectional morphology) of the hybrid membranes. An interesting observation is that the dark parts corresponding to the water channels [20,21] become larger as the silane hydrophilicity increases. It is apparent that, while the water-channel size of Nafion115/DEDMS (hydrophobic silane) hybrids is 20.5 nm, Nafion115/TEOS (hydrophilic silane) hybrids show a larger water-channel size (27.4 nm). This clearly demonstrates the influence of silane hydrophilicity on the morphological change in the hybrid membranes. Compared to the bi-functional DEDMS, the tetra-functional TEOS has more chance to yield polar  $-\text{OH}$  groups after hydrolysis, which could generate higher hydrophilic silicates, attracting a larger number of water molecules. FT-IR and  $^{29}\text{Si}$  NMR studies [22,23] also reported that the smaller number of organic groups in silanes leads to a larger number of  $-\text{OH}$  groups. This morphological change of hybrid membranes is further evidenced by measuring the water uptake (Table 1). The water uptake becomes higher with the increase of silane hydrophilicity, which is 26.1 wt.% for Nafion115/DEDMS, 29.3 wt.% for Nafion115/MTES, and 34.9 wt.% for Nafion115/TEOS, respectively. The higher water uptake at more hydrophilic silanes may indicate that a larger amount of water exists in the water channels. Consequently, this contributes to enlarging the water-channel size, as observed in Fig. 2. As supplementary evidence, the contact angle (toward water) of hybrid membranes was examined. Table 1 exhibits that the contact angle decreases with the increase of silane hydrophilicity, evidently indicating that the hybrid membranes are more hydrophilic.

The effect of silane hydrophilicity on the state of water in the hybrid membranes was investigated by analyzing DSC thermograms and discussed in terms of freezable water and non-freezable water.

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