

## Theoretical Methodology for Calculating Water Uptake and IEC Parameters of Ionic Exchange Membranes with Applications in Fuel Cells

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### ABSTRACT

The water uptake (WU) and ion exchange capacity (IEC) are two important parameters for PEMs, which represent their water retention and the proportion of exchangeable protons in the membrane, respectively. According to the vehicle mechanism of proton transport, an appropriate amount of water content and a suitable value of IEC in PEMs is necessary for achieving high proton conductivity. In this work, studies based on Density Functional Theory (DFT), Molecular Mechanics and Dynamics Simulations were realized in order to develop a theoretical methodology to obtain water uptake and ionic exchange capacity parameters. Unlike other methods, our proposal considers the molecular structure of the monomers of the membrane, the solvation medium and the various interactions between the monomer and water molecules. The methodology is applied to structures of sulfonated poly (ether-imide) (SPEI) with  $(-\text{SO}_3\text{H})_n$  ( $n=1, \dots, 6$ ) groups. These structures were built and optimized aiming to obtain above properties as a function of the number of sulfonyl groups. The comparative study demonstrates that the SPEI with four sulfonyl groups in its backbone is the polymer having better properties for successful operation in fuel cells.

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**Keywords:** Sulfonation, Poly (ether-imide), polymers.

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## 1. Introduction

Polyelectrolyte membranes have been extensively investigated lately due to their potential applications in different types of electrochemical devices such as ion conducting membranes in fuel cells <sup>[1]</sup>. Since years ago, polymer electrolyte membrane fuel cells (PEMFCs) are regarded as a source of clean energy because of features such as high efficiency, high energy density, and environmental friendliness <sup>[2]</sup>. The perfluorinated sulfonic acid membrane, which is known as DuPont™ Nafion®, has been used for years as electrolyte in PEMFC. However, despite great successes with this membrane, it presents many disadvantages during the operation mechanism of the PEMFC <sup>[3]</sup>, and besides they are expensive.

Hydrogen and fuel cells technology is facing three main challenges related to new polymeric materials for membranes: reducing the high cost of production, increasing durability and chemical and mechanical stability at temperatures above 100 °C, and improving proton conductivity at temperatures above 120 °C.

Nowadays, many efforts are being directed towards developing new non-DuPont™ Nafion® electrolyte polymers, possessing excellent overall properties in order to build proton exchange membranes for fuel cell <sup>[4]</sup>. However, most of the efforts have been focused on the experimental developments, thereby neglecting the development of theoretical methods. A theoretical methodology is necessary, since it could significantly contribute to guide the experimental work, which would reduce the experimental time and resource savings. Some of the main problems that the ionic membranes, for use in PEM cells, have presented are the low proton conductivity at low relative humidity and the low mechanical properties at high temperatures and humidities. Ion conduction is a thermally activated process and its magnitude varies dramatically from one material to the other. The type of electrolyte, which may be either liquid or solid, determines the temperature at which the fuel cell may be operated. The main limitation to obtain a polymeric material with a high value of conductivity at high temperatures is necessary to maintain the polymeric membrane hydrated, since their ionic conductivity increase <sup>[5-17]</sup>. Two of the parameters which determine and predict the proton conductivity of the membrane are water uptake (WU) and ion exchange capacity (IEC). The rapid increase in computing resources and the progress in software offer new possibilities to rapidly gain new information from molecular modeling and simulation of the conductivity phenomena.

In the present approach, studies based on Density Functional Theory (DFT), Molecular Mechanics and Dynamics Simulations were realized in order to develop a theoretical methodology to obtain water uptake and ionic exchange capacity parameters. The methodology was applied to structures of sulfonated poly (ether-imide) (SPEI) with  $(-\text{SO}_3\text{H})_n$  ( $n=1,\dots,6$ ) groups. Poly (ether imide)s modified by sulfonation are particularly interesting as PEMs because the sulfonide groups  $(-\text{SO}_3\text{H})_n$  show good water retention and excellent adhesive ability with polyimides and inorganic materials <sup>[18-22]</sup>. These structures were built and optimized aiming to obtain above properties as a function of the number of sulfonyl groups.

Our theoretical results are in good agreement with experimental values reported in literature for similar structures to those studied here <sup>[23, 24]</sup>.



## 2. Methodology and computational details

Repeat unit structure of poly(ether imide) (Utem-type), Figure 1, was used in this work in order to build molecular computer models of sulfonated poly(ether imide), PEI-(SO<sub>3</sub>H)<sub>n</sub>,  $n = 1, 2, 3, 4, 5, 6$ . Once the structures were built, it is necessary to carry out the geometry optimization or energy minimization since after they have been sketched, they are often in high energy configurations. Starting dynamics simulations from such unoptimized structures can lead to simulations of systems at temperatures much higher than room temperature. In this work three aspects were considered to select a geometry optimization method and quality level: system size, convergence threshold and basis set used. In this study, the calculations were carried out using functional GGA PW91, DFT semi-core pseudopotentials as approximation for treatment of core electrons. This treatment replaces core electrons by a single effective potential, reducing the computational cost; the DNP (Double Numerical plus polarization) atomic orbital basis set was used in the calculation. In order to obtain structural, vibrational, reactivity, selectivity and thermodynamics properties of each PEI-(SO<sub>3</sub>H)<sub>n</sub>, the following computational scheme was performed: (a) building of the structures, (b) determination of the lowest energy structure of each structure, and (c) calculation of physical properties.

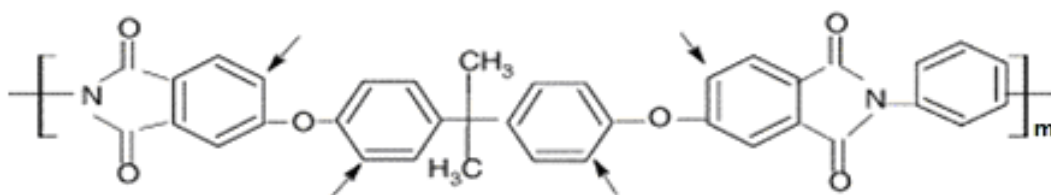


Figure 1. Backbone of repeat unit structure of poly(ether imide). Arrows indicate sites where sulfonyl groups are inserted

The next step was to obtain properties of water uptake and ion exchange capacity (IEC) of each polymer SPEI. The simulated water uptake was calculated using the following equation:

$$\text{Water uptake} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100 \quad (1)$$

where,  $W_{\text{wet}}$  and  $W_{\text{dry}}$  are molecular weight of wetted and dried polymers, respectively. The IEC is the equivalents per gram of dry polymer, and it can be calculated using the following equation:

$$\lambda = \frac{\text{Water uptake}}{18 \times \text{IEC}} \quad (2)$$

where 18 is the molecular weight of water and  $\lambda$  is the number of water molecules per sulfonic group.

The  $\lambda$  parameter was calculated using computational simulation following the next procedure: for each SPEI, a 3D simulation cell containing a single SPEI molecule was built by using the interface of Materials Studio (MS) from Accelrys Inc<sup>[28]</sup>. Each simulation cell was first minimized through molecular mechanics using the steepest-descents method up to 10,000 steps and using the Compass forcefield, as included in the MS Discover module. Then, water molecules were added, one by one to each simulation cell and the minimization process was repeated until it is found the hydrated cell possessing the lowest energy, being the number of water molecules at this step the value of  $\lambda$  parameter.

In order to obtain molecular weight and water uptake for each SPEI, molecular dynamics was carried out in two stages: equilibration and production. The duration of each stage depends on the system, as well as on the purpose of the run. The purpose of equilibration stage is to lead the system to the most probable configuration consistent with the target temperature and pressure, obtaining in this way the cell density. Equilibration stage was carried out using an NPT ensemble with a target temperature of 298 K, and an external hydrostatic pressure of 0 GPa (i.e., the simulation cell is not under compression). The time step was 1 fs and total simulation duration time was 30,000 fs. Integration method used in this process was Velocity Verlet method<sup>[29]</sup>. After equilibrating the system, we setup the production stage, during which data and statistics are collected. The molecular dynamics during the production stage was made using the NVT ensemble and the Berendsen method<sup>[30]</sup> for temperature control. The temperature used was 298 K. Simulation duration time was 80,000.00 fs. We use the automatic method of calculating charges from COMPASS forcefield<sup>[31, 32]</sup>.

Once MD simulations were made, the cell volume  $V_p$  and the density of each polymer SPEI ( $\rho$ ), were then estimated. The molar volume  $V_M$  and the molecular weight  $W$  for (both wet and dry) models were obtained as follows<sup>[33]</sup>:

$$V_M = N_A V_P \quad (3)$$

$$W = \rho V_M \quad (4)$$

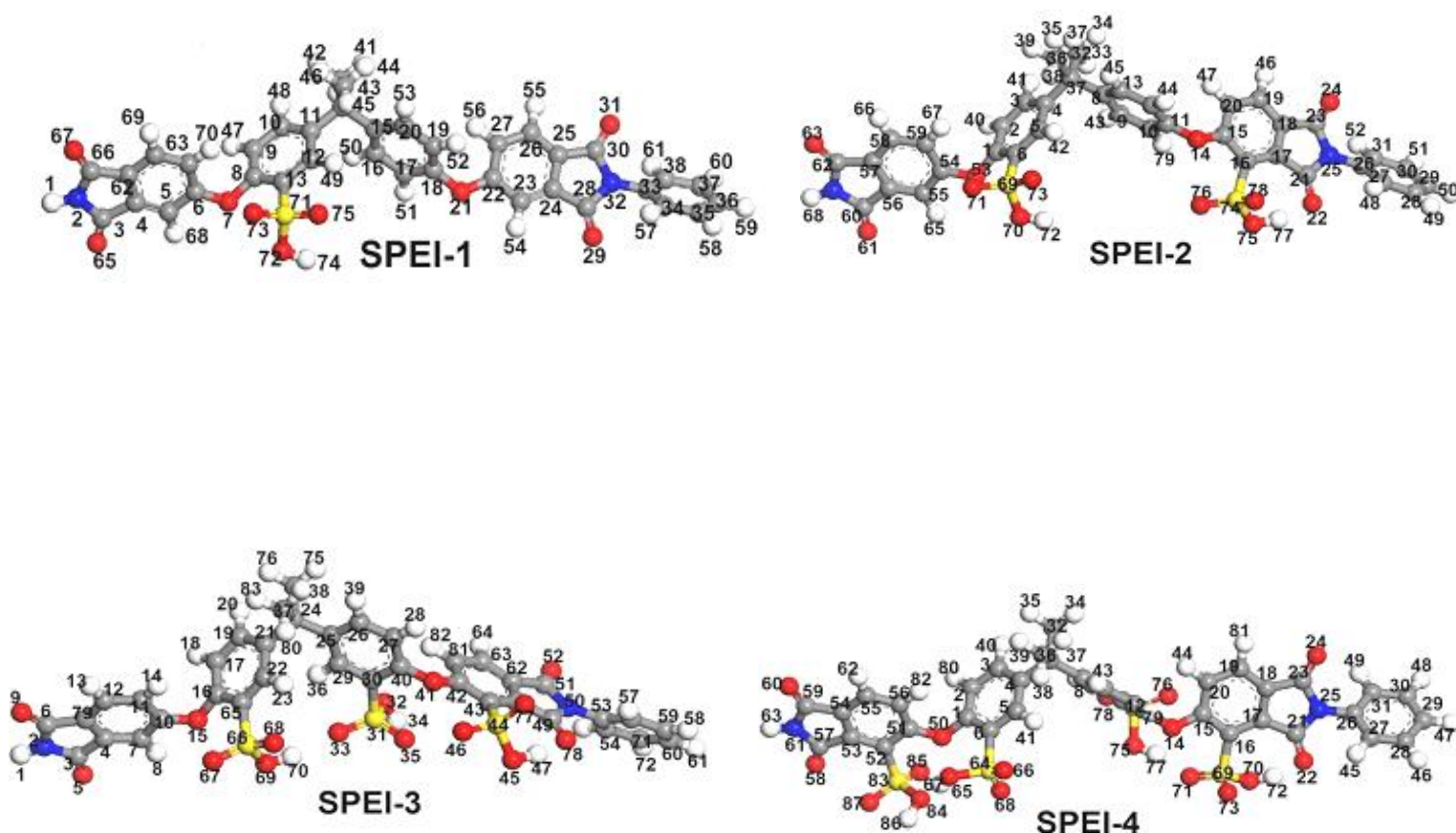
where  $N_A$  is Avogadro number.



### 3. Results and discussion

#### 3.1 Geometry structural properties and stability

The chemical structures of minimum energy for each simulated SPEI, along with atom numbering, are showed in Figure 2. These structures are constituted by a combination that had both polyimide and polyether units in the backbone. SPEIs were obtained by sulfonation of the PEIs on the electron-rich benzene rings.





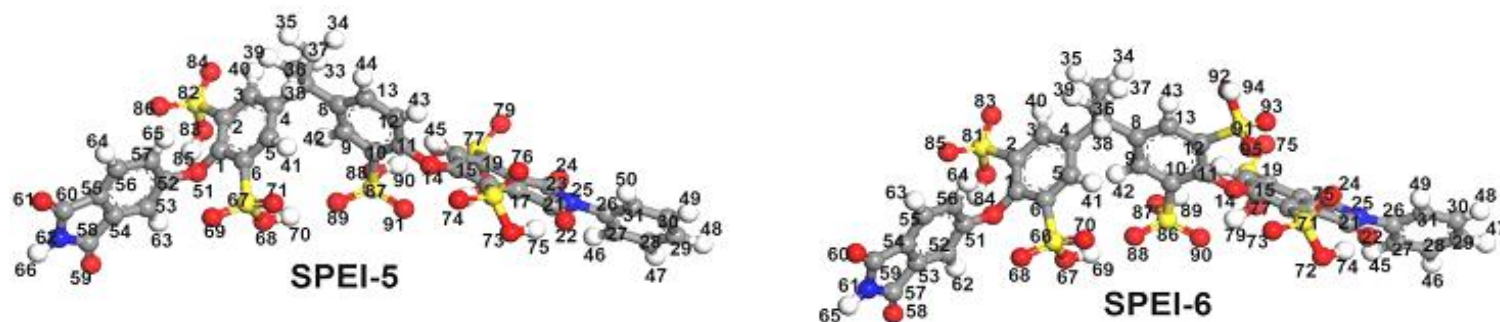


Figure 2 Chemical structures at minimum energy for each SPEI simulated in this work, along with atom numbering.

The SPEIs contain twelve different kinds of bonds, namely: (C-C in imide ring, C-C in benzene ring, C-C connecting two aromatic rings, C-O at diphenyl-ether groups, C=O at carbonyl groups, C-N at imide, C-H at diphenyl-ether groups, C-S at ortho position of diphenyl ether, N-H at imide, O-S at sulfonic groups, O=S at sulfonic groups and O-H sulfonic groups), whose DFT-calculated lengths are listed in Table 1. The lengths obtained are in agreement with those typical reported in the literature <sup>[34]</sup>. For example, the known C-C covalent-bond-lengths in molecules such like C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub> (ethane, ethylene, acetylene and C-diatomic molecules, respectively), are correspondingly 1.54 (single bond), 1.34 (double bond), 1.21 and 1.24 Å (triple bonds) bonds, respectively. In particular, at aromatic rings in SPEIs, the calculated bond lengths are slightly lower than the one in single C-C bonds of benzene, 1.4 Å.

Table 1. Most relevant bond lengths for the six different polymers studied

SPEI	C-C Imide ring (Å)	C-C Benzene ring (Å)	C-C Connected two aromatic rings (Å)	C-O Diphenyl- ether groups (Å)	C=O Carbonyl groups (Å)	C-N Imide (Å)	C-H Diphenyl- ether groups (Å)	C-S Ortho position diphenyl (Å)	N-H Imide (Å)	O-S Sulfonic groups (Å)	O=S Sulfonic groups (Å)	O-H Sulfonic groups (Å)
1	1.456	1.396	1.540	1.385	1.222	1.416	1.093	1.782	1.021	1.634	1.449	0.988
2	1.457	1.400	1.540	1.383	1.226	1.413	1.093	1.801	1.021	1.608	1.448	1.012
3	1.457	1.415	1.542	1.378	1.225	1.412	1.093	1.798	1.021	1.617	1.449	1.005
4	1.443	1.395	1.530	1.382	1.224	1.409	1.092	1.797	1.021	1.615	1.448	1.013
5	1.460	1.397	1.541	1.383	1.224	1.411	1.093	1.411	1.021	1.610	1.448	1.004
6	1.460	1.351	1.541	1.383	1.224	1.411	1.093	1.803	1.021	1.616	1.447	0.999

Bonds lengths may give some information about both mechanical and chemical stability of each SPEI structure <sup>[35]</sup>. The shorter bonds are those requiring more energy to break it, thereby the structure degradation is hard. According to Table 1, the SPEI containing four SO<sub>3</sub>H groups is that which have greater chemical stability because among all of the twelve types of bonds shown by the structures, it has greater number of bonds with lowest bond lengths in comparison with the ones of the other five structures.

### 3.2 Water Uptake and Ionic Exchange Capacity Parameters

The  $\lambda$ , IEC and water uptake values are important parameters because they are related to the proton conductivity of the membranes when they are used in fuel cell. In this work, these parameters were obtained according to methodology described in section 2. In Figure 3 are showed simulation cell of all SPEIs in conjunction with  $\lambda$  water molecules number which energy minimize of system.



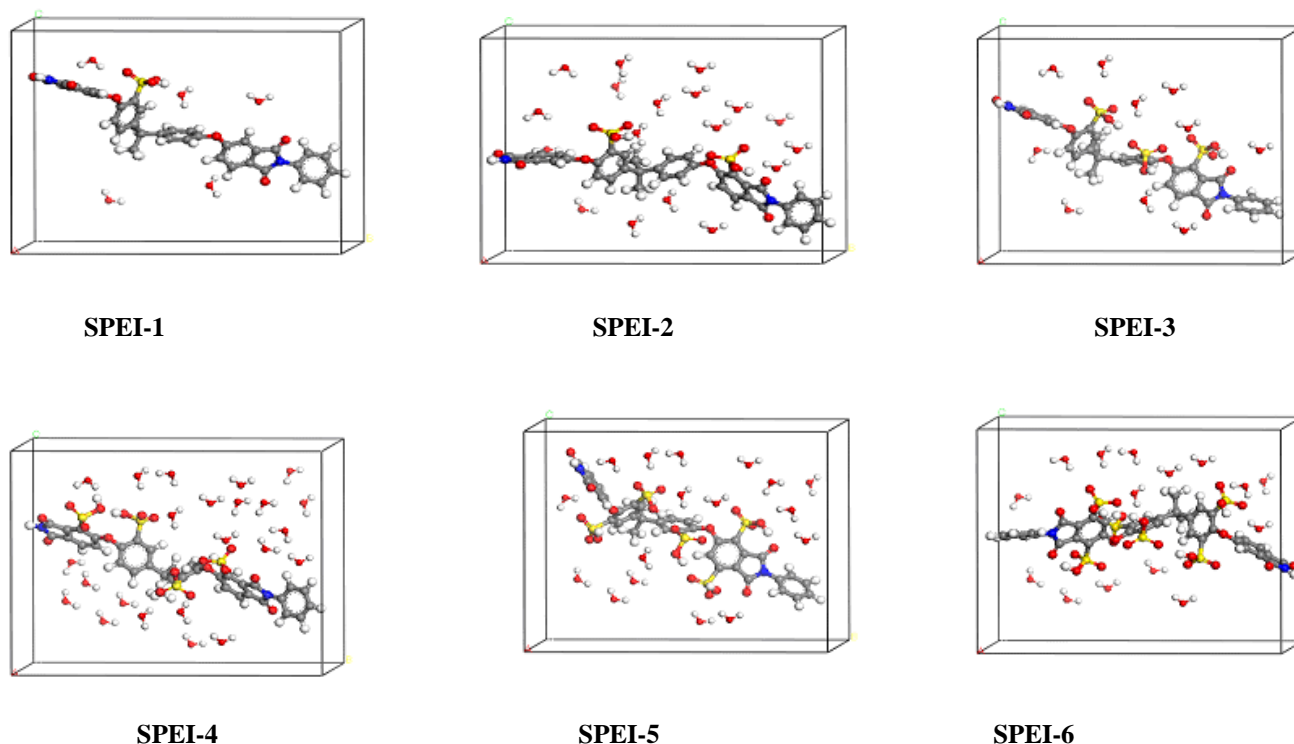


Figure 3 Simulation cell of wetted polymer in ground state for each SPEI

Table 2 presents theoretical values of  $V_P$ ,  $\rho$ ,  $V_M$ ,  $W_M$ , parameters in dry and wet, besides of  $\lambda$ , IEC and water uptake values for SPEI-n ( $n=1,2,3,4,5,6$ ), they were calculated according to methodology described in section 2. In all cases, the theoretical value of both  $\lambda$ , IEC and water uptake are agree with the experimental ones <sup>[18]</sup>, indicating that our theoretical methodology is reliable. It is observe from Table 2 that IEC value decreases as number of sulfonyl groups in PEI increases, this indicate that as more sulfonyl groups are added to the backbone of PEI, the material will go losing the ability to undergo displacement of ions of ( $\text{SO}_3\text{H}$ ), previously attached and loosely incorporated into its structure, by oppositely charged ions present in the surrounding solution, such as  $\text{OH}^-$  or  $\text{H}_3\text{O}^+$ . However, the results of IEC show also that, for all cases, the sulfonyl groups were successfully incorporated into polymer backbone.



Table 2.  $\lambda$ , IEC and water uptake values in conjunction with values of density, and cell volume, molecular volume, molecular weight in conditions wet and dry

SPEI-n	$V_p(\text{cc}) \times 10^{-21}$		$\rho \text{ (g/cc)}$		$V_M(\text{cc/mol})$		$W_M \text{ (g/mol)}$		$\lambda$	Water absorption	IEC (meqH/gPol)
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet			
<b>1</b>	1.85	1.22	0.60	1.05	1116.6	732.0	675	<b>766</b>	5.06	13.5	1.48
<b>2</b>	2.04	1.68	0.61	1.06	1229.0	1010.5	755	1072	17.62	42.0	1.32
<b>3</b>	2.24	1.55	0.62	1.09	1347.2	935.4	835	1019	10.21	22.0	1.20
<b>4</b>	2.42	1.98	0.63	1.12	1454.9	1193.7	915	1340	23.64	46.5	1.09
<b>5</b>	2.62	1.91	0.63	1.13	1577.1	1151.5	995	1303	17.14	31.0	1.01
<b>6</b>	2.79	1.95	0.64	1.14	1679.9	1175.0	1075	1338	14.63	24.5	0.93

From the water uptake data, it can be concluded that the hydrophilicity of PEI was improved by the incorporation of sulfonyl groups. The ability to take up water is one of the important properties of sulfonated polymers that enable them to be used in fuel cells. The proton conductivity of the polymer generally increases with water uptake: the uptake of more water improves the formation of the hydrophilic domain that conducts protons <sup>[12]</sup>. The water uptake of the polymer can be increased by an increase in the ionic group content in the polymer chain, but most often, the uptake of more water increases the swelling of a membrane, leading to the loss of the mechanical stability of membranes and high methanol permeability.

Therefore, from Table 2, we can observe the SPEI with n=4 is the polymer who better optimize properties of IEC and water uptake for successful operation in fuel cells. Similar phenomenon was also observed in the literature <sup>[7, 12, 18]</sup>.



## Conclusion

We have presented general ideas to develop a theoretical methodology, based on molecular simulations and considering a great number of atoms for obtaining water uptake and ionic exchange capacity parameters of ionic exchange membranes with applications in Fuel Cells. The methodology was applied to poly (ether imide) with different degrees of sulfonation. Processes of geometry optimization and energy minimization yielded results on the chemical stability of all SPEIs. The SPEI with  $n=4$  is the polymer who better optimize properties of IEC and water uptake for successful operation in fuel cells. Similar phenomenon was also observed in the literature. We found that the SPEI-4 presents shorter average bond lengths than SPEI- $n$  ( $n=2, 3, 5, 6$ ). So, SPEI-4 is the polymer that will have better characteristics for ionic conductivity than others SPEI- $n$ . From the water uptake data, it can be concluded that the hydrophilicity of PEI was improved by the incorporation of sulfonated group. The methodology can be applied to others molecular structures for polymeric membranes in fuel cell.

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