



# Anisotropic diffusion of water in perfluorosulfonic acid membrane and hydrocarbon membranes

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## ABSTRACT

Polymer electrolyte membranes that are applied for polymer electrolyte fuel cell (PEFC) retain water in their three-dimensional network structure. Diffusion behavior of water in the membranes was analyzed by pulsed field gradient (PFG)-NMR method to estimate diffusion coefficient of proton species as water or hydronium ion. The membrane samples were put in a sample tube vertically or horizontally toward to the field gradient axis under determined temperature and humidity conditions. As the results, anisotropic diffusion behavior of water in the membranes was indicated. Anisotropic properties depended on the sample type, preparation conditions of the wet membranes, and measurement conditions. A perfluorosulfonic acid membrane tended to have smaller anisotropy while hydrocarbon membranes showed greater anisotropy.

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## 1. Introduction

Polymer electrolyte membrane (PEM) for the use of electrolyte material in polymer electrolyte fuel cell (PEFC) is being developed with the aim at popularization as fuel cell vehicles, mobile devices, power stations for home use and so on. For this purpose, in general, cost performance and durability of the PEM are significant key points of research and development. Here, various measurements for the PEMs are promoted in our group with these key points in mind. As one of the useful estimation tool of water behavior in the PEMs, the present study employed a pulsed field gradient (PFG)-NMR. This technique is often utilized for the evaluation of diffusion coefficient of proton nuclei as many reports can be found in literature [1–17]. In the PFG-NMR measurements of wet PEM, a signal originated by proton derived from incorporated water molecules is completely separated from that by liquid water. Thus, water behavior in the PEM can be evaluated with this method under various conditions.

One of the crucial physical properties of the PEM is proton conductivity. Anisotropic property of the proton conductivity is not a principal topic for the membrane property, while only several reports regarding the anisotropy of the proton conductivity were

found [18,19]. However, in many cases, conductivity measurements were performed with a rectangular piece of the membrane to give the proton conductivity with in-plane direction, that is, the direction parallel to membrane area. This may be caused by two reasons. One is the difficulty of precise measurements in through-plane direction, that is, the direction across the membrane. The PEM is too thin such as several tens of micrometers to put electrodes for the accurate conductivity measurement in a proper way when one wants to obtain data in through-plane direction. The other reason for giving in-plane measurement priority is concerning that water domain in the membrane assumes to have isotropic nature. To our knowledge, no paper discussed anisotropy when they treated both diffusion and conductivity data, and they would assume that the water domain in the PEM was isotropic. However, the water domain in the PEM may have some anisotropy although a preferable direction of proton conduction is through-plane direction for the PEM in the fuel cell stack. The present study mentions anisotropic nature of proton diffusion under several membrane conditions to focus on this point.

In principle, PFG-NMR is applied for liquid samples to evaluate diffusion behavior of chemical species in the liquid. Translational diffusion of a nucleus in a certain chemical species (for example, H in water) occurs between two field gradient pulses, and derives signal reduction. A principle of the PFG-NMR is based on the self-diffusion of the species on the assumption that they diffuse isotropically to three-dimensional direction. On the other hand, water molecules and proton species in the PEM have a potential

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**Table 1**  
Structure and properties of hydrocarbon membranes

Code	IEC (meq/g)	Unit structure
HC-1	2.80	—Ph[(C=O)PhOPhSO <sub>3</sub> H]—
HC-2	1.87	—OPh(SO <sub>3</sub> H)OPh(C=O)Ph—
HC-3	1.60	—[OPhPhOPh(SO <sub>3</sub> H)SO <sub>2</sub> Ph(SO <sub>3</sub> H)]—

IEC = ion exchange capacities; Ph indicates C<sub>6</sub>H<sub>4</sub> or C<sub>6</sub>H<sub>3</sub>, here.

to diffuse anisotropically depending on the three-dimensional network structure of the polymer. A travelling distance during PFG-NMR can be estimated as micrometer-order (average distance of travelling the species equal to  $(2D\Delta)^{1/2}$  where  $D$  is diffusion coefficient, and  $\Delta$  is diffusion time;  $D = 10^{-10}$  m<sup>2</sup>/s;  $\Delta = 10^{-2}$  to  $10^{-3}$ ). Such the magnitude of travelling distance is larger than the size of water domain proposed by SAXS measurements [20], while PFG-NMR in porous media gave restricted diffusion of the species as an apparent diffusion. In case that polymer network has anisotropic morphology and the water behavior became anisotropic, anisotropic nature of water diffusion can be evaluated with a system equipped two or three axis of field gradient option [21]. However, such the apparatus is often used to imaging experiment with wide-bore type, while it is sure to be unusual for narrow-bore type. Instead of preparing two or three axis of field gradient option, the present work investigated the anisotropy of water domain in the PEM by contriving a method for setting the preparation direction of the membrane samples toward field gradient axis. While similar reports treated one membrane [22,23], the present work focused on comparison of different membranes and preparation conditions under determined temperature and humidity.

## 2. Experiment

### 2.1. Membrane samples

As a perfluorosulfonic acid membrane, commercially available Nafion® (NRE-212CS, thickness was 50 μm) was used. Polymer electrolyte membranes consisting of hydrocarbon were provided by a university and chemical companies. Here, we call these membranes as HC-1, HC-2, and HC-3 in the following text. These polymers contain *p*-phenylene, phenylene ketone, and phenyl sulfone functionalities as backbone structures. Ion exchange capacities and unit structures of their hydrocarbon membranes were listed in Table 1. Sulfo groups, that act as hydrophilic sites, were substituted at main chain or side chain depending on the type of the polymer. Preparation and characterization of HC-1 was found in the literature [24] as S-PPBP. HC-2 and HC-3 were prepared as follows: HC-2 was synthesized by the sulfonation of a commercial PEEK polymer using concentrated sulfuric acid [25]. HC-3 was synthesized by direct aromatic nucleophilic substitution polycondensation [26]. They were cast from *N*-methyl-2-pyrrolidone solution onto a glass substrate and dried at 80 °C under vacuum. The membranes were immersed in 0.5 M sulfuric acid overnight for complete protonation, then rinsed with deionized water and dried under ambient conditions. Their thicknesses were 60 μm (HC-2) and 50 μm (HC-3). Prior to their use for measurements all the membrane samples were pretreated for the purpose of removing contamination as follows: soaking in 2 M H<sub>2</sub>SO<sub>4</sub>(aq) at 80 °C for 2 h, then, washing out the acid with deionized water at 80 °C for 2 h. Detailed measurement results for some of hydrocarbon membranes will be reported from our group in the separate paper.

**Table 2**

Water contents ( $\lambda$ , the number of water molecules per sulfo group) in the PEMs under different preparation conditions

Prep. cond. <sup>a</sup> °C, %RH	Nafion	HC-1	HC-2	HC-3
50, 70	5.7	5.4	3.7	4.7
80, 80	7.2	6.4	— <sup>b</sup>	—
40, 100	9.5	10.5	—	—

<sup>a</sup> Preparation conditions of the PEM.

<sup>b</sup> No data.

### 2.2. Preparation of temperature and humidity-controlled membranes

A glass tube containing the pretreated membranes was put into a chamber that can control temperature and relative humidity to the determined values. The membrane sample loaded into an NMR sample tube was kept in the chamber for 3 h or more to hold equilibrium state. The both sides of the NMR tube were capped with silicone rubber pieces. Thus, temperature and humidity-controlled membrane samples were prepared. In the latter context, this preparation was called as exposing. Water content of the PEMs under each preparation conditions was estimated by weight with separate experiment. The data were summarized in Table 2.

### 2.3. Pulsed field gradient NMR measurement

PFG-NMR measurements for evaluation of diffusion coefficient were performed using JEOL ECA-500 spectrometer with 11.7 T of superconducting magnet. In order to avoid influences of local current due to field gradient pulses, bipolar pulsed pairs—stimulated echo pulse sequence, that is also mentioned as the 13-interval pulse sequence [27], was applied in the present study. A diffusion time,  $\Delta$  was 20 ms and a duration of each gradient pulse,  $\delta$  was 1 ms. Maximum amplitude of the pulsed field gradient,  $G_{\max}$  was 13.3 T/m. Diffusion coefficient of water,  $D$  was estimated from signal reduction against the magnitude of  $G$  using following equation:  $\ln(I/I_0) = -(\gamma G \delta)^2 (2/\pi)^2 4(\Delta - \tau/2 - \delta/8)D$ , where  $I$  and  $I_0$  corresponds to the signal intensity at each  $G$  and no  $G$ , respectively,  $\tau$  equals to the sum of  $\delta$  and gradient recovery (this was set to the both side of field gradient pulses, 0.2 ms in the present experiment),  $\gamma$  is a gyromagnetic ratio. Estimated error derived from the data treatment was 5% of each value.

## 3. Results and discussion

### 3.1. Evaluation strategy of diffusion coefficient of proton species contained in the membrane

PFG-NMR technique was commonly used to evaluate diffusion coefficient of various nuclei and species, and also applied to proton species containing in the polymer membrane [1–17]. The proton signal could be observed in liquid state measurement mode since the proton exists as mobile (liquid-like) species such as hydronium ion (H<sub>3</sub>O<sup>+</sup>), sulfo group (—SO<sub>3</sub>H) and water. Typical spectra (Fig. 1) showed single signal corresponding to the proton species in the membrane due to rapid exchange over various sites, they mainly existed as water. In the present study, the membrane samples were prepared in two ways as shown in Fig. 2. One method is to put the membrane samples vertical direction that is equivalent to the direction of the field gradient [28]. Another method is to put them horizontally, namely perpendicularly to the direction of field gradient. The former setting method may be able to evaluate in-plane diffusion of proton in the PEM; the latter corresponds to through-plane diffusion. In each case, diffusion coefficient was evaluated at

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