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Water dynamics within a highly rigid sulfonated polyphenylene

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ABSTRACT

Complex water molecule interactions within the confined environments of a sulfonated polyphenylene (sPP) ionomer were studied using ^{1}H nuclear magnetic resonance (NMR), and Fourier transform infrared (FTIR) spectroscopy. Multiple water environments were observed due to variations in hydrophilicity created by its structure, and chemical composition. Confined water properties are strongly dependent upon water content, degree of ionization, and temperature. Increasing the degree of sulfonation (DS) results in the creation of more water states and sites. The chemical shifts of water depend upon its environment with a smaller dependence on temperature. Confined water relaxation time T_1 is than significantly lower bulk water and increases with temperature. Pulse field gradient (PFG) NMR studies reveals that water self-diffusion coefficients increase with. Water molecules diffuse faster in sPP than Nafion, which implies that diffusion is facilitated by bundled hydrophilic pathways. Time-dependent FTIR reveals that bound water evaporates slower than unbound water during drying, which illustrates the difference of bulk and confined water within sPP ionomers. Hindered water evaporation is due to a reduction in the degrees of freedom for ion containing domains and mass transfer limitations at interfacial boundaries between hydrophobic and hydrophilic domains.

1. Introduction

Water dynamics within an ionomer is important to many current and future applications ranging from fuel cells to separation membranes [1–4]. Water is often a critical operational parameter in these applications with excess water hindering function. For example, hydration of an ionomer facilitates proton transport within a hydrogen fuel cell. However, excess water floods electrodes and impacts performance [1,5–7]. Consequently, a delicate water balance must be maintained in order to guarantee optimal electrochemical performance.

The need to control water transport within ionomers and its impact on applications has led to a significant effort discerning the mechanisms of transport [8–10]. Nafion™ developed by DuPont is still the most prevelant polymer electrolyte membrane (PEM) for fuel cells [1,8–10]. This ionomer has a semiflexible tetrafluoroethylene backbone that is substituted with sulfonated perfluorovinyl ethers. Upon hydration, it forms a bicontinuous nanometer-sized hydrophilic and hydrophobic domains [11]. Water resides predominantly in the hydrophilic regions, where specific sites depend on the hydrated ionomer structure. Interfacial boundaries arising from the microstructure of the ionomer physically constrains the mobility of water molecules through electrostatics, hydrogen bonding, and other intermolecular forces [12–17]. While water molecules preferentially partition at hydrophilic sites, three states of water have been proposed to include bulk water, loosely bound

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water, and non-freezable water [18–20]. Bulk water molecules interact weakly with ionomer groups exhibiting bulk-water diffusion dynamics. Loosely-bound water includes solvent molecules located at the polymer/water internal interfaces. Slow water molecule dynamics are associated with loosely-bound and bound water. Non-freezable water is bound strongly to ionic groups.

This study focuses on water dynamics in hydrated polyphenylene ionomers, which represents a class of fluorine-free rigid polymers with high thermal and chemical stability. The chemical formula of SPP is shown in Fig. 1. Water relaxation times and diffusivity studies using ^{1}H NMR was used to identify water binding sites and quantify mobility in the hydrated ionomers [17,21–24]. Both NMR resonance frequencies and line shape distinguish between water molecules residing in different environments, reflecting provide information about the bonding sites and the nature of interactions between the ionomer network and absorbed water. The magnetic spin lattice relaxation time (T_1), is sensitive to the degree of water molecule confinement. PFG NMR studies were used to determine the water self-diffusion coefficients in these ionomers. These studies together with FTIR probe the water dynamics in hydrated rigid ionomers for the first time.

2. Experimental

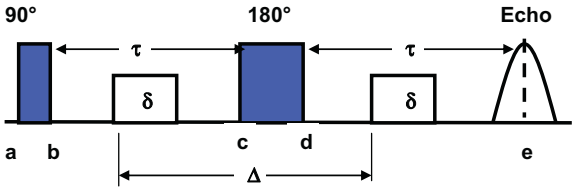
2.1. Materials

Polyphenylenes were synthesized using a Diels–Alder polymerization reaction of 1,4-bis(2,4,5-triphenylcyclopentadienone)benzene and 1,4-diethynylbenzene as described elsewhere [25]. A post-sulfonation reaction was done with a stoichiometric amount of chlorosulfonic acid to create sPP ionomers. Membranes with different ion exchange capacities (IEC) were obtained by controlling the concentration of chlorosulfonic acid. Dissolving sPP into *N*-methyl-2-pyrrolidone (NMP) was done to create 5 wt% solutions [25]. Solutions were cast upon glass plates, and the solvent was evaporated at 60 °C in a vacuum oven for 24 h to form membranes. sPP were washed with deionized water to remove excess N-methyl-2-pyrrolidone [25].

Table 1
IEC, water uptake, and DS of sPP.

	IEC[a] (mmol/g)	Water uptake 100% RH (wt%)	DS (wt%)
sPP1	0.98	13	13.5
sPP2	1.60	49	20.0
sPP3	2.20	137	33.3

[a] IEC = Ion Exchange Capacity.



Scheme 1. Stejskal–Tanner pulse sequence [26–28].

The relative concentration of the sulfonic acid groups is characterized IEC or degree of sulfonation (DS). In this study, three IECs corresponding to 13.5 wt%, 20.0 wt%, and 33.3 wt% were studied. The IEC, water uptake, and DS of sPP are summarized in Table 1.

2.2. NMR and T_1 relaxation time measurement

^{1}H NMR measurements and T_1 relaxation times were carried out on a JEOL 500 MHz Fourier Transform NMR liquid spectrometer. This instrument is equipped with a variable temperature unit that controls temperature to ±0.5 °C. Ionomer films were cut into strips and placed into a standard 5-mm NMR tube with d-chloroform used as an internal reference. Inversion Recovery Pulse Sequence p-τ-p/2-$t_1$where p corresponds to a 180 ° pulse, τ is the delay between the 180 ° and the 90 ° pulses and t_1 is the time between the 90 ° pulse and detection was used to measure the relaxation times. T_1 is obtained by fitting the signal intensity at different times τ where $M_{z,eq}$ is the magnetization at equilibrium with a measurement duration of π/2 equal to 13.8 μs. The details of each experiment are given in each figure. The equilibrium magnetization is given by:

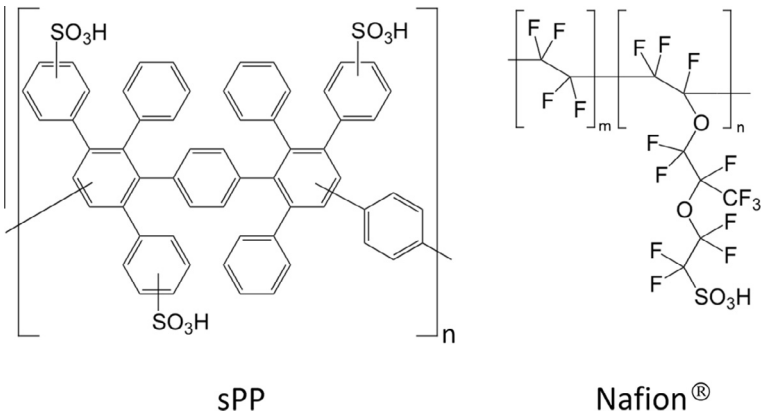


Fig. 1. Chemical structures of sPP and Nafion. N and m are the number of repeating units.