

First-Principles Study on Proton Dissociation Properties of Fluorocarbon- and Hydrocarbon-Based Membranes in Low Humidity Conditions

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We present a theoretical study on the proton dissociation properties of the membranes for polymer electrolyte fuel cells. A density functional theory method is used to study the influence of fluorocarbon and hydrocarbon backbones on proton dissociation, the interaction of water molecules with the sulfonic acid group, and the energy barriers for proton dissociation. Better proton dissociation properties of $\text{CH}_3\text{SO}_3\text{H}$ compared to $\text{CF}_3\text{SO}_3\text{H}$ are observed from statistical analyses of the optimized structures for both systems. However, the calculated energy barriers for proton dissociation are lower for $\text{CF}_3\text{SO}_3\text{H}$ than for the $\text{CH}_3\text{SO}_3\text{H}$ system. At the same time, the interaction of water molecules is stronger for $\text{CH}_3\text{SO}_3\text{H}$ than for $\text{CF}_3\text{SO}_3\text{H}$. Also, the analysis of the hydrogen-bonding network in both systems shows that the number of hydrogen bonds formed around the sulfonic acid group in $\text{CH}_3\text{SO}_3\text{H}$ is larger than that in $\text{CF}_3\text{SO}_3\text{H}$. Therefore, the decrease of the energy barrier with increasing number of coordinating water molecules, pronounced in the case of $\text{CH}_3\text{SO}_3\text{H}$, may lower the barrier, which enhances good proton conductivity of a hydrocarbon-based polymer in low humidity conditions. Thus the hydration ability of a sulfonic acid group is an important factor for realizing better proton dissociation in low humidity conditions.

Introduction

Polymer electrolyte fuel cells (PEFCs) are a promising power generation technology for mobile applications. One of the key issues in the commercialization of PEFCs is the development of electrolyte materials with higher conductivity and stability. Fluorocarbon-based membranes such as Nafion are used as the electrolyte of a PEFC because of their favorable chemical, mechanical, and thermal properties along with high proton conductivity when sufficiently hydrated.^{1–7} To keep membranes well hydrated, the humidity of the supplied fuel and air must be maintained as high as possible, which causes various problems such as the condensation of water in gas flow channels and the high economic cost of the system. In this regard, several attempts have been made to design alternative materials that exhibit good proton conductivity in lower humidity conditions.^{8–11}

New proton-conducting polymer electrolytes such as partially fluorinated membranes, composite membranes, or aromatic polymer membranes have been developed over the past decade. Among them, a hydrocarbon-based membrane was found to be a promising candidate as an electrolyte material for next-generation PEFCs. So far sulfonated hydrocarbon polymers such as sulfonated polyether ether ketone (S-PEEK),^{11–13} sulfonated poly(4-phenoxybenzoyl-1,4-phenylene) (S-PPBP),¹⁴ sulfonated polyimides (SPI),^{15–20} and sulfonated polybenzimidazole (S-

PBI)^{21–32} have been developed and extensively studied. Rikukawa et al.^{28,33} reported that the water uptake property and the proton conductivity of PBI–propanesulfone (PBI–PS) were similar to those of perfluorosulfonated polymers below 80 °C, while it showed better properties above 80 °C. The proton conductivity of Nafion remarkably drops above 100 °C because of the loss of the absorbed water. By contrast, the high proton conductivity of hydrous PBI–PS is retained even above 100 °C. They also observed the physical states of the absorbed water in hydrous PBI–PS polymers and suggested that the sulfonic acid groups in PBI–PS were more water attracting than those in Nafion membrane, which would explain the higher conductivity of PBI–PS even at high temperature. Although the different physical states of water molecules in fluorocarbon- and hydrocarbon-based membranes were clearly observed, the nature of the difference and its influence on dissociation and the conduction of protons in those membranes are not well understood. For the development of materials with better proton conductivity especially under low humidity operation, studies on the essential influence of the chemical structure of polymers on the proton conductivity of membranes are important. Theoretical methods are effective for understanding proton conduction at the electronic and atomic levels.³⁴ Paddison et al. studied the effect of the structure of the side chain on proton dissociation under low humidity conditions using the first-principles method.^{35–39} However, the good water uptake property and proton conductivity for hydrocarbon sulfonated polymers in low humidity conditions still remain unexplored. In this study, we investigated the influence of absorbed water molecules surrounding the sulfonic acid group on the proton

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TABLE 1: Geometric Criteria for Classification of Optimized Structures

group	classification criteria		
	$d_{\text{P-Os}}$ (Å)	$d_{\text{P-Ow}}$ (Å)	explanation
a	<1.2		no proton dissociation
b	>1.2 and <1.4	<1.4	proton shared between sulfonic acid group and water
c	>1.4	<1.4	formation of H_3O^+ or H_5O_2^+ ion

dissociation characteristics of fluorocarbon- and hydrocarbon-based membranes using density functional theory (DFT) method.

Computational Method

All DFT calculations were carried out using the Amsterdam Density Functional (ADF) program.^{40–42} A small core was used for the calculations, and triple- ζ plus double polarization function basis sets were applied to all atoms. For the calculations, scalar relativistic corrections within Pauli formalism were adopted and no molecular symmetry was applied. The local density approximation (LDA) with Vosko–Wilk–Nusair local functional⁴³ was employed to optimize geometry. For the optimized geometry, the energy was calculated using generalized gradient approximation (GGA) with Perdew–Wang 1991 exchange and correlation functionals.⁴⁴ We selected LDA for the geometry optimization and GGA for the energy evaluation because the previous study reported LDA gives better geometric structures while GGA provides better energy estimations.⁴⁵ The self-consistent field (SCF) convergence criterion was set as 1×10^{-6} hartree. The charges were evaluated from Hirshfeld population analysis. To investigate the nature of fluorocarbon- and hydrocarbon-based membranes with a minimum computational cost, the smallest subunit models, $\text{CF}_3\text{SO}_3\text{H}$ and $\text{CH}_3\text{SO}_3\text{H}$, were used for fluorocarbon sulfonated and hydrocarbon sulfonated polymers, respectively.

Results and Discussion

1. Proton Dissociation Properties for $\text{CF}_3\text{SO}_3\text{H}$ and $\text{CH}_3\text{SO}_3\text{H}$. To study the dissociation properties of proton in low humidity conditions, geometry optimizations of $\text{CF}_3\text{SO}_3\text{H}$ and $\text{CH}_3\text{SO}_3\text{H}$ were carried out for models with different numbers of surrounding water molecules, λ ($\lambda = 1–6$). Ten initial geometries with different configurations of water molecules were prepared for every λ to analyze interactions as globally as possible because the conformational freedom of water molecules is extremely large. We admit that even 10 different initial structures would not fully suppress the fluctuations due to the conformational freedom of water molecules; however, we believe that good trends in the dissociation properties can be obtained. To systematically analyze the results of geometry optimization, we classified the optimized structures into three categories depending on the distance between the proton of sulfonyl parentage and the oxygen atoms of sulfonic acid group, $d_{\text{P-Os}}$, and the distance between the proton and the oxygen atoms of water molecules, $d_{\text{P-Ow}}$. The detailed criterion is shown in Table 1, and typical optimized structures for each of three categories are shown in Figure 1.

First we checked the energies for respective 10 optimized structures of $\text{CF}_3\text{SO}_3\text{H}$ and $\text{CH}_3\text{SO}_3\text{H}$ systems at $\lambda = 3$. For $\text{CF}_3\text{SO}_3\text{H}$ and $\text{CH}_3\text{SO}_3\text{H}$ systems, we obtained standard deviations of 0.32 and 0.052 eV, respectively. While the overall standard deviation for the $\text{CF}_3\text{SO}_3\text{H}$ system is large, when the structures are classified into three categories according to the criterion shown in Table 1, standard deviations within each

group fall into a range similar to that for $\text{CH}_3\text{SO}_3\text{H}$ (less than 0.1 eV). Then we sorted all results obtained from optimized structures as shown in Figure 2. Figure 2 clearly shows that the proton dissociates from the sulfonic acid group of $\text{CF}_3\text{SO}_3\text{H}$ when it is relatively well hydrated, i.e., with three or more water molecules. This agrees with results observed in the previous work by Paddison on the proton dissociation condition of $\text{CF}_3\text{SO}_3\text{H}$ with λ water molecules ($\lambda = 1–6$) using an ab initio calculation program.³⁸ By contrast, two water molecules abstract the proton from the sulfonic acid group in $\text{CH}_3\text{SO}_3\text{H}$. This implies that the proton dissociates more easily from $\text{CH}_3\text{SO}_3\text{H}$ under low humidity conditions compared to $\text{CF}_3\text{SO}_3\text{H}$. Moreover, by general comparison of proton dissociation results in both systems, we can see a smaller fraction of “nondissociation” and a larger fraction of “dissociation” in the $\text{CH}_3\text{SO}_3\text{H}$ system. This tendency shows the predominance of proton dissociation from $\text{CH}_3\text{SO}_3\text{H}$ in these conditions, corresponding well to the experimentally observed higher proton conductivity of PBI–PS than that of Nafion membrane in low humidity conditions or at high temperature.^{28,33} With five or six water molecules, no statistical difference between these two systems was observed. To clarify the influence of the interactions between the sulfonic acid group and surrounding water molecules on the proton dissociation properties, we analyze in detail in subsequent sections the hydrogen-bonding network formed around the sulfonic acid group, hydration of the sulfonic acid group, and the energy barriers for proton dissociation.

2. Analysis of Interactions between Sulfonic Acid Group and Surrounding Water Molecules. *2.1. Interaction of a Water Molecule with Sulfonic Acid Group.* The interaction energy, E_{int} , of a water molecule with the sulfonic acid group was calculated using the following equation:

$$E_{\text{int}} = E_{\text{interacting system}} - (E_{\text{CX}_3\text{SO}_3\text{H}} + E_{\text{water}})$$

where $E_{\text{CX}_3\text{SO}_3\text{H}}$, E_{water} , and $E_{\text{interacting system}}$ represent the energies of the $\text{CX}_3\text{SO}_3\text{H}$ ($X = \text{F}$ or H), a single water molecule, and the system including both $\text{CX}_3\text{SO}_3\text{H}$ and interacting water molecules, respectively. For a water molecule interacting with the sulfonic acid group, the interaction energies are -69.2 and -76.6 kJ/mol for $\text{CF}_3\text{SO}_3\text{H}$ and $\text{CH}_3\text{SO}_3\text{H}$ systems, respectively. It is clear that a water molecule interacts more strongly with $\text{CH}_3\text{SO}_3\text{H}$ than with $\text{CF}_3\text{SO}_3\text{H}$. To further study the difference, we investigated the atomic charges of each fragment without surrounding water molecules. The average atomic charges of the three oxygen atoms of the sulfonic acid groups in $\text{CF}_3\text{SO}_3\text{H}$ and $\text{CH}_3\text{SO}_3\text{H}$ are -0.217 and -0.249 , respectively. This difference can be attributed to the electron-withdrawing and electron-donating properties of fluorine and hydrogen atoms in the backbone side chain, respectively. We also analyzed the charges on water molecules interacting with the sulfonic acid group. For water molecules interacting with the sulfonic acid group, the average charges are -0.11 and -0.14 in $\text{CF}_3\text{SO}_3\text{H}$ and $\text{CH}_3\text{SO}_3\text{H}$ systems, respectively. For water molecules in the second shell, i.e., water molecules forming hydrogen bonds with the water molecules forming direct hydrogen bonds with the sulfonic acid group, average charges are -0.05 and -0.09 for $\text{CF}_3\text{SO}_3\text{H}$ and $\text{CH}_3\text{SO}_3\text{H}$ systems, respectively. These results indicate that the larger electron transfer from the sulfonic acid group to surrounding water molecules resulted in the stronger interaction energy in the $\text{CH}_3\text{SO}_3\text{H}$ system. These theoretical results gave good support to the experimental suggestion that the water in hydrocarbon-based PBI–PS was attracted more strongly by sulfonic acid groups on the polymer chains compared with fluorocarbon-based Nafion.^{28,33}

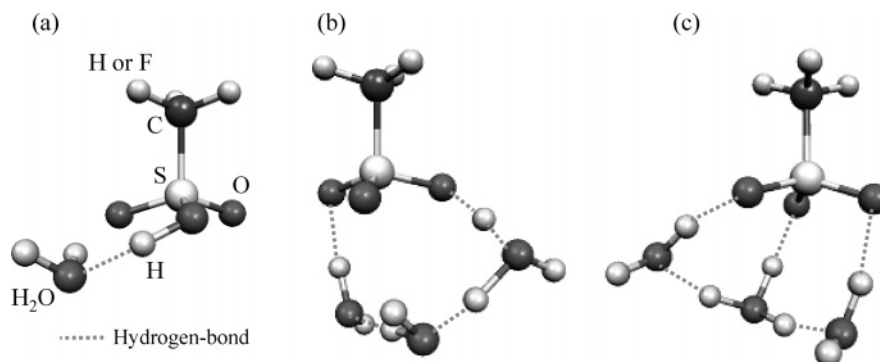


Figure 1. Typical optimized structures for different proton dissociation states: (a) no proton dissociation; (b) proton shared between sulfonic acid group and water; (c) formation of H_3O^+ or H_5O_2^+ ion.

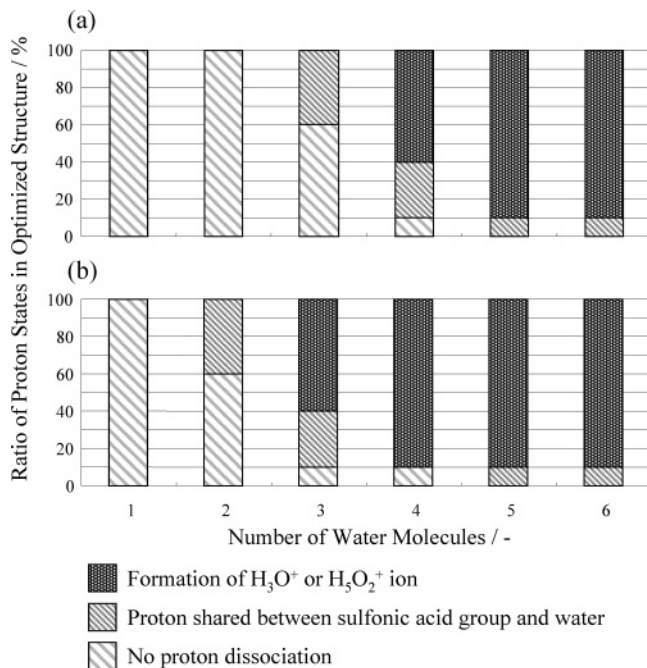


Figure 2. Dependence of proton dissociation states (see Table 1 and Figure 1) on number of surrounding water molecules for (a) $\text{CF}_3\text{SO}_3\text{H}$ and (b) $\text{CH}_3\text{SO}_3\text{H}$.

2.2. Hydration of Sulfonic Acid Group. To further study the interaction of water molecules with sulfonic acid groups in $\text{CF}_3\text{SO}_3\text{H}$ and $\text{CH}_3\text{SO}_3\text{H}$, water distribution around a sulfonic acid group was investigated. For the geometry-optimized $\text{CH}_3\text{SO}_3\text{H}$ and $\text{CF}_3\text{SO}_3\text{H}$ systems, the ratio of water oxygen atoms found within 0.02 Å intervals from 0 to 10 Å was calculated, taking three oxygen atoms of the sulfonic acid group as the center atoms. Because our models include at most six water molecules in the system, all data obtained from 60 trials for both $\text{CH}_3\text{SO}_3\text{H}$ and $\text{CF}_3\text{SO}_3\text{H}$ systems are shown in Figure 3 to give a statistical insight with minimizing statistical noise. The sharp peak of the first hydration shell of sulfonic acid groups is observed at 2.6 Å in both systems (see Figure 3). Water molecules found in this region are classified as directly coordinated with oxygen atoms of the sulfonic acid group through hydrogen bonds. This observation is in good agreement with the reported radial distribution function between sulfonic acid groups and water molecules in fluorocarbon sulfonated polymers.^{46–49} According to our results a remarkable preference for the $\text{CH}_3\text{SO}_3\text{H}$ system with respect to the number of water molecules existing in the first hydration shell is observed even though the distance for the first hydration shell of the sulfonic acid group in both systems is the same. On the other hand, the

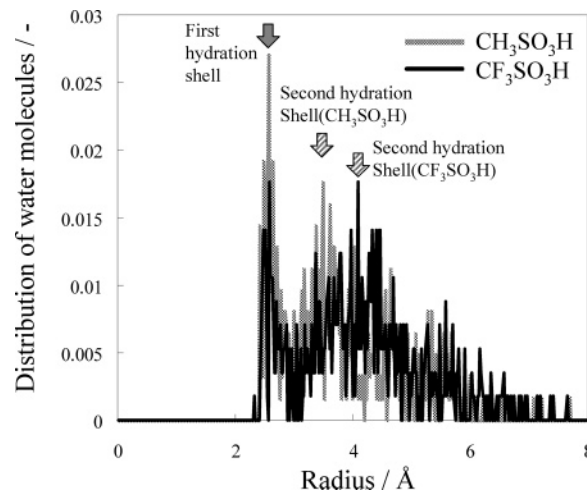


Figure 3. Radial distributions of water molecules around oxygen atoms in sulfonic acid group for $\text{CF}_3\text{SO}_3\text{H}$ and $\text{CH}_3\text{SO}_3\text{H}$.

broad peaks around 3.5 Å for the $\text{CH}_3\text{SO}_3\text{H}$ system and 4.1 Å for the $\text{CF}_3\text{SO}_3\text{H}$ system in Figure 3 are attributed to the second hydration shell of the sulfonic acid group. Contrary to the first hydration shell, the height of the peak in the second hydration shell is nearly the same in both systems. However, the peak observed for $\text{CH}_3\text{SO}_3\text{H}$ (3.5 Å) is shorter than that for the $\text{CF}_3\text{SO}_3\text{H}$ system (4.1 Å), which directly means that water molecules in the second hydration shell are more closely attracted by the sulfonic acid group. This in conjunction with the larger number of water molecules in the first hydration shell for $\text{CH}_3\text{SO}_3\text{H}$ clarifies the better proton dissociation in the $\text{CH}_3\text{SO}_3\text{H}$ system. These results support the experimental observation that hydrocarbon polymers have a tendency to include a large amount of water molecules around the polar groups of polymer chains, which may result in higher conductivities in low humidity conditions or at high temperature.^{28,33}

2.3. Hydrogen-Bonding Network. In this section, we analyze the hydrogen-bonding network for both hydrated $\text{CF}_3\text{SO}_3\text{H}$ and $\text{CH}_3\text{SO}_3\text{H}$ systems to study its influence on proton dissociation properties. It was reported that the average distance between oxygen atoms of water molecules in the hydrogen-bonding network is 2.72 Å with the standard deviation of 0.15 Å.⁵⁰ Tentatively we assume the hydrogen bond is formed when the distance between oxygen atoms is in the range of 2.57–2.87 Å. With this distance criterion we analyzed the number of hydrogen bonds formed in 60 optimized structures for six different λ values with 10 different initial structures as shown in Figure 2. We classified the hydrogen bonds into three types, i.e., hydrogen bonds between (A) the sulfonic acid group and water molecules or H_3O^+ , (B) H_3O^+ or a water molecule directly

TABLE 2: Average Number of Hydrogen Bonds in Categories A, B, and C for $\text{CF}_3\text{SO}_3\text{H}$ or $\text{CH}_3\text{SO}_3\text{H}$ with λ Water Molecules ($\lambda = 2-6$)

1	$\text{CF}_3\text{SO}_3\text{H}$			$\text{CH}_3\text{SO}_3\text{H}$		
	A	B	C	A	B	C
2	1.14	1.00	1.00	1.14	1.00	1.00
3	1.71	1.14	2.00	2.86	1.71	2.00
4	2.29	1.57	2.43	3.14	2.14	3.43
5	1.71	1.71	4.57	3.57	2.14	5.00
6	2.00	2.14	5.57	3.57	2.42	6.43

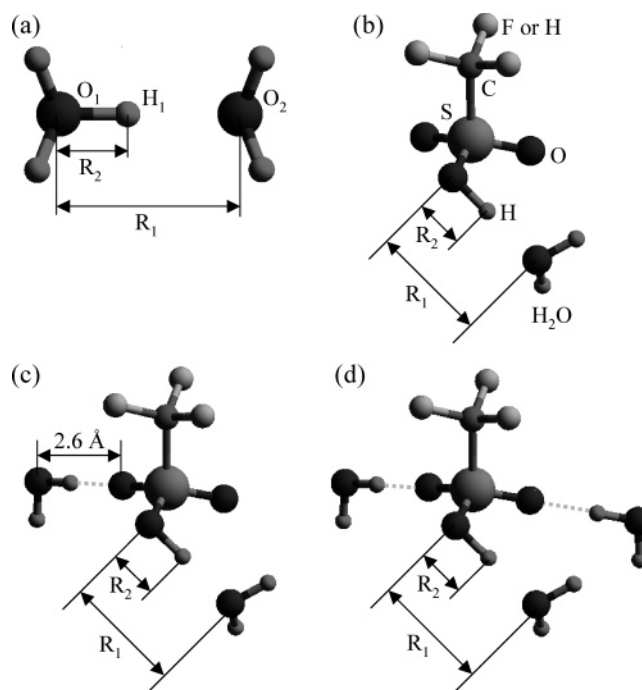
forming a hydrogen bond with the proton in the sulfonic acid group and surrounding water molecules, and (C) within all water molecules (including H_3O^+) in the system.

The numbers of hydrogen bonds obtained from 10 samples for every λ are averaged and summarized in Table 2. Results for $\lambda = 1$ and the highest and the lowest values for the remaining λ are excluded from the statistical analysis. Comparing the overall number of hydrogen bonds formed in both systems over the entire range of water contents, a larger number of hydrogen bonds was found for $\text{CH}_3\text{SO}_3\text{H}$ than for the $\text{CF}_3\text{SO}_3\text{H}$ system. In particular, the number of direct hydrogen bonds between oxygen atoms of the sulfonic acid group and surrounding water molecules is remarkably larger for $\text{CH}_3\text{SO}_3\text{H}$ than that for the $\text{CF}_3\text{SO}_3\text{H}$ system (compare 3.57 vs 2.00 at $\lambda = 6$).

Thus we can conclude that the good hydration property of $\text{CH}_3\text{SO}_3\text{H}$ compared to $\text{CF}_3\text{SO}_3\text{H}$ shown in Figure 3 corresponds to the significant difference in the formation of hydrogen bonds, which can explain the high dissociation ability of $\text{CH}_3\text{SO}_3\text{H}$ in low humidity conditions.

3. Energy Barriers for Proton Transfer. As shown earlier, we have found that the number of water molecules forming hydrogen bonds with the sulfonic acid group was remarkably different for $\text{CH}_3\text{SO}_3\text{H}$ and $\text{CF}_3\text{SO}_3\text{H}$ systems. To study the proton dissociation of $\text{CH}_3\text{SO}_3\text{H}$ and $\text{CF}_3\text{SO}_3\text{H}$ systems with different water coordination states, we investigated the energy barriers for proton transfer from the sulfonic acid group of $\text{CH}_3\text{SO}_3\text{H}$ or $\text{CF}_3\text{SO}_3\text{H}$ to the coordinating water molecules. Before estimating the energy barriers for proton transfers in $\text{CH}_3\text{SO}_3\text{H}$ and $\text{CF}_3\text{SO}_3\text{H}$ systems, we calculated the potential energy profiles for proton transfer from H_3O^+ to its neighboring H_2O using a model of the H_5O_2^+ ion. The coordinates used to investigate the potential energy profiles for the proton transfer were the $\text{O}_1\text{--O}_2$ distance, R_1 , and the $\text{O}_1\text{--H}_1$ distance R_2 , which are shown in Figure 4a. For each curve, R_1 was kept constant while R_2 was increased with an increment of 0.1 Å. The energy barrier predicted by ADF in this study was 15.56 kJ/mol at $R_1 = 2.80$ Å, which is in reasonable agreement with previously reported ab initio calculations with BP86 functional (17.10 kJ/mol) and with B3LYP functional (26.26 kJ/mol).^{51,52} This comparison indicates that the computation scheme adopted in this section gives reasonable estimates of the energy barriers for proton-transfer reactions.

In the investigation of the energy barriers for proton transfer from the sulfonic acid group from $\text{CH}_3\text{SO}_3\text{H}$ or $\text{CF}_3\text{SO}_3\text{H}$ to a coordinating water molecule, we focused on the dependence of

**Figure 4.** Models for estimating the energy barrier for proton transfer: (a) H_5O_2^+ ; (b) $\text{CX}_3\text{SO}_3\text{H} + \text{H}_2\text{O}$; (c) $\text{CX}_3\text{SO}_3\text{H} + 2\text{H}_2\text{O}$; (d) $\text{CX}_3\text{SO}_3\text{H} + 3\text{H}_2\text{O}$. X = F or H.

the energy barriers on the number of water molecules coordinated to the sulfonic acid group. We focused on the analyses for lower λ , i.e., $\lambda = 1, 2$, and 3, to obtain insights on the proton dissociation in low humidity conditions while reducing the extremely numerous degrees of freedom for water configurations. Models for the analyses are shown in parts b, c, and d, respectively, of Figure 4 in which one, two, and three water molecules are included. The distance between an oxygen atom of the sulfonic acid group and an oxygen atom of additionally coordinated water molecule was set to 2.6 Å, corresponding to the peak of the first hydration shell. We prepared these models by geometry optimization after fixing the distance between oxygen atoms of the sulfonic acid group and the coordinating water molecules. Then we evaluated the barriers for the proton dissociation following the procedure for proton transfer in the H_5O_2^+ system described above. Apart from R_1 and R_2 all degrees of freedom were fixed for simplification when we evaluated the energy barriers.

The potential energy profiles for $\text{CH}_3\text{SO}_3\text{H}$ and $\text{CF}_3\text{SO}_3\text{H}$ interacting with two water molecules are shown in Figure 5. For small R_1 the energy profiles show single minimum well shapes without any energy barriers. However, the potential energy curves show asymmetrical double minimum well shapes with energy barriers when R_1 becomes longer than 3.06 Å. The energy barriers for proton transfer are shown in Table 3. Comparing the energy barriers in both systems with single water coordination and the R_1 distance of 3.06 Å where a well-defined double minimum exists, the $\text{CF}_3\text{SO}_3\text{H}$ system shows an energy barrier of 142.5 kJ/mol, lower than that for the $\text{CH}_3\text{SO}_3\text{H}$ system

TABLE 3: Energy Barriers (E_a) for Proton Dissociation in $\text{CX}_3\text{SO}_3\text{H}$ with λ Water Molecules at $R_1 = 3.06$ Å^a

E_a (kJ/mol)					
$\text{CF}_3\text{SO}_3\text{H}$			$\text{CH}_3\text{SO}_3\text{H}$		
$\lambda = 1$	$\lambda = 2$	$\lambda = 3$	$\lambda = 1$	$\lambda = 2$	$\lambda = 3$
142.5	134.3	123.9	170.8	153.0	144.5
	($\Delta E_2 = -8.2$)	($\Delta E_3 = -18.6$)		($\Delta E_2 = -17.8$)	($\Delta E_3 = -26.3$)

^a ΔE_k is defined as the difference of E_a at $\lambda = k$ and $\lambda = 1$.

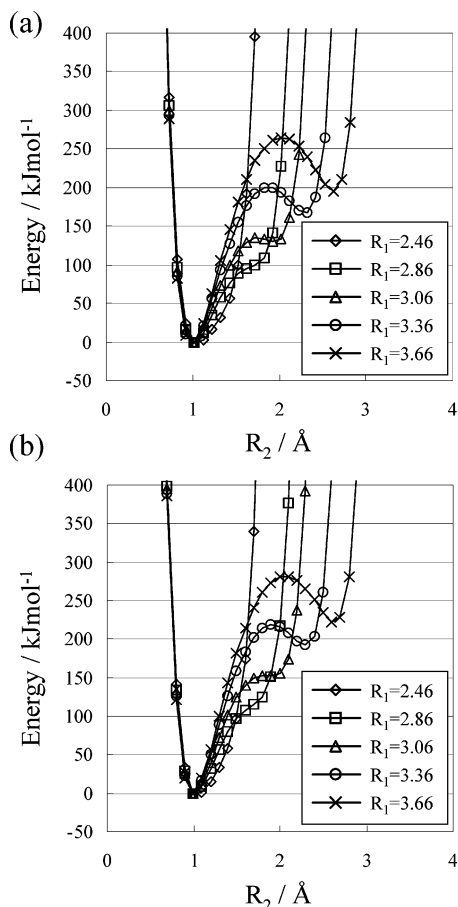


Figure 5. Energy profiles for proton transfer in (a) $\text{CF}_3\text{SO}_3\text{H} + 2\text{H}_2\text{O}$ and (b) $\text{CH}_3\text{SO}_3\text{H} + 2\text{H}_2\text{O}$.

(170.8 kJ/mol). This corresponds to the experimentally reported fact that the energy barriers for proton dissociation from fluorocarbon sulfonated polymers are lower than those for hydrocarbon sulfonated polymers. However, when the coordination number of water increases, the energy barrier decreases more profoundly for $\text{CH}_3\text{SO}_3\text{H}$ than for $\text{CF}_3\text{SO}_3\text{H}$ (compare -17.6 vs -8.2 kJ/mol for $\lambda = 2$ or -26.3 vs -18.6 kJ/mol for $\lambda = 3$). Even if the calculated energy barrier for $\text{CH}_3\text{SO}_3\text{H}$ at $\lambda = 3$ is still higher than that for $\text{CF}_3\text{SO}_3\text{H}$ (possibly due to geometric restrictions), our results show clearly that hydration lowers the energy barrier much more for $\text{CH}_3\text{SO}_3\text{H}$ than for $\text{CF}_3\text{SO}_3\text{H}$. This trend in conjunction with the better hydration properties of $\text{CH}_3\text{SO}_3\text{H}$ (Figure 3) can qualitatively explain its better proton dissociation ability in low humidity conditions (Figure 2).

The conventional design concept for a polymer electrolyte with better proton dissociation property was to use an electron-withdrawing group in the backbone side chain of a sulfonic acid group. However, in low humidity conditions, the importance of a better hydration of a sulfonic acid group, which lowers the energy barrier of the proton dissociation, becomes more significant. Thus our results indicate clearly that both factors, the intrinsic lower energy barrier for the proton dissociation and the better hydration properties of a sulfonic acid group promoting proton dissociation, should be considered to account for efficient proton transfer in low humidity conditions.

Conclusion

Density functional theory calculations for $\text{CF}_3\text{SO}_3\text{H}$ and $\text{CH}_3\text{SO}_3\text{H}$ with surrounding water molecules were performed in

order to understand the influence of fluorocarbon and hydrocarbon backbones on proton dissociation properties in low humidity conditions. From the analysis of the optimized structures, it is observed that the proton dissociation rate is higher for $\text{CH}_3\text{SO}_3\text{H}$ compared to $\text{CF}_3\text{SO}_3\text{H}$. Radial distributions of water molecules around the sulfonic acid group illustrate the better hydration property of $\text{CH}_3\text{SO}_3\text{H}$ than that of $\text{CF}_3\text{SO}_3\text{H}$. Also, the overall number of hydrogen bonds formed in the case of the $\text{CH}_3\text{SO}_3\text{H}$ system is larger than that in the $\text{CF}_3\text{SO}_3\text{H}$ system. These findings agree well with the better proton dissociation property of $\text{CH}_3\text{SO}_3\text{H}$ in low humidity conditions. In contrast, the energy barriers for proton transfer from the sulfonic acid groups of $\text{CH}_3\text{SO}_3\text{H}$ and $\text{CF}_3\text{SO}_3\text{H}$ to a coordinating water molecule studied under the same water coordination are lower for $\text{CF}_3\text{SO}_3\text{H}$ than for the $\text{CH}_3\text{SO}_3\text{H}$ system, which agrees with generally accepted better proton dissociation in fluorocarbon sulfonated polymers than in hydrocarbon sulfonated polymers. However, our study shows that the decrease of the energy barriers with increasing coordination number of water molecules is more pronounced for $\text{CH}_3\text{SO}_3\text{H}$ than for the $\text{CF}_3\text{SO}_3\text{H}$ system, which rationalizes the better performance of $\text{CH}_3\text{SO}_3\text{H}$ under low humidity conditions. This indicates that the realization of better hydration ability is the additional factor critical for low humidity conditions, to be considered to achieve better proton dissociation performance.

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