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# The effect of side chain connectivity and local hydration on proton transfer in 3M perfluorosulfonic acid membranes

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ABSTRACT

We present a molecular modeling study on the role the connectivity of adjacent acid groups of 3M perfluorosulfonic acid (PFSA) membranes has on proton dissociation and transfer through a consideration of oligomeric fragments with different poly(tetrafluoroethylene) (PTFE) backbone segments separating the side chains. Electronic structure calculations were performed at the B3LYP/6-311G** level of theory on fragments with chemical formula: $CF_3CF(-O(CF_2)_4SO_3H)(CF_2)_nCF(-O(CF_2)_4SO_3H)CF_3$, where n = 5 or 7, corresponding to membrane equivalent weights of 590 and 690 g/mol, respectively. Fully optimized structures of these fragments with and without the addition of water molecules revealed that connectivity of the $SO_3H$ groups through hydrogen bonding is critical for proton dissociation and the state of the dissociated proton. Proton dissociation was first observed in the EW 590 fragment at a water content of only 1 $H_2O/SO_3H$; the system with greater separation of the side chains (EW 690) did not exhibit proton dissociation until four water molecules (i.e., 2 $H_2O/SO_3H$) were added as the greater side chain separation precluded the cooperative interaction through hydrogen bonding that promotes proton dissociation at low hydration in membranes of this type. Second proton dissociation in the EW 590 system occurred upon addition of three water molecules; this required five water molecules in the EW 690 fragment. The differences in dissociation and the state of the dissociated proton were mitigated after six water molecules were added to each system where one of the dissociated protons exists as a 'Zundel-like' cation and the other as more of an 'Eigen-like' complex. These calculations further substantiate prior work on the importance of the interaction of sulfonic acid groups through hydrogen bonding in the transfer and state of the dissociated protons.



## 1. Introduction

Interest in the use of fuel cells as highly efficient, clean energy conversion devices has been rapidly increasing over the past twenty years. Currently, proton exchange membrane (PEM) fuel cells are regarded as the paramount type of fuel cell due to their wide range of applicability [1]. The PEM functions not only as the electrolyte in current hydrogen fuel cells but also as the separator of the electrodes and reactant gases and importantly as the internal ion conductor [2]. Efficient operation of PEM fuel cells in diverse applications (i.e., vehicular, portable, and stationary) places demands on the PEM which include: long-time thermal and chemical stability (including resistance to oxidation and degradation by reactive species) at temperatures as high as 120 °C and high proton conductivity ($\approx 10^{-1}$ S cm$^{-1}$) under low humidity conditions (25–50% relative humidity) [3]. Although a large number of strategies have been devised in the pursuit to design membrane materials that meet these requirements, current PEM fuel cells still utilize perfluorosulfonic acid (PFSA) ionomers such as Nafion®. PFSA membranes consist of a poly(tetrafluoroethylene) (PTFE) backbone functionalized with pendant side chains each terminated with a single sulfonic acid group. Substantial research on the chemical structure, properties, and functionality in PFSA membranes and other PEMs has been reviewed by several authors and continues to expand the overall understanding crucial for further development of these materials [2,4–13]. However, utilization of current materials is limited due to high production costs and the high levels of hydration necessary for sufficient proton conductivity [14]. Considerable effort is being undertaken toward improving the efficiency and reducing the economic cost of PFSA membranes along with efforts to develop membranes with structural and chemical variations to the acidic side chains and/or protogenic groups [15–17]. The potential PFSA membranes have for wide spread application as the electrolyte in PEMFCs operating under relatively dry conditions will not only be enhanced through extensive testing and characterization but also through obtaining a molecular-level understanding of proton transfer and primary hydration of the protogenic groups in materials of this type.

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Molecular modeling can be used in the progression towards one of the primary goals of current PFSA membrane research, the development of materials that exhibit high proton conductivity at elevated temperatures and low hydration levels, by providing insight into the mechanisms of proton transport within these systems [2]. Hydration is essential to proton transfer in PFSA membranes. Theoretical and experimental studies suggest aggregation of the sulfonic acid groups occurs to some extent in nominally dry membranes and to a greater degree in hydrated membranes where the acidic groups are solvated by the water molecules; the solvation of these acidic groups leads to proton dissociation into the aqueous domain. Dissociated protons in these systems are mobile which facilitates long-range proton transport through the aqueous domains of the material [18–21]. The protons may not only move through the aqueous medium through simple vehicular diffusion but also via a Grotthuss or structural diffusion mechanism [22–24] resembling that of bulk-water [25–30]. This structural diffusion involves proton shuttling through the hydrogen bond network through a series of transformations between an Eigen cation ($H_9O_4^+$) and a Zundel cation ($H_5O_2^+$). Hence, an understanding of the formation and the nature of hydrogen bond networks between acidic groups and water molecules is a necessary requirement for the further development of PEM materials. Within PFSA membranes, the connectivity and cooperativity exhibited by the side chains are critical to the formation of complex hydrogen bond networks and, thus, crucial for facilitation of proton transport [31,32]. Full understanding of this requires insight into the formation and breaking of hydrogen bonds within these complex systems. As there are few experimental techniques that can reach this level of resolution, molecular simulations have been utilized to describe these interactions.

We continue our investigations in the present work on understanding the role side chain connectivity [33–35] and local hydration [36–38] have on proton dissociation and separation. Specifically, we report electronic structure calculations of fragments of the 3 M PFSA ionomer consisting of two side chains ($-O(CF_2)_4SO_3H$) with different separation along the PTFE backbone: $CF_3CF(-O(CF_2)_4SO_3H)(CF_2)_n CF(-O(CF_2)_4SO_3H)CF_3$, where $n=5$ and 7 which correspond to equivalent weights (EWs) of 590 and 690 grams of ionomer per mole acid, respectively. The nomenclature EW 590 and EW 690 is henceforth used to distinguish the two different fragments.

## 2. Computational methods

All electronic structure calculations of the oligomeric fragments were performed using the GAUSSIAN 03 suite of programs [39]. Each of the initial structures were constructed by adding the two acidic side chains with a specified spacing between them to fully optimized perfluorinated alkanes of two different lengths (i.e., $C_9F_{20}$ and $C_{11}F_{24}$). The initial backbone geometry exhibited the expected structure of PTFE (i.e., staggered fluorine atoms along an all *trans* arrangements of the carbon atoms thereby exhibiting an alpha helical pitch when viewed down the length of the backbone). Two side chains ($-O(CF_2)_4SO_3H$) were added to each alkane with a variety of different initial configurations. Full optimizations (i.e. over all degrees of freedom) were then carried out by conjugate gradient methods [40] without symmetry constraints initially invoking Hartree–Fock theory with the 6–31G** split valence basis set [41]. The resulting structures were then refined with hybrid density functional theory (DFT) employing Becke's 3-parameter functional (B3LYP) [42,43] and the same basis set. Final optimizations were then performed at the B3LYP/6–311G** level of theory [44]. Subsequent to the 'dry' optimizations (i.e., without explicit $H_2O$ molecules), water molecules were individually added to the optimized system at a variety of initial positions and full optimization was performed using the protocol described above. Vibrational frequencies and zero point energies (ZPEs) were determined for all global minimum energy structures at the B3LYP/6–311G** level. The binding energies of water molecules to the oligomeric fragments were calculated using both uncorrected and ZPE corrected minimum electronic energies using the equation

$$\Delta E = \frac{\left[E_{elec}^{total} - \left(E_{elec}^{frag} + n_{H_2O}E_{elec}^{H_2O}\right)\right]}{n_{H_2O}}$$

where $E_{elec}^{total}$ is the total electronic energy of the system including the water molecules, $E_{elec}^{frag}$ is the electronic energy of the initial 'dry' fragment, $E_{elec}^{H_2O}$ is the electronic energy of a single water molecule, and $n_{elec}^{H_2O}$ is the number of water molecules in the system. The counterpoise (CP) method of Boys and Bernardi [45] was also employed to explore the effects of basis set superposition error (BSSE) on the water binding energies calculated from the CP-corrected optimized geometries and vibrational frequencies. Lastly, partial atomic electrostatic charges were obtained using the CHelpG scheme for the fully optimized structures (B3LYP/6–311G**) in both systems at all levels of hydration.

## 3. Results and discussion

### 3.1. 'Dry' fragments

As it is well known that hydrogen bonding is a critical feature of proton transport in materials of this type, these interactions were a primary focus in this study. The requirements for a hydrogen bond in these electronic structure calculations were an O···O distance between 2.45 and 3.25 Å and an O–H···O bond angle greater than 145°. Throughout this paper, the global minimum energy structures (i.e., lowest of all fully optimized structures determined) at each hydration level are presented in the top panel of the figures discussed throughout the text; the bottom panel of the figures shows a rotated bottom view of the sulfonic acid/sulfonate groups and water molecule(s) (with the exception of the 'dry' case) with hydrogen bonds denoted by dotted lines and the O···O distance reported, all other atoms have been removed for clarity. The global minimum energy structure of the EW 590 fragment exhibits double hydrogen bonded sulfonic acid groups (shown in the bottom panel of Fig. 1a) with a fully extended PTFE backbone and side chains, the latter exhibiting no kinking or distortion, as shown in Fig. 1a (top panel). The doubly hydrogen bonded configuration was significantly lower in energy than systems where there was no hydrogen bonding of the acid moieties; this result is consistent with results obtained using fragments of the short-side chain (SSC) PFSA membrane consisting of a PTFE backbone and two pendant $-O(CF_2)_2SO_3H$ side chains separated by only four $-CF_2-$ backbone units [9]. The EW 690 fragment, on the other hand, does not exhibit the same 'relaxed' interaction (i.e. does not require forced distortion or kinking of bond and dihedral angles of the backbone or side chains) between the side chains under 'dry' conditions due to the additional tetrafluoroethylene unit in the backbone separating them. Instead, to maintain a fully extended backbone and 'relaxed' side chains, the side chains remain well separated without any hydrogen bonding between them, shown in Fig. 1b (as hydrogen bonds are not present in this configuration, no bottom view of this 'dry' system has been included). The 'relaxed' and well separated configuration of the side chains seen in the EW 690 system was also observed in electronic structure calculations on oligomeric fragments of the SSC PFSA membrane having a fully extended backbone with side chains separated by 5, 7, and 9 $-CF_2-$ units [33–35]. The extension of the side chains of the SSC ionomer by an additional tetrafluoroethylene unit (as is the case for the 3M PFSA membranes in this study) evidently allows for favorable hydrogen bonding between the sulfonic acid groups when the side chains are separated by five $-CF_2-$ groups. However, increasing side chain separation to seven $-CF_2-$ groups in the 3M PFSA ionomer does not lead to this type of configuration for fragments with an all *trans* (i.e. fully extended) backbone.