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ScienceDirect
Magnetic Resonance Imaging 25 (2007) 501–504
MAGNETIC RESONANCE IMAGING

Water dynamics in ionomer membranes by field-cycling NMR relaxometry

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Abstract

The dynamic behavior of water within two types of ionomer membranes, Nafion and sulfonated polyimides, has been investigated by field-cycling nuclear magnetic relaxation. This technique, applied to materials prepared at different hydration levels, allows to probe the proton motion on a time scale of the microsecond. The NMR longitudinal relaxation rate R_1 measured over three decades of Larmor angular frequencies ω is particularly sensitive to the host–water interactions and thus well suited to study fluid dynamics in restricted geometries. In the polyimide membranes, we have observed a strong dispersion of $R_1(\omega)$ following closely a $1/\sqrt{\omega}$ law in a low-frequency range (correlation times from 0.1 to 10 μs). This is indicative of a strong interaction of water with "interfacial" hydrophilic groups of the polymeric matrix (wetting situation). On the contrary, in the Nafion, we observed weak variations of $R_1(\omega)$ at low frequency. This is typical of a nonwetting behavior. At early hydration stages, the proton–proton inter-dipolar contribution to $R_1(\omega)$ evolves logarithmically, suggesting a confined bidimensional diffusion of protons in the microsecond time range. Such an evolution is lost at higher swelling where a plateau related to 3D diffusion is observed.

Keywords: Ionomer membranes; Nafion; Sulfonated polyimides; Fast field-cycling relaxometry; NMRD; Water dynamics; Confined motions; Water diffusion; Porous media

1. Introduction

Nowadays, ionomer membranes are extensively studied, notably for polymer electrolyte fuel cell (PEFC) applications. These membranes have the property to be good ionic conductors when hydrated. The hydration state of the membranes is characterized by the number of water molecules per ionic group λ. A considerable effort has been made in the last years to understand the proton conduction processes as a function of λ and thus the water's role in enhancing conductivity, with the clear objective to improve the performances in view of further industrial application. Presently, the perfluorinated ionomer membranes stand for the best materials for PEFC applications: among them, the so-called Nafion is the most popular (Fig. 1A). Its hydrophobic polytetrafluoroethylene backbone carries fluorether side chains terminated by hydrophilic sulfonic acid groups. Although the Nafion exhibits remarkable performances and notably an unchallenged protonic conductivity under operating conditions in fuel cell power-supplied prototypes, it has numerous drawbacks (high cost, low glass transition temperature T_g) that strongly encourage the development of alternative and competitive materials. Polyaromatic compounds, such as sulfonated polyimides (Fig. 1B), are one of these new promising systems with lower cost synthesis and highly tunable properties through a wide choice of chemical units [1]. In both cases, ionomer membranes exhibit a nanoscale separation between hydrophilic and hydrophobic domains [2] creating a multi-connected "pore" network available for water sorption. A strong difference concerns the structural evolution with the relative humidity (RH): Nafion membranes exhibit a strong swelling, the sulfonated polyimides do not. Moreover, at low RH, the macroscopic conductivity of Nafion is much higher than that of sulfonated polyimides. In this paper, we report the results obtained by NMR relaxometry (NMRD) on Nafion and polyimide

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doi:10.1016/j.mri.2007.01.002

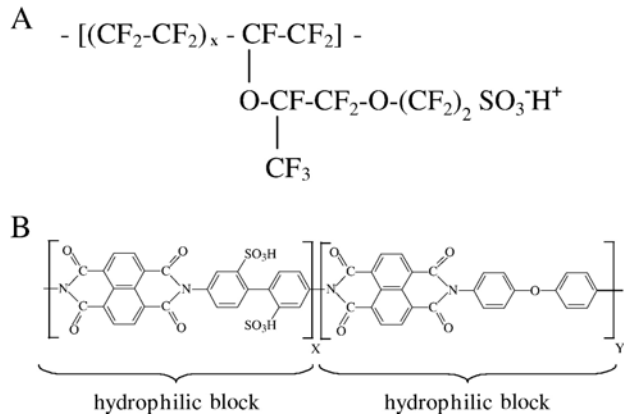

Fig. 1. (A) Nafion 112 ($X=7$, IEC=0.91 meq/g) and (B) sulfonated polyimide 5/5 ($X=5$, $Y=5$; IEC=1.98 meq/g).

membranes equilibrated at various relative humidities (from almost dry to saturated).

2. Experimental section

2.1. Materials

Fifth-micrometer-thick membranes have been used in this work. Nafion membranes with an ionic exchange capacity (IEC) of 0.9 meq/g (i.e., 0.9 mmol of SO_3H per gram of polymer) and a density of about 2.1 g/cm^3 have been chosen (Nafion 112, see Fig. 1A). In the case of polyimides, the polymers are composed of a hydrophilic sulfonated block based on naphthalenic structure and a hydrophobic block obtained with an oxydianiline monomer (see Fig. 1B). The repetition rate of the blocks is 5/5 ($X=5$ and $Y=5$), corresponding to an IEC of 1.98 meq/g for a polymer density close to 1.4 g/cm^3. If n_s is the number of sulfonated groups and n_p the total number of polar groups (including, for instance, carbonyl groups that are present in the polyimides), the ratio defined as $f_s=n_s/n_p$ is a chemical characteristic of each polymer (in the case of a fully perfluorinated polymer such as Nafion 112, $f_s=1$). The ratio $\lambda=N/n_s$, with N being the total number of water molecules in the material characterizing the hydration state.

2.2. Sample preparation

The Nafion 112 membranes were purchased from Dupont Company. Strips of Nafion 0.7 cm wide were cut from the raw sheet. To ensure a complete acidification, they were soaked in 800 ml of 2 mol/L hydrochloric acid solution at 80°C for 2 h and rinsed in distilled–deionized water at 80°C for 2 h. They were then soaked in 800 ml of 1 mol/L nitric acid solution at 80°C for 2 h and rinsed in distilled–deionized water at 80°C for 2 h. Paramagnetic impurities introduced during the manufacture of Nafion have been removed by applying a cleaning protocol close to the one described by MacMillan et al. [3]. The purification was achieved by chelation with ethylenediaminetetraacetic acid (EDTA). The strips are soaked in EDTA 0.015 mol/L at room temperature for 1 day and rinsed in distilled–deionized water at 80°C for 2 h. This step was repeated two times. The efficiency of the protocol has been checked by electronic paramagnetic resonance. The sulfonated polyimide membranes were provided by LMOPS Laboratory (Vernaison, France). Strips of sulfonated polyimide were soaked in 500 ml of 0.5 mol/L sulfuric acid solution at room temperature for 4 h. They were then soaked in distilled–deionized water at 50°C for 4 h and rinsed with fresh distilled water. Nafion and sulfonated polyimide strips were rolled inside 10-mm-diameter NMR tubes (typical weight of one sample in the dry state is 500 mg). A series of samples at different water content have been prepared by controlling the relative humidity (RH) inside the NMR tube. For doing so, a small glass tube containing well-chosen saturated salt solutions has been placed above the membrane in the 10-mm-diameter tube. The nature of the salt fixes the vapor pressure P/P_0 at room temperature and thus imposes a known RH that can be translated into λ through the sorption isotherms.

2.3. NMR relaxometry experiments

^{1}H NMRD and ^{2}H NMRD experiments related to water molecules inside the membranes have been performed at 298 K with a Stelar Spinmaster-FFC2000 relaxometer.

3. Results and discussion

3.1. Sulfonated polyimides

At all relative humidities, a strong $R_1(\omega)$ dispersion is observed, following a $\omega^{-\alpha}$ trend, with α close to 0.5. As shown elsewhere [4], this is the signature of a noticeable interaction between the entrapped fluid and the polymeric interface, typical of a good wetting. Similar results were also observed for deuterated water, strongly suggesting that the

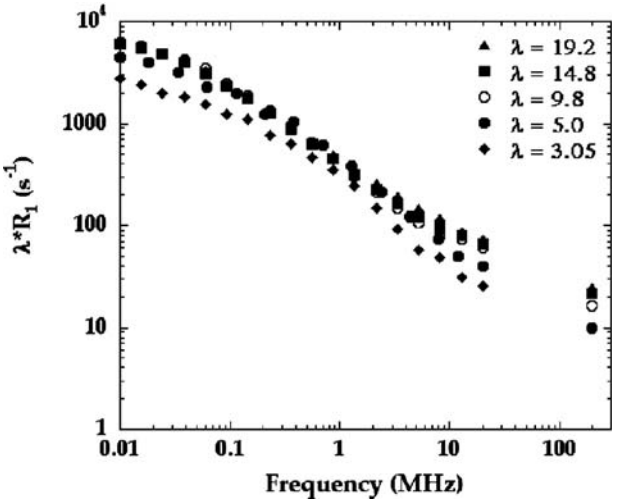

Fig. 2. Reduced coordinate dispersion law $\lambda R_1(\omega)$ for the sulfonated polyimide 5/5 at room temperature and at different humidities, showing the existence of a master curve at RH >52%.