

## Behavior of ionic species in sulfonated PEI using DFT simulations: A study to determine ionic conductivity

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### ABSTRACT

Compared with internal combustion engines, proton exchange fuel cells (PEMFC) are able to operate without polluting emissions. Increasing the operating temperature of the fuel cell above 100 °C is one of the major objectives in this field as it would facilitate the commercial development of electric vehicles powered by fuel cells. To achieve this objective, it is important to develop new types of membranes to replace Nafion®. The poly (ether imide) sulfonated are presented as a new alternative in order to use as an electrolyte in PEMFC. In this work, DFT theory has been used to study the interaction between ionic species charged of hydrogen as hydroxyl ((OH)<sup>-</sup>) or hydronium ((H<sub>3</sub>O)<sup>+</sup>) and sulfonated poly (ether imide). The analysis of molecular reactivity through frontier MO (HOMO and LUMO) allows determine the mechanism of ionic conductivity which takes place over the polymeric membrane. This study is addressed to improve the efficient of PEM fuel cells.

**Keywords:** Ion conductivity, DFT Theory, sulfonated poly (ether imide)

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## 1. Introduction

The polymer exchange membrane (PEM) is the heart of the fuel cell. Based on the research, it has been determined that protonic exchange membrane fuel cell (PEMFC) has a huge variety of applications like: portable, mobile and stationary power<sup>[1-4]</sup>.

Because of their importance new polymers structures have been studied with the promise of enhance the disadvantages that the membrane perfluorosulfonic acid called Nafion® does have. New proposals are, **sulfonated poly(arylene ether sulfone)s**<sup>[5-6]</sup>, **poly(arylene ether ketone)s**<sup>[7]</sup>, **poly(arylene ether)**<sup>[8]</sup>, polyimides<sup>[9-12]</sup>, polyphosphazenes<sup>[13]</sup>, chitosan<sup>[14]</sup>, polybenzimidazoles<sup>[15]</sup> and other polymers<sup>[16-17]</sup>.

All the materials proposed for the development of PEM must have a high protonic conductivity, and, at the same time must avoid the electron transport through of its structure. A high chemical, mechanical and thermal stability are required in conditions of operation of the PEMFC<sup>[18]</sup>.

In a previous work, we proposed polymers based on sulfonated ether imide (SPEI) with sulfonic groups different ((SO<sub>3</sub>H) *n* *n* = 1, ..., 6)<sup>[19-21]</sup>. These sulfonic groups at the matrix of the SPEI provide charge sites that produced and guided the ionic species as hydronium (H<sub>3</sub>O)<sup>+</sup> and hydroxyl (OH)<sup>-</sup> in its conduction throughout membrane. The SPEI have been studied both theoretical and experimental, they were found to have chemical, mechanical and thermically stable and these became themselves in a perfect candidate for development of the PEMFC's with properties equals or better than Nafion®<sup>[22-23]</sup>.

In this paper, we present some theoretical results regarding the behavior between ionic species and the SPEI's. These results give us information about the intermolecular interactions like van der Waals, ionic and electrostatic interaction which determine the mechanism of ionic conductivity throughout membrane. The Mulliken population analysis is an important factor to charge sites localized in the membranes that guide some species with hydrogen charge.

Finally, results give us information about which chemical structure will do much better the protonic conductivity in order to improve the efficiency of PEMFC's.

## 2. Methodology and computational details

Both computational simulations and theoretical studies of the mechanism of the protonic conductivity in a lot of membranes have been studied for many scientific groups into different research centers<sup>[24-27]</sup>. The polymers based on sulfonated ether imide (SPEI) with sulfonic groups are the structures that we proposed to develop proton exchange membranes.



For the study of interaction between SPEI and ionic species, we took one after another the polymers sulfonated, then, we obtained their frontier orbitals HOMO-LUMO. Subsequently, the hydronium molecule was placed near the highest occupied molecular orbital of each SPEI and hydroxyl molecule was putted close to the lowest unoccupied molecular orbital of each SPEI.

When the ionic structures were put, the geometry optimization took place. We used the Density Functional Theory (DFT) with general gradient approximation (GGA) of Perdew and Wang PW91 and DFT semi-core pseudopotentials as approximation for treating core electrons, the DPN (double numerical plus polarization) atomic orbital basis set was used in the calculation<sup>[28-29]</sup>.

In order to determine the stability and the grade of the reactivity for each group (between each ionic specie and each SPEI), we calculated HOMO and LUMO energy differences for each single molecule,  $E_{\text{LUMO}} - E_{\text{HOMO}}$  terms and between pairs of molecules  $E_{\text{LUMO}}$  (ionic species)-  $E_{\text{HOMO}}$  (SPEI's) and conversely.

To obtain another parameter that confirm us the chemical interactions, we calculated the Mulliken population analysis<sup>[30-32]</sup>

### 3. Results and discussion

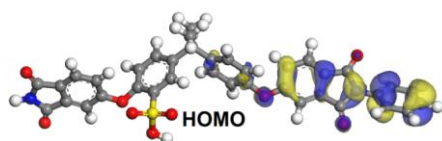
As mentioned above, in general Membrane is the core component of the PEM fuel cell. Triple roles of the polymeric membrane in the PEM fuel cells are as follows: charge carrier for protons, to separate of the reactant gases, and electronic insulator for not passing of electrons through the membrane (due to have a negative charge from  $\text{SO}_3\text{H}$  and electron repelling).

In this work, chemical reactivity was studied in terms of frontier orbital HOMO-LUMO between each SPEI and ionic species. In Figure 1, the frontier orbitals of each SPEI are presented in conjunction with energy corresponding. For each SPEI these frontier orbitals are built from sulfur 3p, carbon 2p, nitrogen 2p and oxygen 2p atomic orbitals; thus, the corresponding molecular orbital type is the type  $\pi$ .

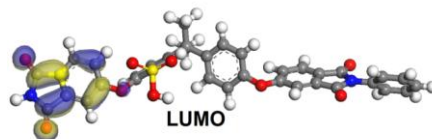
From Figure 1, we can observed, for polymers from 1 to 4 sulfonyl groups, the HOMO orbital is bonding-type, while polymers with 5 and 6 sulfonyl groups is antibonding-type. The lowest unoccupied molecular orbital is antibonding for all SPEI's. Hybridization of the ionic species is  $sp^2$  y  $sp^3$  for the hydroxyl and hydronium respectively; based on hybridization, both ions have  $\sigma$ -type molecular orbitals. Since the LUMO antibonding character in all cases of the polymers, it appears that this region is suitable for interacting with the ionic species and promote the proton conduction.



SPEI\_1

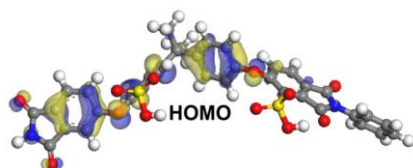


E= -5.843 eV

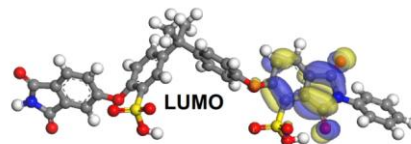


E= -3.245 eV

SPEI\_2

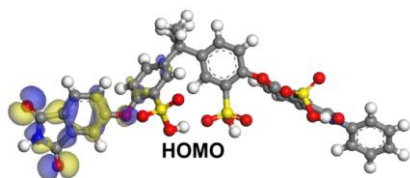


E= -5.053 eV

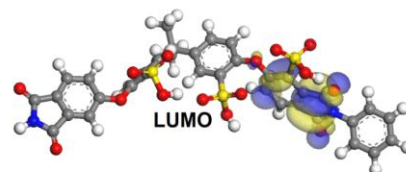


E= -4.052 eV

SPEI\_3

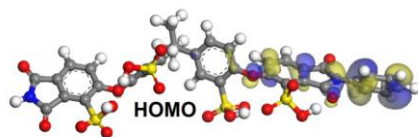


E= -5.080 eV

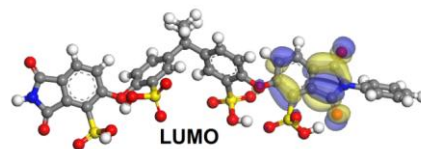


E= -4.049 eV

SPEI\_4

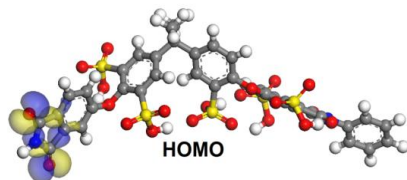


E= -5.295 eV

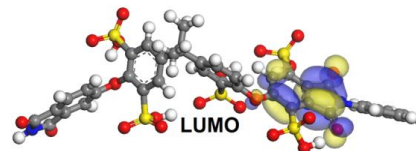


E= -4.443 eV

SPEI\_5

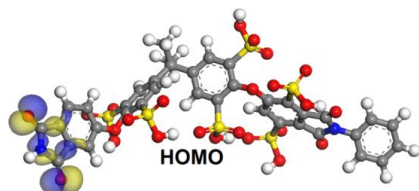


$$E = -5.356 \text{ eV}$$

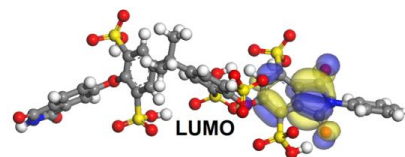


$$E = -4.508 \text{ eV}$$

SPEI\_6



$$E = -5.350 \text{ eV}$$



$$E = -4.508 \text{ eV}$$

Figure1. Frontier molecular orbital of SPEI

HOMO and LUMO orbitals for the hydroxyl and hydronium are plotted in Figure 2. The forms of these frontier orbitals illustrate type bonds in each molecule, these are  $\sigma$  bonds. Both HOMO-LUMO for hydroxyl turn out to be antibonding  $\sigma$  bonds, this indicate that hydroxyl will have low reactivity with each SPEI, therefore, the interactions determining hydroxyl mobility inside of each SPEI will be electrostatic-type or Van der Waals-type; this characteristic is an indication that, at a molecular level, the ionic transport of hydroxyl in the hydrated polymeric matrices is in general is a vehicular mechanism. In this mechanism ion ( $\text{OH}^-$ ) diffuses through the aqueous medium in response to the electrochemical difference. In vehicular mechanism, the water connected ions in the result of the electroosmotic drag carry the one or more molecules of water through the membrane and itself are transferred with them<sup>[33]</sup>.

HOMO for hydronium is antibonding while LUMO is bonding  $\sigma$ -type, this characteristic favors the mechanism “proton hopping” or “Grotthus mechanism” type, since, in proton hopping mechanism, protons hop from one hydrolyzed ionic site ( $(\text{SO}_3)^-$ ,  $(\text{H}_3\text{O})^+$ ) to another across the membrane. The produced proton by oxidation of hydrogen in anode adheres to water molecule than the provisional hydronium ion is

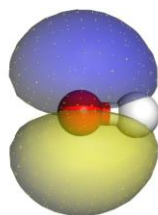
formed and one different proton from same hydronium ion hops on the other water molecule. In this mechanism, ionic clusters were swelled in presence of water and formed the percolation mechanism for proton transferring. The simple scheme of the hydronium hopping mechanism has been shown in Figure 3<sup>[34]</sup>.

To have an indicator of the interaction between the SPEI and ionic species, were calculated the energy differences between pairs  $E_{LUMO}(hidronio) - E_{HOMO}(SPEI_n)$  y  $E_{LUMO}(hidroxilo) - E_{HOMO}(SPEI_n)$  and viceversa. They are specified in Table 1.

Table1. Energy differences (in eV) among LUMO and HOMO for pairs of molecules

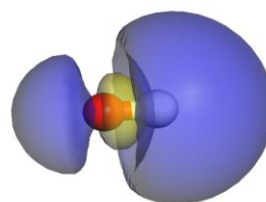
Molecule	$E_{LUMO}(\text{Hydronium}) - E_{HOMO}(\text{SPEI})$	$E_{LUMO}(\text{Hydroxyl}) - E_{HOMO}(\text{SPEI})$	$E_{LUMO}(\text{SPEI}) - E_{HOMO}(\text{Hydronium})$	$E_{LUMO}(\text{SPEI}) - E_{HOMO}(\text{Hydroxyl})$
SPEI_1	-2.083	15.949	10.898	-10.441
SPEI_2	-2.873	15.159	10.091	-11.248
SPEI_3	-2.846	15.186	10.094	-11.245
SPEI_4	-2.631	15.401	10.012	-11.327
SPEI_5	-2.570	15.462	9.635	-11.704
SPEI_6	-2.576	15.456	9.7	-11.639

#### Hydroxyl



HOMO

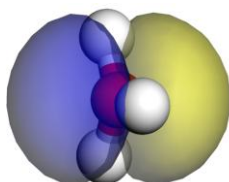
E= 71.96 eV



LUMO

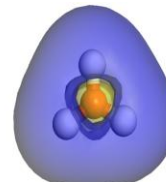
E= 10.106 eV

#### Hydronium



HOMO

E= -14.143 eV



LUMO

E= -79.26 eV



Figure2. Frontier molecular orbital for ionic species

According to the results of Table 1, for that an electron is transferred from the hydroxyl at SPEI must release a large amount of energy of about 11 eV which would require very strong collisions between hydroxyl and SPEI, while it is required very high energies, around 15 eV, to excite an electron from the hydroxyl to SPEI. This indicates that there is little possibility that the hydroxyl and SPEI can form chemical bond, which favors the diffusion mechanism of the hydroxyl in the membrane, as mentioned above.

Moreover, in Table 1, we can see that the hydronium have greater difficulty in moving through the membrane because the released energy for transfer an electron from the SPEI to this ionic specie is relatively low, about 2 eV, so that there is some likelihood of the ionic specie form a chemical bond with SPEI so that the hydronium be anchored in the membrane structure. However, the interaction will not be so strong, because the electron require high relatively energy, at least 10 eV, to be transferred from hydronium to SPEI, so there is the probability that a hydrogen atom is apparent from the hydronium and this could lead to proton conduction type "proton hopping" or "Grotthus mechanism" that is consistent with those found in the analysis of the frontier orbitals.

Based on these results, we carried out a qualitative analysis of the mechanism of ion conductivity of hydronium inside different SPEI. For this, the hydronium was placed close LUMO of each SPEI, then the geometry optimization was performed. The final state of interactions hydronium-SPEIs is seen in Figure 3. In this figure, dipole-dipole interactions and electrostatic interactions at the final state of interactions hydronium-SPEI's are too observed.

For the polymer with a group  $\text{SO}_3\text{H}$  (Figure 3a) shows that because the nitrogen atom is more electronegative than hydrogen atom  $\text{H}_3$ , it gives up electron and consequently N atom attracts  $\text{H}_3$ .

In Figure 3b (SPEI\_2), we observe an interesting effect: as a result of the different interactions between hydronium and SPEI\_2, the atom  $\text{H}_3$  is attracted to the atom  $\text{O}_2$  because it has the same feature that the nitrogen atom, under this process,  $\text{H}_3$  belongs to the sulfonyl group, and, in turn the hydrogen atom  $\text{H}_4$  is detached from sulfonyl group and attracted to the atom  $\text{O}_3$ . Similar process occurs in Figures 3c and 3d (SPEI\_3 and SPEI\_5 respectively).

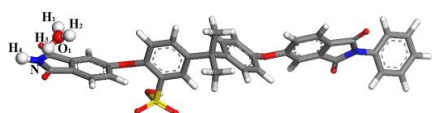
In SPEI\_4 (Figure 3e) follows the same mechanism, the difference is the involvement of two groups  $\text{SO}_3\text{H}$ . In the three cases we have a good indication that the conduction mechanism is much closer to the type of mechanism Grotthus, as predicted above.

In Figure 3f a  $\text{C}_1\text{-S}_1$  bond break is observed and no detachment of atoms from hydronium.

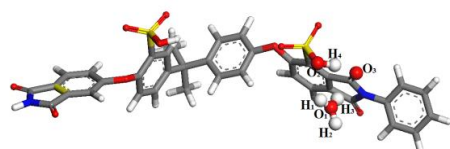
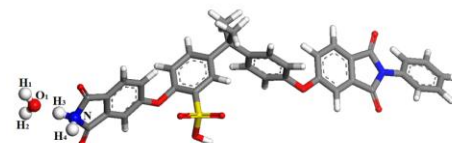
Table 2 contains information on atomic charges distribution on atoms indicate in figure 3 corresponding to the initial and final states of the optimization, since this quantity is not only an index of ionicity of a bond,



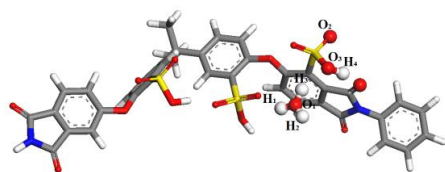
but can also be considered as an index of reactivity when charged species are involved in a chemical process like the one we are studying here. The mechanism of chemisorption and further breaking is revealed from both Mulliken electron population on atoms <sup>[32]</sup> (Table 2) and the analysis of interaction of frontier orbital HOMO-LUMO between hydronium and SPEI (Figure 3)



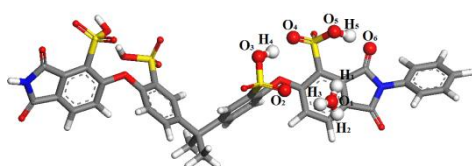
3a. SPEI\_1 y  $H_3O^+$



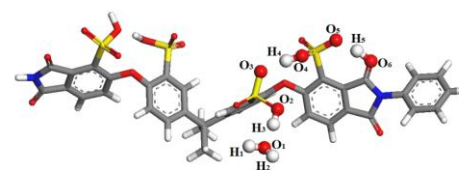
3b. SPEI\_2 y  $H_3O^+$



3c. SPEI\_3 y  $H_3O^+$



3d. SPEI\_4 y  $H_3O^+$





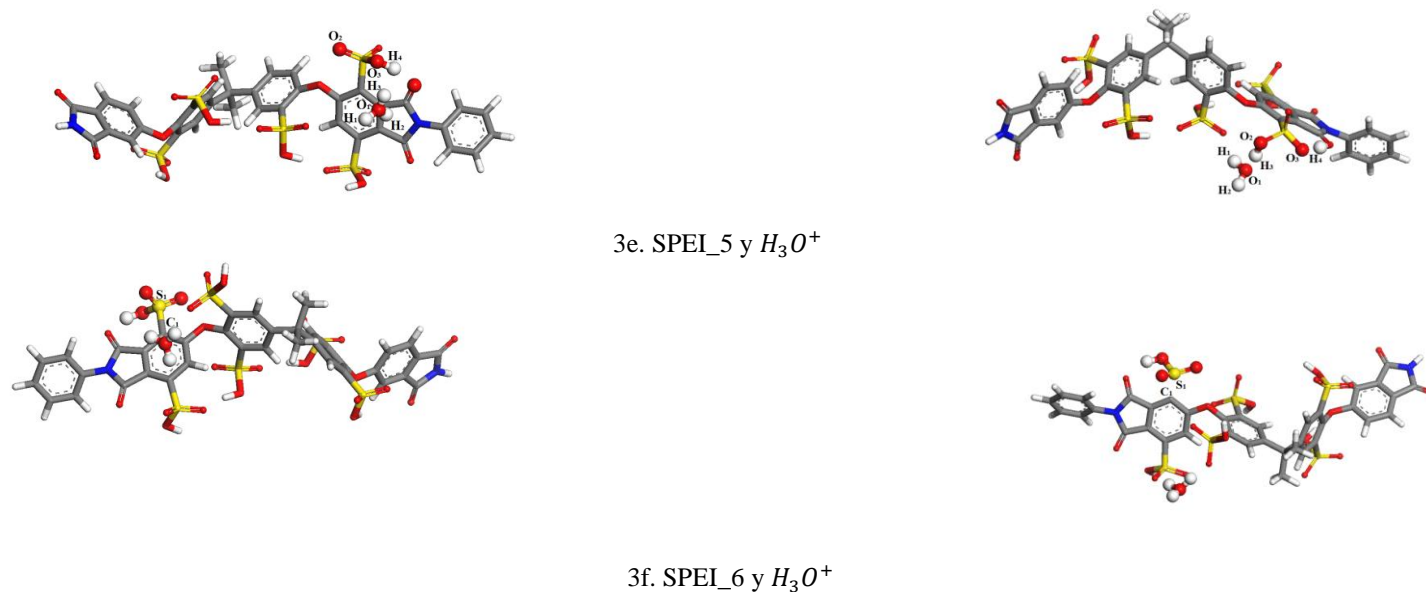


Figure 3. Interaction between ion hydronium with each SPEI's

Table2. Charge distribution on atoms of figure 3

atom SPEI_1	Initial State (e)	Final State (e)
H <sub>1</sub>	0.357	0.326
H <sub>2</sub>	0.369	0.326
H <sub>3</sub>	0.224	0.373
H <sub>4</sub>	0.284	0.302
O <sub>1</sub>	-0.275	-0.595
N	0.351	-0.543

atom SPEI_3	Initial State (e)	Final State (e)
H <sub>1</sub>	0.315	0.341
H <sub>2</sub>	0.331	0.324
H <sub>3</sub>	0.364	0.386
H <sub>4</sub>	0.366	0.377
O <sub>1</sub>	-0.335	-0.589
O <sub>2</sub>	-0.415	-0.418
O <sub>3</sub>	-0.461	-0.517

atom SPEI_2	Initial State (e)	Final State (e)
H <sub>1</sub>	0.243	0.328
H <sub>2</sub>	0.349	0.326
H <sub>3</sub>	0.378	0.398
H <sub>4</sub>	0.366	0.379
O <sub>1</sub>	-0.197	-0.576
O <sub>2</sub>	-0.461	-0.582
O <sub>3</sub>	-0.471	-0.401

atom SPEI_4	Initial State (e)	Final State (e)
H <sub>1</sub>	0.212	0.325
H <sub>2</sub>	0.327	0.319
H <sub>3</sub>	0.342	0.357
H <sub>4</sub>	0.353	0.367
H <sub>5</sub>	0.375	0.377
O <sub>1</sub>	-0.255	-0.580
O <sub>2</sub>	-0.484	-0.460
O <sub>3</sub>	-0.396	-0.385
O <sub>4</sub>	-0.434	-0.385
O <sub>5</sub>	-0.422	-0.505
O <sub>6</sub>	-0.463	-0.386



atom SPEI_5	Initial State (e)	Final State (e)
H <sub>1</sub>	0.250	0.337
H <sub>2</sub>	0.344	0.326
H <sub>3</sub>	0.351	0.389
H <sub>4</sub>	0.357	0.376
O <sub>1</sub>	-0.173	-0.587
O <sub>2</sub>	-0.456	-0.417
O <sub>3</sub>	-0.487	-0.512

## Conclusion

Theoretical studies based on density functional theory provide valuable information on mechanism of proton conductivity in sulfonated poly (ether imide). Our results indicate that the hydroxyl presents a vehicular mechanism. In this mechanism ion (OH)<sup>-</sup> diffuses through the aqueous medium in response to the electrochemical difference. In this vehicular mechanism, we can infer that the water may connect ions in the result of the electroosmotic drag carry the one or more molecules of water through the membrane and itself are transferred with them. On other hand, proton specie (H<sub>3</sub>O)<sup>+</sup> meets all of the features to perform a mechanism of proton transport “proton hopping” or “Grotthus mechanism” since the results of this study show the detachment of hydrogen atoms from the hydronium and other hydrogen hop from one hydrolyzed ionic site to another across the sulfonated poly(ether imide). These results show that sulfonated poly (ether imide) is a promising material for development of proton exchange polymeric membranes.

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