

# Selective hydration of the ‘short-side-chain’ perfluorosulfonic acid membrane. An ONIOM study

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## Abstract

We evaluate the hydration of the short-side-chain perfluorosulfonic acid membrane through a comparative study of the energetics of an oligomeric fragment of the polymer using ONIOM DFT/HF molecular orbital calculations. Extensive searches for minimum energy conformations of the three pendant side chain oligomeric fragment of the polymer,  $\text{CF}_3(\text{CF}(\text{O}(\text{CF}_2)_2\text{SO}_3\text{H})(\text{CF}_2)_7)_2\text{CF}(\text{O}(\text{CF}_2)_2\text{SO}_3\text{H})\text{CF}_3$ , at the B3LYP/6-31G\*\*/HF/3-21G\*\* level with from 6 to 9 explicit water molecules revealed that at the lower range of the examined hydration (i.e. 2  $\text{H}_2\text{O}/\text{SO}_3\text{H}$ ) the uniform hydration of the sulfonic acid groups results in the lowest energy and therefore most favorable state of the system. Our calculations showed, however, that as the degree of hydration is increased the energetic preference for uniform hydration decreases, disappearing altogether at 3  $\text{H}_2\text{O}/\text{SO}_3\text{H}$ . Furthermore, we found that water distributions that facilitate a higher degree of dissociation and separation of the protons are important factors in stabilizing the fragments. These calculations provide a base line set of results for which the effects of distinct backbone and side chain chemistry maybe explored on hydration in minimally hydrated candidate polymer electrolyte membranes.

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## 1. Introduction

Although the perfluorosulfonic acid (PFSA) ionomer Nafion<sup>®</sup> (DuPont) was first used as the electrolyte in GE designed fuel cells forty years ago [1], it remains the archetypical membrane in proton exchange membrane (PEM) fuel cells under development today. This is despite well recognized drawbacks which include: high manufacturing cost; limitations in thermal stability; the requirement that the material remain fully hydrated during operation of the device; and the undesirable “cross-over” of water and methanol due to permeation and electro osmotic drag. It is also notwithstanding significant research into the development of electrolytes that exclusively transport protons and possess both chemical and mechanical stability at temperatures above 100 °C under low humidity conditions [2].

Several different approaches [3] have been explored towards this goal including: (1) modification of the chemistry of the polymer (i.e. backbone [4,5], side chain [6], or protogenic group [7,8]) of existing PEMs; (2) addition of inorganic particles (i.e.  $\text{SiO}_2$ ,  $\text{ZrO}_2$ , etc.) [9] to various PEMs; (3) replacement of the water with liquid heterocycles [10] such as imidazole, benzimidazole, triazole, etc.; and (4) synthesis of entirely novel proton conductors [11]. The success and suitability of these materials as proton conductors for medium temperature fuel cells has been varied but the development of a PEM superior to Nafion<sup>®</sup> has yet to emerge.

Of specific relevance to the present work has been the observation that modification of the length of the side chain in a PFSA ionomer may substantially alter either the proton diffusion and/or proton conductivity at low degrees of hydration [12,13]. Synthesis and testing of a ‘short-side-chain’ (SSC) PFSA membrane (i.e. the Dow<sup>®</sup> membrane [14]) showed significantly higher proton conductivity than Nafion<sup>®</sup> despite a similar hydrated morphology. This was recently substantiated

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by Solvay-Solexis [15] in the testing of the same SSC ionomer (i.e. their Hyflon® Ion) by a much simpler synthetic route and by the Fuel Cell Components group at 3M in their ionomer with  $-\text{O}(\text{CF}_2)_4\text{SO}_3\text{H}$  side chains [16]. Why PFSA membranes at similar degrees of hydration (i.e. # of  $\text{H}_2\text{O}$ s/ $\text{SO}_3\text{H}$ ) and possessing the same PTFE backbone but with different side chain length should exhibit substantially different proton mobilities is not understood.

Recent reviews [2,17] of what has been measured and modeled in both experimental and theoretical studies of proton transport in hydrated PEMs indicate that the underlying factors are complex and incompletely elucidated. This is despite the substantial effort undertaken during the past two decades [18–31]. A helpful framework in understanding proton conductivity in PEMs may be constructed through considering the mobility of protons in both the solid state [30] (e.g. cubic perovskite-type oxides [31]) and in bulk water [32,33]. These may be viewed as limiting cases in the range of hydration of the electrolyte (i.e. from dry to fully hydrated) with the common feature that the excess protonic charge follows the symmetry of a dynamic and fluctuating coordination of hydrogen bonds [34]. With solids this is typically within direct proximity of the mobile proton while in water the proton-hopping is coupled to the dynamics of the hydrogen bonds in at least the second hydration shell. The diffusion of protons in a hydrated PEM is more complicated than in either of these media due to the heterogeneous nature of the polymer (i.e. co-organized crystalline and ionic domains) and the nano-confinement of the water subject to a high density of tethered anionic groups (e.g.  $-\text{SO}_3^-$ ) and hydrated protons. In some respects the situation is more analogous to proton transport in biological membranes [35].

Molecular modeling of acidic functional groups [36,37], polymeric fragments [38–40], proton self-diffusion [41–43], and dielectric saturation of the confined water [44] in several different PEMs has suggested that the critical ingredients of proton conduction include: *complexity*, *connectivity*, and *cooperativity*. Complexity encompasses dissociation of the proton from the acidic site, subsequent transfer of the proton to the aqueous medium, formation of a solvent separated (i.e. from the conjugate base) pair, and finally diffusion of the proton in the confined water within ionomer. Connectivity involves not only hydrogen bonding of the water to the protogenic groups but also includes longer scale connection of the water domains within the polymeric matrix. Cooperativity includes enhanced mobility due to flux of water, transport aided by the flexibility of the side chains and/or backbone, and the amphotericity of the protogenic groups. All of these chemical and physical processes govern the transport of protons in PEMs and necessitate examination over diverse length and time scales for appreciation of the subtleties involved. The present study aims to elucidate aspects of all these three ingredients at the molecular scale.

In recent investigations [39,40] we sought to understand the role of the side chain in facilitating proton dissociation in oligomeric fragments of the SSC ionomer consisting of two side chains with varying degrees of side-chain separation (i.e.  $-(\text{CF}_2)_x-$ ,  $x=5-9$ ) along with the effects of conformational changes in the perfluorinated backbone on both hydration and

proton transfer through DFT electronic structure calculations that treated all atoms at the B3LYP/6-311G\*\* level. As these fragments with 7 water molecules approach the computational limit in what maybe practically treated at this high level of theory, we extend our investigation with an ONIOM (DFT/HF) study of the relative energetic effects of varying the manner in which a larger three side chain fragment of the SSC membrane may be hydrated.

## 2. Computational methods

We used the ONIOM [45,46] method as implemented in the Gaussian G03 suite of programs [47]. The ONIOM method partitions the molecular system in up to three different levels of computational complexity. For our investigations, however, we only used two levels (medium and high). As we wished to capture the chemical effects of both proton dissociation and the separation of the hydrated protons from the sulfonate groups, the high level was selected to consist of the sulfonic acid groups and the terminal  $\text{CF}_2$  group of each side chain along with all water molecules. The high level used hybrid DFT methods at the B3LYP/6-31G(d,p) level, which combines Becke's three parameter functional [48] with the nonlocal correlation of the functional of Lee et al. [49]. This level of theory was selected to provide for a meaningful comparison with our previous electronic structure calculations on smaller two side chain fragments of the SSC polymer treated entirely at the B3LYP/6-311G(d,p) level [39,40]. The unsatisfied valences in the high level were satisfied by using the default method of capping them with a hydrogen atom. An extensive search of various MM (i.e. DREIDING, Amber, etc.) and semi-empirical (i.e. AM1 [50]) methods for implementation as the medium level ultimately resulted in the selection of HF/3-21G\*\* for treatment of the entire backbone and the  $-\text{OCF}_2$  portion of each side chain. This choice was made due to the observation that full optimizations of oligomeric fragments with out the addition of water molecules using either the MM or semi-empirical methods resulted in backbone conformations that did not possess the expected [51,52] helical pitch due to splitting of *trans* states caused by electrostatic repulsions due to polarity in the C–F bond (i.e. ca 165°).

## 3. Results and discussion

After identifying the B3LYP/6-31G(d,p):HF/3-21G\*\* level of theory as reproducing the earlier results obtained with the two side chain fragments (at the B3LYP/6-311G(d,p) level), we constructed oligomeric fragments possessing three uniformly separated pendant side chains along the backbone, i.e.  $\text{CF}_3(\text{CF}(-\text{O}(\text{CF}_2)_2\text{SO}_3\text{H})(\text{CF}_2)_7)_2\text{CF}(-\text{O}(\text{CF}_2)_2\text{SO}_3\text{H})\text{CF}_3$ , by fully optimizing the 'dry' fragment from five different arrangements of the side chains. These distinct conformations were selected so as to avoid any bias in the conformation of the global minimum energy conformation selected for the further hydration studies involving the water molecules. The water molecules were then sequentially added (i.e. one at a time) to assess the hydrogen bonding and proton dissociation on the

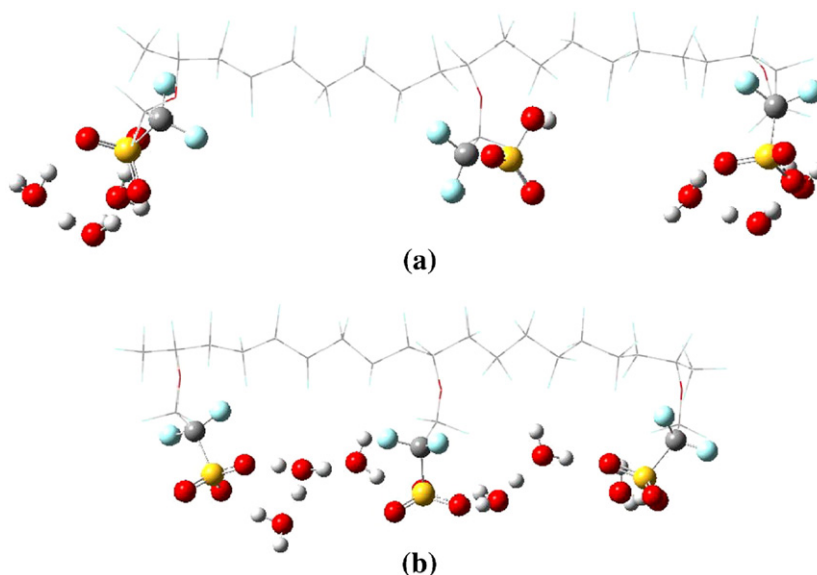


Fig. 1. Fully optimized (B3LYP/6-31G(d,p):HF/3-21G\*\*) structures of a three side chain fragment of the SSC polymer with 6 explicit water molecules: (a) three water molecules hydrate the outer two sulfonic acid groups; and (b) each of the sulfonic acid groups are uniformly hydrated with two water molecules. The PFC backbone and  $-\text{OCF}_2-$  portion of each side chain are treated at the medium level indicated by the wire frame atoms, high level atoms are shown as spheres: light blue are fluorine; grey are carbon; yellow are sulfur; red are oxygen; and white are hydrogen. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

preferential hydration of the oligomeric fragment through full optimization at the B3LYP/6-31G(d,p):HF/3-21G\*\* level. Initial structures were prepared by placing the water molecule in from 6 – 15 different positions around the sulfonic acid groups. In this brief communication we have selected two fully optimized structures at four different water contents that exhibit qualitatively distinct hydration of the three sulfonic acid groups.

### 3.1. Oligomeric fragment with 6 H<sub>2</sub>O molecules

Two fully optimized structures of the oligomeric fragment each with six water molecules were selected, from a total of 10 different minimum energy conformations that display qualitatively different hydration of the sulfonic acid groups and are presented in Fig. 1. In Fig. 1(a) three water molecules are associated with the outer two sulfonic acid groups leaving the central sulfonic acid isolated and unhydrated. This is distinctly different to Fig. 1(b) where the two water molecules hydrogen bonded to each sulfonic acid group form a connected water/acid network. Despite the obvious hydration differences between these structures, the conformation of the backbone is quite similar with the majority of the C–C–C–C dihedral angles between 155° and 173°, very similar to what was observed in our previous B3LYP/6-311G(d,p) calculations on two side chain fragments [40] and possessing the expected helical pitch. The position of the side chains relative to one another, however, is quite different in comparing the two fragments. Only two of the side chains in Fig. 1(a) are on the same side of the backbone, whereas all three are similarly orientated with respect to the backbone in the fragment in Fig. 1(b). Although the perspective of the two structures might suggest that the conformation of the side chains are distinctly different in the two hydrated fragments, an examination of the dihedral angles along the

length of the side chains indicate they are actually quite similar and all fall into the expected ranges as derived in our complete torsional energy profiles [40]. It is clear from Fig. 1 that the sulfonic acid groups are much closer to one another in (b) due to the bridging water molecules with distances between the sulfur atoms of 8.82 and 8.70 Å, as compared to the much longer S...S distances in (a) of 14.8 and 9.13 Å, the latter due to the orientational difference in the first side chain (i.e.  $\approx 90^\circ$  out of the plane made by the second and third side chains).

Examination of these two hydrated fragments also reveals an interesting and important similarity in the dissociation of the protons. In our earlier electronic structure calculations on the two side chain oligomeric fragments of this SSC polymer we observed that proton dissociation dramatically affected the overall energetics of the molecular system and the binding of the water to the fragment [40]. In both fragments the hydration with six water molecules has effected the dissociation of two protons. In the minimum energy conformation in Fig. 1(a) the proton from the left most sulfonic acid is stabilized as a Zundel-like ion with an O...H–O contact distance of 2.59 Å and O...H separation distance of 1.61 Å; and the proton from the sulfonic acid on the right side chain exists as a hydronium ion-sulfonate contact ion pair with an O...H separation distance of 1.491 Å. Protons dissociated in the uniformly hydrated fragment (Fig. 1(b)) from the left and central sulfonic acids and both formed contact ion pairs with their conjugate sulfonate anions with  $\text{SO}_2\text{O...H-OH}_2$  distances of 2.49 and 2.43 Å and O...H separation distances of 1.44 and 1.34 Å, respectively.

### 3.2. Oligomeric fragment with 7 H<sub>2</sub>O molecules

Fully optimized structures of the same oligomeric fragment with two distinctly different distributions of seven water

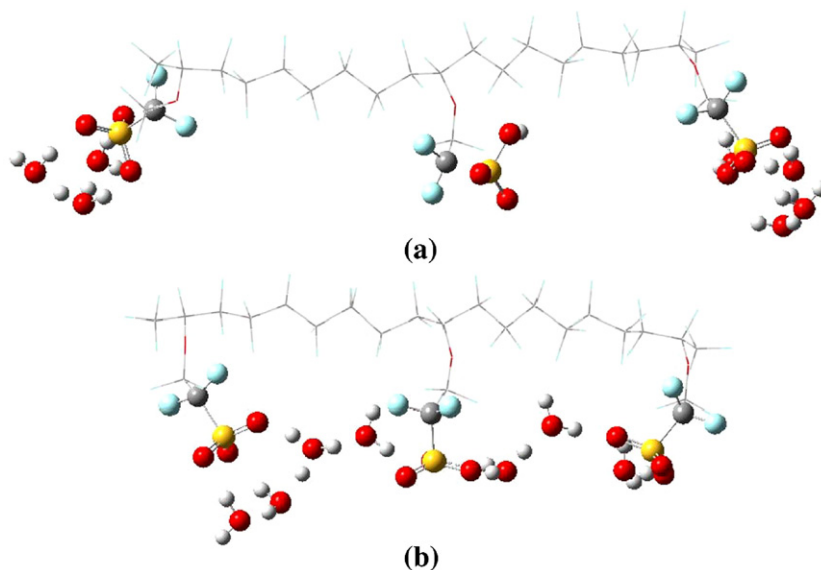


Fig. 2. Fully optimized (B3LYP/6-31G(d,p):HF/3-21G\*\*) structures of a three side chain fragment of the SSC polymer with 7 explicit water molecules: (a) clusters of three and four water molecules hydrate only the outer two sulfonic acid groups; and (b) the water molecules hydrate each sulfonic acid group forming a continuous hydrogen bonded network.

molecules are displayed in Fig. 2. These were selected from 12 different minimum energy conformations at this water content with the arrangement in (b) possessing the lowest energy. Comparison with the oligomeric fragment with six water molecules reveals that the addition of another water molecule has not brought about any significant changes to the conformations of either the backbone or side chains in either of the arrangements of water. The separation of the side chains is also quite similar with the sulfur-sulfur distances in the fragment in Fig. 2(a) of 14.8 and 10.6 Å for the left and right pairs,

respectively. Thence, with the addition of the water molecule to the cluster around the right most sulfonic acid some further separation of the side chains has occurred. The (global) minimum energy structure with the water connecting the side chains (i.e. Fig. 2(b)) shows essentially no change in the separation of the side chain termini with S?S distances of 8.81 and 8.69 Å.

With seven water molecules two protons are once again dissociated in both of the arrangements of water molecules. Both the O...H–O and O...H separation distances in the Zundel-

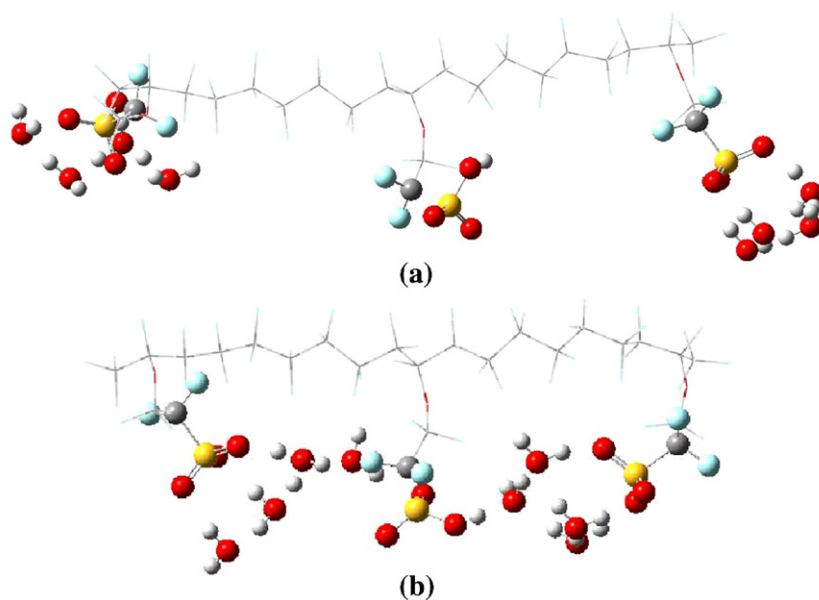


Fig. 3. Fully optimized (B3LYP/6-31G(d,p):HF/3-21G\*\*) structures of a three side chain fragment of the SSC polymer with 8 explicit water molecules: (a) four water molecules hydrate the outer two sulfonic acid groups; and (b) the outer two sulfonic acid groups are each hydrated with three water molecules and the central sulfonic acid group with two water molecules forming a continuous connection of the sulfonic acids.



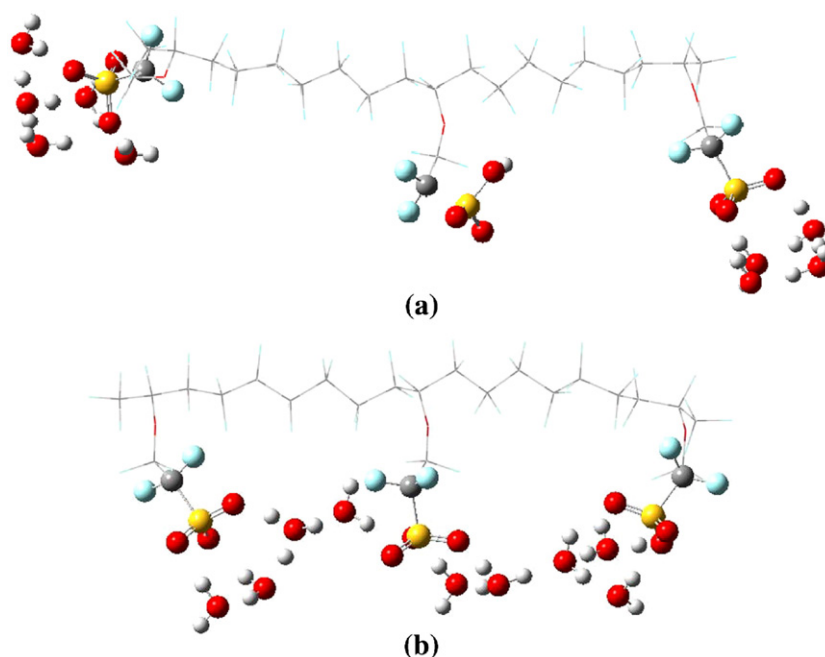


Fig. 4. Fully optimized (B3LYP/6-31G(d,p):HF/3-21G\*\*) structures of a three side chain fragment of the SSC polymer with 9 explicit water molecules: (a) clusters of five and four water molecules hydrate the outer two sulfonic acid groups; and (b) three water molecules are associated with each sulfonic acid group.

like contact ion pair on the left water cluster in Fig. 2(a) remain the same at 2.59 and 1.61 Å, respectively. With the addition of a water molecule to the cluster on the right a further separation of the hydronium ion from the sulfonate occurs with O...H–O and O...H separation distances of 2.61 and 1.64 Å, respectively. The additional water molecule around the sulfonate group on the right side chain (now coordinated with three water molecules) in the fragment in Fig. 2(b) has also resulted in further separation of the hydronium ion with O...H–O and O...H separation distances of 2.55 and 1.55 Å, respectively. The water molecules and hydronium ion to the right of the central sulfonic acid group are unperturbed with hydrogen bonding that is indistinguishable from the arrangement in Fig. 1(b).

### 3.3. Oligomeric fragment with 8 H<sub>2</sub>O

Fully optimized (B3LYP/6-31G(d,p):HF/3-21G\*\*) conformations of the oligomeric fragment possessing qualitatively distinct hydration with 8 water molecules were selected from among 14 different minimum energy structures and are displayed in Fig. 3. Similar to the structures with six and seven water molecules, the pair consists of the oligomeric fragment with well separated hydration of only two of the sulfonic acid groups (Fig. 3(a)) and another where all three sulfonic acid groups are hydrated and are connected with the water (Fig. 3(b)), the global minimum energy structure. Examination of the conformations of the backbone and side chains in both arrangements of the water molecules, indicates very little change from their counterparts with six and seven waters with the exception in the terminal portion of the right side chain in the uniformly hydrated fragment where a slight rotation of  $\approx 10^\circ$  has occurred in the C–C bond with the result

that the sulfonic acid groups are about 1 Å closer to each other. Three water molecules are coordinated with this sulfonic acid (in contrast to only two in the fragment in Fig. 2(b)) and have effected the dissociation of its proton forming a Zundel-like ion with an O...H–O contact distance of 2.60 Å and O...H separation distance of 1.60 Å. Proton dissociation of the sulfonic acid group on the right has seemingly come at a cost in that the proton has returned to the central sulfonic acid group thus resulting in only two dissociated protons similar to the fragment with either six or seven water molecules. With four water molecules hydrated each of the outer two sulfonic acid groups in the fragment in Fig. 3(a), the two water clusters are quite symmetrical with sulfonate–hydronium ion contact pairs with O...H–O and O...H separation distances of 2.61 and 1.62 Å, respectively.

### 3.4. Oligomeric fragment with 9 H<sub>2</sub>O

Of 16 fully optimized structures of the SSC oligomeric fragment with nine water molecules a similar pair of water arrangements were selected: the first with well separated hydration of only two of the sulfonic acid groups shown in Fig. 4(a); and the second with uniform and connected hydration where each sulfonic acid group is hydrogen bonded to three water molecules displayed in Fig. 4(b). Once again both the backbone and side chains possess very similar conformation as was observed at the lower water contents. An important difference with 3 H<sub>2</sub>O/SO<sub>3</sub>H is the formation of a solvent separated Eigen ion in the cluster of five water molecules around the left sulfonic acid group in the fragment in Fig. 4(b). The average distance of the hydronium ion in this cluster from the sulfonate oxygen atoms is 3.80 Å, considerable greater than

Table 1  
Energies of optimized  $\text{CF}_3(\text{CF}(-\text{O}(\text{CF}_2)_2\text{SO}_3\text{H})(\text{CF}_2)_7)_2$   $\text{CF}(-\text{O}(\text{CF}_2)_2\text{SO}_3\text{H})$   $\text{CF}_3$  fragments<sup>a</sup>

+ n H <sub>2</sub> O, Fig. #	$E_{\text{elec}}^b$	$\Delta E^c$ (kcal/mol)	$\Delta E/\text{H}_2\text{O}^d$ (kcal/mol)
6, 1(a)	−8349.808591659976	8.94	1.35
6, 1(b)	−8349.822831845624	0	
7, 2(a)	−8426.252121664536	7.64	1.09
7, 2(b)	−8426.264293492772	0	
8, 3(a)	−8502.712291026058	6.56	0.82
8, 3(b)	−8502.722745051057	0	
9, 4(a)	−8579.164290619111	0	
9, 4(b)	−8579.164612982593	0.20	0.02

<sup>a</sup>For structures optimized at the B3LYP/6-31G\*\*: $\text{HF}/3-21\text{G}^{**}$  level.

<sup>b</sup>Total electronic energy in Hartrees.

<sup>c</sup>Energy difference from global minimum energy conformation.

<sup>d</sup>Energy difference per water molecule.

the O...H–O separation distances observed in any of the contact ion pairs. We previously observed the significant energetic preference for separation of the solvated proton in single trifluorosulfonic acid molecules [37]. The cluster of four water molecules around the right sulfonic acid group is essentially identical with that displayed in Fig. 3(b). Of some interest is the observation that in the uniformly hydrated fragment (Fig. 4(a)) only two protons were observed to dissociate. This is despite conducting a substantial number of optimizations with the water molecules placed at various initial positions.

### 3.5. Energetics

The total electronic energies and relative energy difference at each of the degrees of hydration for all the oligomeric fragments are reported in Table 1. Examination of the energy differences between the fragments with the uniform hydration (i.e. Figs. 1–4(b)) versus those featuring separate and disconnected hydration of the sulfonic acid groups (i.e. Figs. 1–4(a)) reveal that without exception the former is lower in energy than the latter. At the lowest degree of hydration (i.e. 2 H<sub>2</sub>O/SO<sub>3</sub>H) the energy difference is significant with the fragment possessing the connected hydrogen bond network 1.35 kcal/mol/H<sub>2</sub>O lower in energy than its counterpart (i.e. Fig. 1(a)). The energetics also reveal the interesting and systematic trend of a decrease in the energy difference between the fragments with isolated water clusters versus those with uniformly distributed water molecules when 7 and 8 waters hydrate the fragment. However, when a hydration of 3 H<sub>2</sub>O/SO<sub>3</sub>H is reached the preference for uniform hydration disappears. The probable reason for this is likely due to the formation of a solvent separated Eigen ion in the sulfonic acid group on the left in the Fig. 4(a) as a result of the completion of a solvation shell consisting of 5 water molecules. In agreement with our previous work [17,40], proton dissociation and eventual separation have a profound affect on the energy of the molecular system. Clearly, when there is a sufficient number of water molecules around a sulfonic acid group to form an intermediate water layer separating the hydrated proton from its conjugate base, the energetics indicate this as the preferred state.

## 4. Conclusions

The hydration of the short-side-chain perfluorosulfonic acid membrane has been explored through comparing the energetics of an oligomeric fragment of the SSC polymer with three side chains. Full optimizations of the oligomeric fragment at the B3LYP/6-31G\*\*: $\text{HF}/3-21\text{G}^{**}$  level with from 6 to 9 explicit water molecules with all the sulfonic acid groups connected through hydrogen bonding with the water. However, as the degree of hydration is increased the energetic preference for uniform hydration decreases, eventually disappearing altogether at 3 H<sub>2</sub>O/SO<sub>3</sub>H. At this water content, hydration of the fragment that facilitates formation of a solvent separated Eigen ion results in substantially lower energy. In general distributions of the water that facilitate a higher degree of dissociation and separation of the protons result in stabilization of the fragment. Our calculations provide a base line set of results for which the effects of distinct backbone and side chain chemistry maybe explored in minimally hydrated candidate polymer electrolyte membranes.

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## References

- [1] W.G. Grot, *Macromol. Symp.* 82 (1994) 161.
- [2] K.D. Kreuer, S.J. Paddison, E. Spohr, M. Schuster, *Chem. Rev.* 104 (2004) 4637.
- [3] R. Souzy, B. Ameduri, *Prog. Polym. Sci.* 30 (2005) 644.
- [4] J.A. Keres, *J. Membr. Sci.* 185 (2001) 3.
- [5] Z.Y. Yang, R.G. Rajendran, *Angew. Chem., Int. Ed. Engl.* 44 (2005) 564.
- [6] J.J. Sumner, S.E. Creager, J.J. Ma, D.D. DesMarteau, *J. Electrochem. Soc.* 145 (1998) 107.
- [7] M. Schuster, T. Rager, A. Noda, K.D. Kreuer, J. Maier, *Fuel Cells* 5 (2005) 355.
- [8] S.J. Paddison, K.D. Kreuer, J. Maier, *Phys. Chem. Chem. Phys.* 8 (2006) 4530.
- [9] G. Alberti, M. Casciola, *Annu. Rev. Mater. Res.* 33 (2003) 129.
- [10] K.D. Kreuer, A. Fuchs, M. Ise, M. Spaeth, J. Maier, *Electrochim. Acta* 43 (1998) 1281.
- [11] D.A. Boysen, T. Uda, C.R.I. Chisholm, S.M. Haile, *Science* 303 (2004) 68.
- [12] T.A. Zawodzinski, T.E. Springer, J. Davey, R. Jestel, C. Lopez, J. Valerio, S. Gottesfeld, *J. Electrochem. Soc.* 140 (1993) 1981.
- [13] C.A. Edmondson, J.J. Fontanella, *Solid State Ionics* 152–153 (2002) 355.
- [14] B.R. Ezzell, W.P. Carl, W.A. Mod, *Inventors; The Dow Chemical Company, Assignee.* 1982. U.S. patent 4,358,412.
- [15] V. Arcella, A. Ghielmi, G. Tommasi, *Ann. N. Y. Acad. Sci.* 984 (2003) 226.
- [16] S. Hamrock, Presented at Advances in Materials for Proton Exchange Membrane Fuel Cell Pacific Grove, CA February 20–23, 2005.
- [17] S.J. Paddison, *Annu. Rev. Mater. Res.* 33 (2003) 289.
- [18] S.C. Yeo, A. Eisenberg, *J. Appl. Polym. Sci.* 21 (1977) 875.
- [19] W.Y. Hsu, T.D. Gierke, *J. Membr. Sci.* 13 (1983) 307.
- [20] K.A. Mauritz, C.E. Rogers, *Macromolecules* 18 (1985) 483.
- [21] M.W. Verbrugge, R.F. Hill, *J. Electrochem. Soc.* 137 (1990) 886.
- [22] J.R. Bontha, P.N. Pintau, *Chem. Eng. Sci.* 49 (1994) 3835.

- [23] G. Gebel, *Polymer* 41 (2000) 5829.
- [24] J.A. Elliott, S. Hanna, A.M.S. Elliott, G.E. Cooley, *Macromolecules* 33 (2000) 4161.
- [25] A. Vishnyakov, A.V. Neimark, *J. Phys. Chem., B* 104 (2000) 4471.
- [26] P. Commer, A.G. Cherstvy, E. Spohr, A.A. Kornyshev, *Fuel Cells* 3 (2002) 127.
- [27] S.S. Jang, V. Molinero, T. Cagin, W.A. Goddard, *J. Phys. Chem., B* 108 (2004) 3149.
- [28] M.K. Petersen, F. Wang, N.P. Blake, H. Metiu, G.A. Voth, *J. Phys. Chem., B* 109 (2005) 3727.
- [29] J.T. Wescott, Y. Qi, L. Subramanian, T.W. Capehart, *J. Chem. Phys.* 124 (2006) 134702.
- [30] M. Eikerling, S.J. Paddison, L.R. Pratt, T.A. Zawodzinski Jr., *Chem. Phys. Lett.* 368 (2003) 108.
- [31] K.D. Kreuer, *Solid State Ionics* 125 (1999) 285.
- [32] M. Tuckerman, K. Laasonen, M. Sprik, M. Parrinello, *J. Phys. Chem.* 99 (1995) 5749.
- [33] H. Lapid, N. Agmon, M.K. Petersen, G.A. Voth, *J. Chem. Phys.* 122 (2005) 014506.
- [34] K.D. Kreuer, *Solid State Ionics* 136–137 (2000) 149.
- [35] T.E. DeCoursey, *Physiol. Rev.* 83 (2003) 475.
- [36] S.J. Paddison, L.R. Pratt, T.A. Zawodzinski Jr., *J. Phys. Chem., A* 105 (2001) 6266.
- [37] S.J. Paddison, *J. New Mater. Electrochem. Syst.* 4 (2001) 197.
- [38] S.J. Paddison, L.R. Pratt, T.A. Zawodzinski Jr., *J. New Mater. Electrochem. Syst.* 2 (1999) 183.
- [39] S.J. Paddison, J.A. Elliott, *J. Phys. Chem., A* 109 (2005) 7583.
- [40] S.J. Paddison, J.A. Elliott, *Phys. Chem. Chem. Phys.* 8 (2006) 2093.
- [41] S.J. Paddison, R. Paul, T.A. Zawodzinski Jr., *J. Electrochem. Soc.* 147 (2000) 617.
- [42] S.J. Paddison, R. Paul, K.D. Kreuer, *Phys. Chem. Chem. Phys.* 4 (2002) 1151.
- [43] R. Paul, S.J. Paddison, *J. Chem. Phys.* 115 (2005) 224704.
- [44] R. Paul, S.J. Paddison, *J. Phys. Chem., B* 108 (2004) 13231.
- [45] K. Morokuma, *Bull. Korean Chem. Soc.* 24 (2003) 797.
- [46] T. Vreven, K. Morokuma, *J. Chem. Phys.* 113 (2000) 2969.
- [47] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, *Gaussian 03, Revision C.02*, Gaussian, Inc., Wallingford CT, 2004.
- [48] A.D. Becke, *J. Chem. Phys.* 98 (1993) 5648.
- [49] C.T. Lee, W.T. Yang, R.G. Parr, *Phys. Rev., B* 37 (1998) 785.
- [50] M.J.S. Dewar, E.G. Zebisch, E.F. Healy, J.J.P. Stewart, *J. Am. Chem. Soc.* 107 (1985) 3902.
- [51] S.S. Jang, M. Blanco, W.A. Goddard III, G. Caldwell, R.B. Ross, *Macromolecules* 36 (2003) 5331.
- [52] M. D'Amore, G. Talarico, V. Barone, *J. Am. Chem. Soc.* 128 (2006) 1099.