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The states of methanol within Nafion and sulfonated poly(phenylene ether ether sulfone) membranes

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ABSTRACT

The states of methanol in proton exchange membranes are considered to have a significant influence on the methanol permeability of membranes for direct methanol fuel cells, however, they have been rarely studied in the literature. Herein, we use high-resolution ^1H solid-state magic-angle-spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy to identify the microenvironment of methanol molecules in sulfonated poly(phenylene ether ether sulfone) (sPEES) and Nafion117 membranes. Our results show that the majority of methanol molecules are bound with the backbone of sPEES, while almost all of the methanol molecules in Nafion are in the "free" state. In particular, both the –OH and –CH_3 of the bound methanol molecules interact with the polymer within sPEES. It demonstrates the existence of a larger amount of bound methanol molecules and stronger interaction between methanol molecules and the background of polymer within sPEES membranes compared to that in Nafion. Such results allow us to understand the mechanism of the low methanol permeability associated with sPEES as opposed to Nafion.

1. Introduction

Direct methanol fuel cell (DMFC) has attracted much attention in recent years because of its significant advantages in simplifying power systems, convenient fuel transportation and storage, high energy efficiency, environmentally friendly, etc. The perfluorosulfonic acid (PFSA) membrane (e.g., Nafion by Dupont) has been widely used as polymer exchange membranes (PEMs) in DMFC. One of the major problems restricting the commercialization of DMFC is the methanol crossover from anode through the membrane to cathode, causing loss of fuel and reduction of cathode voltage, thus decreasing the cell performance.

Up to now, much effort has been focused on the development of PEMs and further modification of Nafion [1–16]. Many kinds of new PEMs have been prepared and reported. However, the reason why those membranes show better performance has yet to fully understand microscopically. It has been known that the structures of membranes and, the states of water and methanol in the membranes greatly influence the diffusion process of methanol within the membrane, thus directly related to the methanol permeability of PEMs. For the Nafion membrane, the cluster-network model of hydrated Nafion has been widely accepted [1–3]. The water–swollen phases of Nafion are composed of ionic clusters that are approximately spherical in shape with an inverted micellar structure. These spherical ionic clusters are interconnected by narrow channels. Two almost completely separated phases, water-phase (hydrophilic) and perfluoro-phase (hydrophobic), are present in Nafion. In addition, the state of water in Nafion has been widely studied by different techniques [4–9] and the water molecules mainly exist in the water-phase. It is known that there are three types of water molecules in the hydrated Nafion [9,10]: (1) nonfreezing water that is strongly bound to the polymer chain; (2) freezable but loosely bound water that is weakly bound to the polymer chain or interacts weakly with nonfreezing water; and (3) free water that is not intimately bound to the polymer chain and behaves like bulk water. The completely separated phases and large amount of water molecules in hydrated Nafion membrane exist as free and loosely bound water [9], which induces large proton conductivity and methanol permeability of Nafion membrane. To understand the reasons for the relatively lower methanol permeability of novel membranes, Kim et al. [9] studied the states of water within Nafion and biphenol-based wholly aromatic sulfonated poly (arylene ether sulfone) (BPSH) membranes by DSC and ^1H NMR, showing a different distribution of the "state of water" in Nafion and BPSH. They indicated that the less amount of free water in BPSH might be the reason for less methanol permeability and better performance. M. A. Hickner et al. discussed the structure

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and properties of Nafion and other PEMs [17], especially BPSH membrane, proposing the schematics of the geometry of the phase separated domains and their interface of BPSH and Nafion. They concluded that the different performance of the two membranes lay in the large degree separation of phases with a large amount of loosely and free water in Nafion as opposed to the less-distinct separation of phases with more tightly bound water within BPSH.

So far, most studies on the methanol-transport mechanism of PEMs have been focused on the states of water, barely on the methanol states, although the latter may be a very important factor influencing the methanol-blocking performance of the membranes. The high-resolution solid-state NMR is a useful tool to study the microenvironment, interaction and dynamics of molecules, which has been applied to investigate the structure [18,19], states of water in polymers [9,20,21], methanol transport [22–25] and proton dynamics [9,26,27] in PEMs. In this work, the solid-state NMR techniques are used to study the states of methanol and the interaction between methanol and membranes. Different chemical environments of methanol within Nafion and sPEES membranes will be illustrated by ^{1}H NMR and a strong interaction between methanol molecules and the backbones of sPEES is confirmed by the ^{1}H two-dimensional (2D) ^{1}H–^{1}H correlation NOESY spectroscopy.

2. Experimental

2.1. Materials

Poly(phenylene ether ether sulfone) was purchased from Aldrich (USA). Nafion117 membranes were purchased from Dupont (USA). Sulfuric acid (98 wt%), hydrogen peroxide (30 wt%), sodium chloride (99.5%), sodium hydroxide (99.5%) and HPLC grade methanol were purchased from the Sinopharm Chemical Reagent Co., Ltd. (China). All the reagents were used as received.

2.2. Membrane preparation

The Nafion117 membranes were pre-treated according to the procedure [28]: soaked in 5 wt% H_2O_2 solution at 80 °C for 60 min, soaked in deionized water at 80 °C for 60 min, soaked in 1 M H_2SO_4 solution at 80 °C for 60 min and finally soaked in deionized water at 80 °C for 2 h.

sPEES samples were synthesized by direct sulfonation of PEES with concentrated sulfuric acid. sPEES samples with different sulfonation degrees were prepared. To prepare sPEES membrane, the sPEES sample was dissolved in NMP ($\sim$0.3 g/10 ml) to get the casting solution, which was cast on a glass plate and dried in an oven at 80 °C for 48 h. sPEES membranes were named according to reaction time, such as sPEES (15 min) means the sulfonation time is 15 min. The Chemical structure of sPEES is shown in Fig. 1.

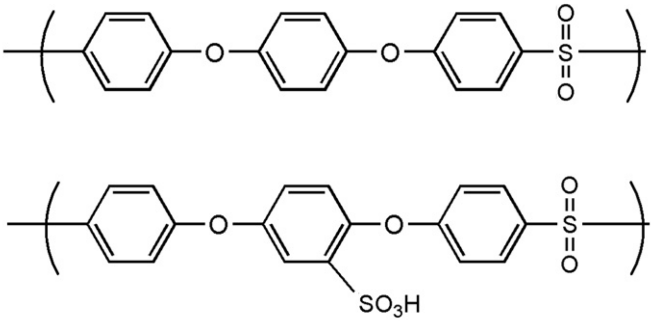

Fig. 1. The chemical structures of unsulfonated (top) and sulfonated (bottom) PEES.

The hydrated membranes were obtained by soaking the dried membranes in deionized water for over 24 h, while the dried membranes were obtained by placing the membranes in a vacuum oven at 80 °C for more than 24 h.

2.3. Characterization of the states of methanol in the membranes

2.3.1. Solid-state ^{1}H NMR

High-resolution ^{1}H solid-state MAS NMR spectra of the membranes absorbed with methanol were obtained to reveal the chemical environment of methanol in the membranes. The membranes were first cut into very small pieces, completely dried and filled into 2.5 mm solid-state NMR rotors, then dried again at 80 °C in a vacuum oven for 48 h. After that, the rotors filled with membranes pieces were quickly transferred to a glove box (MBRAUN, LabMaster100, Germany, $H_2O < 5$ ppm) and placed in a 50 ml short jar with 12 ml pure methanol liquid inside. It is worth noting that the rotors were not immersed or directly touched with the methanol liquid. To ensure reaching the equilibrium, the jar was sealed with a rubber cap and placed in the glove box for more than 5 days before the rotors were taken out from the jar and sealed immediately with rotor caps. The ^{1}H solid-state NMR experiments were performed on a Bruker Avance 400 NMR spectrometer with a ^{1}H Larmor frequency of 400.2 MHz using Bruker 2.5 mm double-resonance MAS NMR probe with a spinning frequency up to 30 kHz. The spectra were referenced to adamantane (1.63 ppm, ^{1}H). The ^{1}H NMR spectra were acquired using direct polarization with a 90° pulse length of 3–5 μs, recycle delay of 1 s and with the bearing gas at room temperature. The ^{1}H MAS NMR spectra before and after the 48 h measurements were identical, indicating that these samples remained in the same physical conditions throughout the measurements. Herein, Nafion117 membrane absorbed with methanol was named Nafion(MeOH) and other samples were named accordingly. The ^{1}H 2D NOESY spectrum of sPEES (15 min) (MeOH) was acquired using the mixing time 50 ms with 1024 increments in the indirect dimension. The quadrature detection in the indirect dimension was achieved by using the TPPI method.

2.4. Physico-chemical characterization of the membranes

2.4.1. Thermo-gravimetric analysis

The degradation process and the thermal stability of dried sPEES membranes with different sulfonation degree were investigated by TG-DTA (Netzsch STA 409 PC). The approximately 5–10 mg samples were characterized with a heating rate of 5 °C/min.

2.4.2. Ionic exchange capacity (IEC) measurement

The quantity of acid equivalents per gram of polymer was obtained according to the following steps. The membrane in the acid form ($\sim$0.3–0.5 g) was first immersed in 1 M NaCl solution for 24 h to convert sulfonic acid into sodium form. Then the released H^+ was back titrated with $\sim$0.01 M NaOH solution using phenolphthalein as indicator. The volume of NaOH solution was recorded to determine the equivalence point. The IEC is the equivalents per gram of dry sample.

2.4.3. Water uptake

Water uptake properties of the semi-IPN membranes were investigated according to the following steps [29]. First, the membranes were fully equilibrated with pure liquid water at