

## Characterization of Morphological and Transport Behavior of Solvated Sulfonated Poly (2,6-Dimethyl-1,4-Phenylene Oxide) Fuel Cell Membranes From Molecular Simulation

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### Abstract

During recent years, polymer electrolyte membranes (PEMs) have attracted intensive research works thanks to their potential usages in both polymer electrolyte membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs). Perfluorosulfonic Nafion membranes, which consists of poly (tetrafluoroethylene) (PTFE) backbone and a sulfonic acid terminated perfluorinated side chain are the most widely adopted membranes, because of their high proton conductivity at optimum hydration levels and acceptable mechanical stability. However, major drawbacks including high methanol crossover (for DMFCs), high production cost and lower proton conductivity at increased temperatures have limited their applications and motivated extensive studies toward the development of alternative membranes especially hydrocarbon-based PEMs such as sulfonated poly (2,6-dimethyl-1,4-phenylene oxide) (SPPO). Therefore, in the current research, molecular dynamics (MD) simulations were used to investigate the structure and dynamics of water and hydronium ion inside the solvated SPPO membranes as a function of hydration level. Simulation results have shown that SPPO membranes become phase separated when they uptake water molecules. Evaluation of radial distribution function revealed that water molecules and hydronium ions form larger aqueous clusters within the hydrated SPPO membranes at enhanced hydrations. Finally, the calculated diffusion coefficients for hydronium ions and water molecules inside SPPO based PEMs were increased as the hydration level is increased.

**Keywords:** Fuel cell, Polymer electrolyte membrane, Sulfonated Poly (2,6-Dimethyl-1,4-Phenylene Oxide) (SPPO), Hydration level, Molecular dynamics simulation

## 1. Introduction

Owing to their potential usages in polymer electrolyte membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs), polymer electrolyte membranes (PEMs) have received research works during recent years [1]. Fuel cell performance of these membranes strongly depends on their physicochemical characteristics. Nafion membrane, a perfluorosulfonic PEM with a poly(tetrafluoroethylene) (PTFE) backbone and a sulfonic acid terminated perfluorinated side chain, is the most frequently used membrane due to acceptable ionic conductivity at optimum water content and good chemical and mechanical strength [2]. However, major drawbacks of high methanol permeability for DMFCs, high cost of production and poor conductivity at higher temperatures have limited its applications as a PEM and motivated research studies toward the development of new membranes especially hydrocarbon-type materials like sulfonated poly(styrene) (SPS), sulfonated poly(ether ether ketone) (SPEEK), sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO) and so forth [3-5].

Various types of SPPO based polymeric membranes have been recently studied as a candidate membrane for PEMFCs and DMFCs usages because they have showed appropriate thermal and mechanical properties and possess simple backbone structure which makes easier their modification [5]. Guan et al. [6] found larger ionic regions inside the SPPO materials with higher degrees of sulfonation which were ascribed to greater water uptakes of membrane. Also, Yang et al. [7] concluded that increased conductivity of SPPO membrane at higher sulfonation levels is mostly because of continuous aqueous channels formed at higher water uptake conditions. Lee et al. [8] measured higher conductivity and lower methanol crossover for sulfonated crosslinked PPO membranes with sulfonation of 30.1% compared to Nafion membrane. In another study, Hasani-Sadrabadi et al. [9] reported that the methanol permeability of nanocomposite PEMs made of SPPO and organically modified montmorillonite clay was decreased as compared to Nafion.

In contrast to these experimental observations concerned with characteristics of SPPO membranes, theoretical studies of these membranes were not addressed in past works. Theoretical techniques, in particular, molecular dynamics (MD) simulations, are very useful tools that are able to provide atomistic information regarding membrane characteristics which cannot be easily achieved by means of experiments [10,11]. Therefore, in the present work, we perform MD simulations over pure SPPO based PEMs to better understand their morphological and dynamical properties as a candidate PEM for fuel cell applications. Since experimental observations about SPPO membranes revealed that their water content (hydration level) is a parameter that greatly influences membrane performance, the current study investigates the impact of water content on properties of pure SPPO membranes by using MD simulations.

## 2. Computational Details

### 2.1. Molecular Models & Amorphous Cell Construction

In order to evaluate the water content effects upon the morphology and dynamics of hydrated SPPO membranes, MD simulations were carried out for SPPO materials containing two different hydration levels of  $\lambda = 3$  and 6 (here,  $\lambda$  is the ratio of the number of water molecules to the number of sulfonic acid groups). For this purpose, two three-dimensional amorphous cells which consist of SPPO polymeric chains, hydronium ions ( $\text{H}_3\text{O}^+$ ) and water molecules were constructed to represent the SPPO membranes behavior under different hydration levels. 20

SPPO chains each consisting of 20 PPO monomers with 25% degree of sulfonation were used in both simulation cells. Degree of sulfonation is defined as the ratio of number of sulfonated PPO monomers to the total number of sulfonated and non-sulfonated PPO monomers, as shown in Figure 1, respectively. Using 25% degree of sulfonation, each SPPO chain contains 5 sulfonated and 15 non-sulfonated monomers. These monomer units were randomly arranged within the SPPO chains. For MD simulations, it was assumed that sulfonic acid groups attached to PPO backbone are completely dissociated, as displayed in part (a) of Figure 1. Therefore, to keep the charge neutrality of the simulation cells, the same number of hydronium ions as the total number of sulfonic acid groups was used for both cells. The number of water molecules was determined by using their corresponding hydration level. Table 1 presents the composition of simulated cells corresponding to solvated SPPO membranes. Finally, using the number of molecules presented in Table 1, initial cell containing SPPO chains, water molecules and hydronium ions was created at initial density of  $0.005 \text{ g/cm}^3$  by means of amorphous cell module of the Materials Studio software package [12]. This very low density was specifically used for construction of amorphous cells to prevent the ring catenation problem of SPPO chains.

**Table 1.** Composition of Solvated SPPO PEMs Used for MD Simulations and Equilibrated Densities and Cell Sizes for Hydration Levels of  $\lambda = 3$  and 6

	Hydration Level ( $\lambda$ )	
	3	6
No. of SPPO Chains	20	20
No. of H <sub>2</sub> O	300	600
No. of H <sub>3</sub> O <sup>+</sup>	100	100
Total No. of Atoms	8440	9340
Density, (g/cm <sup>3</sup> )	0.920	1.010
Cell Size, (Å)	48.525	48.34

## 2.2. Force Field Parameters & MD Simulation

DREIDING and flexible 3-centered (F3C) force fields [13,14] were employed for SPPO chains and water molecules, respectively, which have been previously used in MD analyses of hydrated PEMs [15,16]. Partial charges for SPPO were assigned using charge equilibration procedure. Potential parameters and charges for hydronium ions were from Jang et al. [15].

Once the initial cells were constructed, they were optimized using conjugate gradient (CG) algorithm. Optimized cells were then subjected to equilibration using shrinking box method, as it has been previously used in the MD simulation of hydrated SPEEK membranes [17]. In this method, NPT MD simulations were first performed at 300 K for 10 ps during which operating pressure was increased from 1 to 100 atm. Next, the simulation cells were further compressed from 100 to 150 atm for 1 ns using NPT runs. In these simulations, only the bonded and

repulsive non-bonded Lennard-Jones (LJ) interactions were included. Afterwards, NPT simulations were continued at 150 atm for 10 ps with inclusion of both repulsive and attractive parts of LJ interactions, which was followed by another NPT MD run at 150 atm for 50 ps where coulombic interactions were also turned on. Subsequently, both MD cells were equilibrated for time period of 10 ns in NPT ensemble at 300 K and 1 atm. This equilibration phase of MD simulations was used to accelerate attainment of equilibrated structures. Finally, at the equilibrated densities, NVT simulations were done for 1 ns at 300 K, where trajectories were used every 1 ps for subsequent analyses of membrane properties.

All MD simulations were done by using LAMMPS (large-scale atomic/molecular massively parallel simulator) code [18]. Non-bonded interactions were truncated at 12 Å cutoff distance and the long-range electrostatic interactions were computed using particle-particle particle-mesh (PPPM) method [19]. Newton's equation of motion was integrated using velocity Verlet integrator with a time step of 0.5 fs [20].

During simulations, temperature and pressure were controlled via Nose-Hoover algorithm as thermostat and barostat [21,22]. Periodic boundary conditions were imposed in all directions of simulation box.

### 3. Results & Discussion

#### 3.1. Structural Analysis

Radial distribution function (RDF)  $g_{A-B}(r)$  was used to analyze the morphology of the hydrated SPPO membranes as a function of water content. RDF analysis shows the probability distribution of  $B$  atoms around reference  $A$  atoms, and is defined as equation (1):

$$(1) \quad g_{A-B}(r) = \frac{\left( \frac{n_B}{4\pi r^2 \Delta r} \right)}{\left( \frac{N_B}{V} \right)}$$

where  $n_B N_B$  is the number of  $B$  atoms located around  $AA$  atoms inside a spherical shell of thickness  $\Delta r$ ,  $N_B$  is the total number of  $BB$  atoms employed when constructing simulation cell and  $V$  is the equilibrated cell volume (as its size was collected in Table 1).

Figure 2 (a) and (b) displays the RDFs of hydrogen atoms of water molecules (Hw) and hydronium ions (Hh) with respect to oxygen atoms of sulfonic acid group (Os) at different hydration levels, respectively. For Hw-Os RDFs, there is a sharp peak at about 1.86 Å for both hydration levels of  $\lambda = 3$  and 6. This pronounced peak is owing to the hydrogen bonding interaction between hydrogen atoms of water and oxygen atoms of sulfonic acid. There is also a weak peak at 3.18 Å for all hydration levels. Height of both peaks are seen to decrease with an increase in water content of membrane which is attributed to the stronger solvent effect of water molecules upon water molecules at higher values of hydration. Similar behaviors are observed in Hh-Os RDFs, where there is a significant peak at 1.86 Å and a weaker one at a distance of 2.82 Å. The intensified peak indicates the hydrogen bonding of hydronium ions with sulfonic acid

groups. Comparison of peak height between Hw-Os and Hh-Os RDFs exhibits that the peak height in Hh-Os RDFs is greater than that in Hw-Os RDFs which results from the strong electrostatic interactions between negatively charged sulfonic acid groups attached to backbone of SPPO chains and positively charged hydronium ions. Presence of intense peaks in Hw-Os and Hh-Os RDFs implies that the sulfonic acid groups are hydrophilic and water molecules and hydronium ions solvate sulfonic acid groups. This behavior suggests the phase separated morphology of hydrated SPPO membranes. Parts (c) and (d) in Figure 2 shows the average coordination number of water molecules and hydronium ions around sulfonic acid groups, respectively, which is calculated from integration of Hw-Os and Hh-Os RDFs up to a certain distance. It is observed that by increasing the hydration level, the water coordination number enhances while coordination number of hydronium ions decreases. With increasing the water content, more water molecules surround sulfonic acid groups which pushes hydronium ions away from sulfonic acid groups by reducing their interactions, and thus decreases their coordination number.

To evaluate the structure of water molecules and hydronium ions, the interaction between water and hydronium ion was analyzed using RDFs of hydronium ion oxygen atoms and water hydrogen atoms (Oh-Hw), as illustrated in Figure 3 (a) for both water uptakes of membrane. There is an intensified peak at 3.3 Å corresponding to first hydration shell of water molecules around hydronium ions. This high peak originates from the hydrogen bonding interaction of water and hydronium ion. Increasing hydration level from  $\lambda = 3$  to  $\lambda = 6$  leads to a reduction in peak height since stronger water solvent effects at higher hydrations reduces the water-hydronium ions interactions. Appearance of high peak in Oh-Hw RDFs suggests that water molecules and hydronium ion tend to form aqueous clusters among which transport of water molecules and hydronium ions occurs. Average coordination number of water molecules surrounding hydronium ions was calculated by integrating Oh-Hw RDFs and demonstrated in part (b) of Figure 3. As the value of water content is increased, hydronium ions are coordinated with greater number of water molecules.

### 3.2. Dynamical Analysis

Dynamical characteristics of solvated SPPO membranes were analyzed by using the diffusion coefficients ( $D$ ) of water molecules and hydronium ions inside the hydrated membrane as a function of water uptake. Diffusion coefficient was computed using the slope of mean squared displacement (MSD) or Einstein relation defined as following equation:

$$(2) \quad D = \frac{1}{6} \lim_{t \rightarrow \infty} \frac{dMSD(t)}{dt} = \frac{1}{6N} \lim_{t \rightarrow \infty} \frac{d}{dt} \sum_{j=1}^N [(r_j(t) - r_j(0))^2]$$

where  $N$  is the total number of  $j$  atoms (here, oxygen atoms for water molecules or hydronium ions),  $r_j(t)$  and  $r_j(0)$  are the positions of  $j$  atoms at time  $t$  and at the beginning of production phase of MD simulations, respectively. It should be noted the diffusivity for water and hydronium ion was computed using both hydrogen and oxygen atoms and the results were the same. The simulated diffusion coefficients for water molecules and hydronium ions in SPPO membranes were listed in Table 2. It can be seen that the hydronium ion diffusion coefficient is lower than

that of water molecules since the calculation of diffusivity of hydronium ion via equation 2 only includes the vehicular diffusion mechanism for hydronium ions while transport of hydronium ions inside the membrane happens by two well known mechanisms of vehicular and hopping. The calculated water and hydronium ion diffusion coefficients increase as the degree of hydration is increased. These observations are related to appearance of larger aqueous clusters at increased water uptakes of membrane. Increasing hydration of membrane enhances the solvent effect from water molecules which reduces the interaction of water and hydronium ion with sulfonate groups and thus allows the hydronium ions and water molecules to move quickly inside the water clusters.

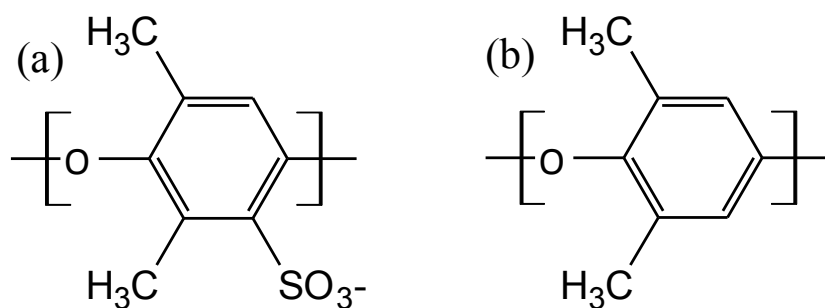
**Table 2.** Diffusion Coefficients of Hydronium Ions and Water Molecules in Hydrated SPPO Membranes

Hydration level ( $\lambda$ )	D ( $\times 10^{-6}$ , cm <sup>2</sup> /s)	
	H <sub>3</sub> O <sup>+</sup>	H <sub>2</sub> O
3	0.032	0.370
6	0.048	0.900

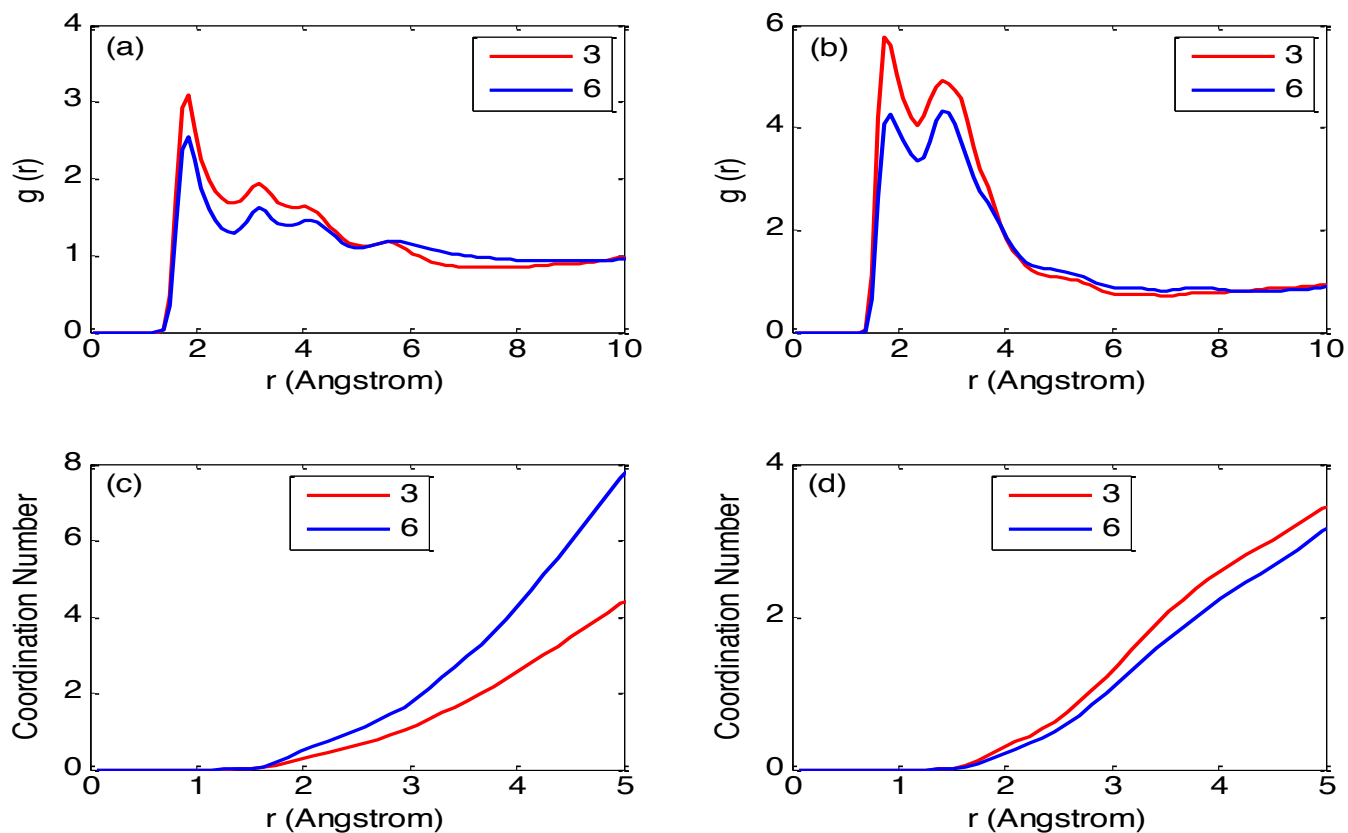
#### 4. Conclusion

MD simulations were used to investigate the morphology and dynamics of the solvated SPPO membranes as a function of water content at 300 K. Obtained simulation results revealed the phase separation of hydrated SPPO PEMs.

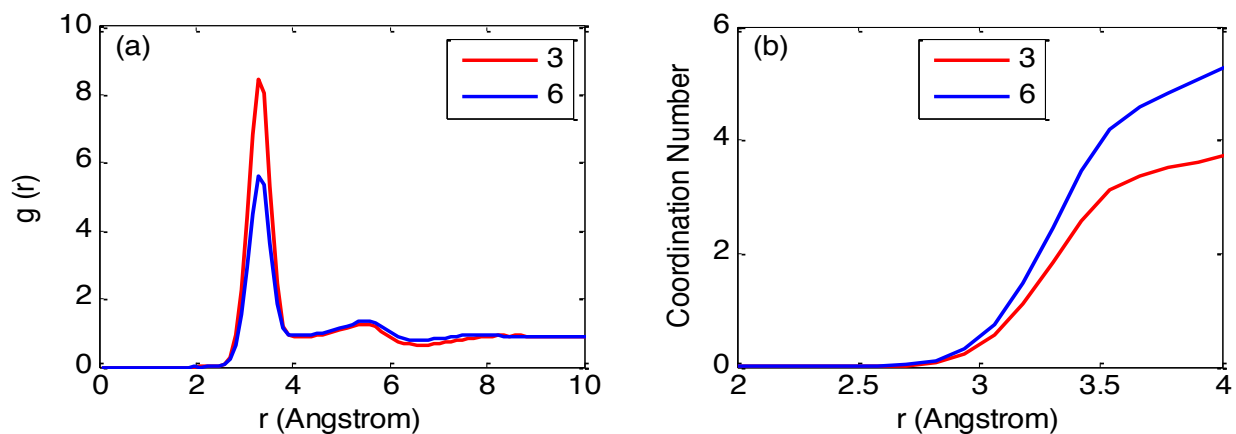
RDF analyses were applied to evaluate the interaction among sulfonic acid groups, water molecules and hydronium ions. It was understood that both the water and hydronium ion solvate sulfonic acid groups. It was also found that water molecules and hydronium ions form aqueous clusters inside the membrane. Additionally, diffusion coefficients for water molecules and hydronium ion enhanced with an increase in water content.



**Figure 1.** Chemical Structure of (a) Ionized Sulfonated and (b) Non-Sulfonated PPO Monomer Used During Simulations



**Figure 2.** RDFs of (a) Hydrogen (Water Molecules)–Oxygen (Sulfonic Acid Group) and (b) Hydrogen(Hydronium Ions)–Oxygen(Sulfonic Acid Group); Coordination Number of (c) Water Molecules and (d) Hydronium Ions around Sulfonic Acid Groups for Different Hydration Levels



**Figure 3.** (a) RDFs of Oxygen(Hydronium Ions)–Hydrogen(Water Molecules), and (b) Coordination Number of Water Molecules around Hydronium Ions for Different Hydration Levels



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