The effect of different environments on Nafton degradation: Quantum mechanics study

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ABSTRACT

Degradation of the Nafton electrolyte in Proton Exchange Membrane Fuel Cells (PEMFCs) limits the lifetime, motivating development of materials that resist degradation. The mechanism for degradation of Nafton under fuel cell conditions remains uncertain. Studies of Nafton degradation in concentrated OH environments, such as Fenton or vapor HOOH tests, show that the main chain significantly degrades in these conditions. However it has not been established whether this applies to fuel cell conditions. We have used quantum mechanics (Density Functional Theory with the B3LYP and M06 functionals) to determine the mechanism of Nafton degradation under both concentrated OH− and fuel cell conditions. These studies confirm that under concentrated OH− conditions Nafton degrades when peroxide radicals attack end groups (−COOH, −CF−CF2, −CF2H); followed by degradation of Nafton along the polymer main chain, as proposed previously. However we find that under fuel cell conditions, Nafton degradation occurs along the polymer side chain starting with H+ attacking the side chain groups such as the sulfonic acid, −SO3−. We find that it is easier for OH− to attack the main chain than H+, while vice versa, it is easier for H+ radical to attack the side chain than OH−.

1. Introduction

Nafton is a critical component of state-of-the-art Proton Exchange Membrane Fuel Cells (PEMFCs). Currently lifetime of Nafton based PEMFCs is limited to ~2000 h [12], well short of the 5000–10,000 h operational requirement needed for successful automotive applications. In order to improve the durability of Nafton, a number of studies have been performed to determine the mechanism of its degradation [13–17]. In our recent paper [18], we showed that Nafton degradation occurs when OH radicals attack the Nafton side chain. These OH radicals are generated on the Pt (111) surface during fuel cell operation from HOOH and OOH ads with calculated barriers of 0.53 and 0.76 eV, respectively. Our work also provides a potential energy map describing how HOOH and OOH ads can be generated as side reactions during the ORR. This energy map is useful in explaining why certain experimental conditions (such as high H2 concentration) can lead to higher concentrations of HOOH, which in turn generates more OH radicals as shown in experiment [15]. We then showed that these OH radicals can attack vulnerable sites on the Nafton side chain, in particular the sulfonic acid group. Nafton degradation is also initiated in the reaction of the OH radical with H2 to form an H radical, which allows additional degradation reactions (1) breaking the C–F bond of a tertiary carbon to form HF; (2) attacking the sulfonic acid group to form H2SO3, which was found to be a barrierless reaction and as a product in experiments [18]. By barrierless, we mean that the reaction is enthalpically barrierless. The reaction is still limited by the concentration of the rare OH− or H+ reactant, which is a free energy barrier for the reaction to occur. Another possible location of Nafton degradation is the polymer main chain [5,13–16]. While the Teflon chain is very strong, the degradation can be initiated when OH radicals attack end groups (R−COOH, R−CF2−CF2, R−CF2H) or C−H bonds in the main chain (R−CFH−R), which are undesired byproducts of the manufacturing process [5,14]. OH radicals can be introduced in high concentrations through ex-situ tests outside a fuel cell. Fenton’s reagents [19] have been shown to degrade Nafton, and are used to simulate OH radicals in PEMFCs [5,15,16]. Treating Nafton with elemental fluorine to eliminate polymer main chain end groups [20,21] showed dramatic improvements in Nafton durability in Fenton reagents [5,15]. This result led to the early conclusion that radical attack of main chain end groups is the principal mechanism for Nafton degradation [5]. Another high concentration ex-situ experiment is H2O2 vapor tests [22–24]. In addition to accelerating degradation with a high concentration of OH radicals, this
experiment also has the advantage that the relative humidity (RH) can be controlled, making it easy to predict the effect of RH on degradation. Many useful results arise from these studies including evidence suggesting that scission of the main chain occurs during Nafion degradation [24].

While concentrated OH experiments are useful ways to introduce OH radicals into the system at an accelerated rate, the conditions differ from those for actual fuel cells, because there is only trace concentration of radicals during fuel cell operation [9,25]. The difference in OH concentration may lead to different degradation pathways. Another aspect to distinguish fuel cell operating conditions from concentrated OH experiments is the presence of O2 and H2 flowing gases, which can change the mechanism [26]. As shown in this study, these gases preferentially react with certain free radical intermediate and change the degradation pattern. In addition, gas crossover of H2 to the cathode and O2 to the anode of a fuel cell can change the Nafion degradation mechanisms. The goal of this study is to demonstrate how the degradation pathways may change in different conditions and to assist with design strategies at the molecular level to improve the chemical stability of Nafion.

2. Computational methods

Non-periodic QM calculations were carried out using the B3LYP [27,28] hybrid Density Functional Theory (DFT) functional with the Jaguar code [29]. In some cases, the M06 functional [30] was used as well to see how much the results change with higher level DFT. Here we employed the 6–31 g** basis set [31]. All geometries were optimized with the analytic Hessian to determine that the local minima have no imaginary frequencies, whereas the transition state structures have exactly one. The potential energies of the reactant/transition/product states are reported in the Supplemental information. The vibrational frequencies from the analytic Hessian were used to calculate zero-point energy corrections at 0 K, which was added to the Jaguar implicit solvation correction [32] and the QM energy (ΔE) to obtain the enthalpy at 0 K. The Jaguar implicit solvation correction take the charges from quantum mechanics to obtain accurate dipole moments which are entered into a Poisson–Boltzmann solver [33] to solve the linear equation.

For periodic calculations, we used the SeqQuest [34] code for the Perdew, Burke, and Ernzerhof [35] (PBE) flavor of (DFT), with a double zeta plus polarization basis set contracted Gaussian functions optimized for periodic calculations (rather than the plane wave basis often used in periodic systems). The density grid was 6 points per angstrom, while the reciprocal space grid was 5 × 5 × 0. We used the climbing nudged elastic band (NEB) [36,37] function of SeqQuest to calculate reaction barriers. The potential energies of the NEB results are reported in the Supplemental information. We predicted the effects due to solvation using a periodic Poisson–Boltzmann solver [33,38] to obtain the free energy of solute–solvent interaction.

3. Results and discussion

3.1. Concentrated OH* conditions versus fuel cell conditions

To distinguish between experiments under concentrated OH* [5,15,23,24], and fuel cell conditions, where the OH radical concentration is limited, we studied the mechanism of Nafion degradation in four different environments. The first, concentrated OH* environment, allows multiple OH radicals as reagents as found in Fenton reagents [5,15] and H2O2 vapor tests [23,24]. The second, the fuel cell environment, is limited by only one OH radical to initiate reaction. In addition, we allow the H2 and O2 gases as reagents in the fuel cell environment, because they are present as fuel and can diffuse into the membrane during crossover processes in a fuel cell. Crossover of the O2 to the anode [25] and H2 to the cathode are known to be accelerated during start/stop operation [39]. To contrast the role of crossover, we designed a third environment, which has low OH radical concentration, high O2 concentration but no H2 available to simulate the cathode side without crossover. The fourth simulates Nafion degradation occurring at the anode without O2 crossover. In this environment, there is high H2 concentration which leads to H radical but no O2 or OH radical. In the literature, debates still continue on whether Nafion damage occurs more at the anode or the cathode, as post-mortem analysis have shown different conclusions [3,26].

3.2. Degradation under concentrated OH* conditions

We examine the possible reaction mechanisms that lead to chemical degradation of the Nafion polymer (Fig. 1). In order for the polymer main chain to degrade, a possible first step is to initiate the process by attacking one of the three end groups: R–CF3H, R–CF2=CF2, and R–COOH, which appear as results of the manufacturing process [5]. The initiation process of the polymer main chain degradation leaves R* which can be further attacked in the propagation steps. Experiments suggest that radical attack of residual non-fluorinated terminal bonds of the main chain of Nafion is the principal degradation mechanism [5]. Here we will examine if this is the case.

3.2.1. R–CF3H polymer main chain end group initiation

When the end group is R–CF3H or if there is a C–H bond in the main chain, the OH radical can attack this end group as follows:

Degradation initiated at R–CF3H: R–CF3H+OH*→R–CF3H+H2O.

The transition state and energetics are described in Fig. 2 with a barrier of 0.02 eV for the initiation of the polymer degradation at a −CF3H end group. The potential energy of the reactant/transition/product states are reported in the supplemental information.

3.2.2. R–CF2=CF2 polymer main chain end group initiation

When the end group is R–CF2=CF2, the OH radical can attack the end group as follows:


The transition state and energetics are described in Fig. 3A to D. Reaction 3D has the highest barrier of 0.22 eV.

3.2.3. R–COOH polymer main chain end group initiation

When the end group is R–COOH, the OH radical can attack the end group as follows:


Fig. 1. Chemical structure of Nafion. Nafion 117 has an average composition of x=6.5, y=1, z=1. N indicates the nonpolar monomeric units, while P indicates the polar monomeric units.
The transition states and energetics are described in Fig. 4A to B. Reaction 4A has the highest barrier of 0.31 eV.

3.2.4. Propagating polymer main chain degradation

After initiation, degradation can propagate along the main chain continuously. The way it propagates may differ depending whether it is in the concentrated OH\textsuperscript{–} or fuel cell environment.

Chain propagation under the concentrated OH\textsuperscript{–} conditions:

\[ \text{R–CF}_2\text{–CF}_2\text{–} + 2\text{OH}^\cdot \rightarrow \text{R–CF}_2\text{–CF}_2\text{OH}^\cdot \rightarrow \text{R–CF}_2\text{–CF}_2\text{O}^\cdot + \text{H}_2\text{O} \rightarrow \text{R–CF}_2\text{–O} + \text{H}_2\text{O} \rightarrow \text{R–CF}_2 + \text{CO}_2 + 2\text{HF}. \]

The reaction can be reproduced continuously with a –CF\textsubscript{2} monomer unit breaking off each time. The product carbonyl fluoride, O\(\equiv\)CF\textsubscript{2}, is known to react spontaneously with water to form HF and CO\textsubscript{2} \[40\]. The energetics and barriers are shown in Fig. 5A to C. Chain propagation in concentrated OH\textsuperscript{–} environments...
has a barrier of 0.09 eV. Rather than reacting with OH radical, the R–CF2–CF2OH can react with H2O alternatively in the following two water catalyzed reaction:

\[
\text{R–CF}_2\text{-CF}_2\text{OH} + 3\text{H}_2\text{O} \rightarrow \text{R–CF}_2\text{-CF} = \text{O} + 2\text{H}_2\text{O} + \text{HF} \quad \text{R–CF}_2\text{-COH} = \text{O} + \text{H}_2\text{O} + 2\text{HF}
\]

This alternative mechanism has a barrier of 0.31 and 0.42 eV and the product is a carboxylic acid. We show the transition states in Fig. 5B-ii and 5C-ii. These calculated water catalyzed barriers were found to be much lower than our previous calculation (1.94 and 1.20 eV, respectively) [18] without considering water spectator specie. There is strong evidence for this water catalyzed reaction, during H2O2 vapor tests, where the concentration of carboxylic acid increased over time, suggesting main chain scission [24]. The main chain scission can occur and form carboxylic acid as follows in a concentrated OH− environment:

1) R–CFH–CF2–R+OH−→R–CF−–CF2–R+H2O (Fig. 2)
2) R–CF–CF2–R+OH−→R–CFOH–CF2–R (Fig. 5A)
3) R–CFOH–CF2–R+OH−→R–CFO−–CF2–R+H2O (Fig. 5B-i)
4) R–CFO−–CF2–R→R–CF−→O+CF2–R (Fig. 5C-i)
5) R–CF=O+′CF2–R+OH−→R–CF=O+COF2–R (Fig. 5A)
6) R–CF=O+COHF2–R→2(R–CF=O)+HF (Fig. 5B-ii)
7) R–CF=O+H2O→R–COH=O+HF (Fig. 5C-ii)

Indeed, the polymer main chain degradation is very fast in concentrated OH− environment agreeing with experiments [5].

3.2.5. Side chain degradation
The degradation of the Nafion side chain was described in detail in our previous work [18]. Three possible degradation mechanisms were described. In the concentrated OH− environment, since there is no H2 gas, the only OH− reacts with the sulfonic acid end group directly.

3.3. Degradation under the fuel cell conditions
In the fuel cell environment, the concentration of OH radical is very low [9,25]. A trace OH radical can initiate the degradation, but more than one OH radical involved in the reaction is unlikely. The presence of O2 and H2 from crossover can continue to degrade the


The barrier for this reaction is 0.96 eV with the dimensions of the transition state described in our earlier work [18]. The SO42− product agrees with side chain degradation products described in Fenton experiments [16], whereas the fuel cell experiments show degradation products of SO32− [3] but no evidence of SO42−.

The product R–CF2 can further degrade the side chain, as described previously [18], forming alkene or epoxide products that can easily react with water to form HF. Also, under concentrated OH− conditions, OH radicals can attack R–CF2 to form R–CF2–OH and then R–CF2–O−, which can break off to form R′+O=C≈CF2 in a way similar to the mechanism described in Section 3.2.4. For all intent and purposes, once the sulfonic acid group is removed, the side chain loses its usefulness. Therefore, the most important step for side chain degradation is the first step that removes the sulfonic acid group with a barrier of 0.96 eV.

We find that, indeed under concentrated OH− environments, the polymer main chain is easier to degrade than the polymer side chain. The barrier to continuously attack the polymer main chain with OH radical is 0.09 eV, while the barrier to attack the polymer side chain is 0.96 eV. In more recent experiments, where Nafion was pretreated to eliminate main chain end groups [15], it was found that Nafion degradation of both the main chain and side chain occurred in a Fenton environment. The product of the side chain degradation was SO32− agreeing with the product of our proposed mechanism.

Fig. 5. Degradation propagation of the polymer main chain in a Fenton environment starting from the products of Figs. 2, 3D, and 5B, with a rate-determining step barrier of 0.09 eV (B3LYP). The product of 5C-i can continue to degrade by starting from reactant 5A. The alternative reaction with water in 5Bii to 5Cii is likely, but has a higher barrier of 0.31 and 0.42 eV. The R–COOH product of 5C-ii was found in H2O2 vapor tests [24] and can continue to degrade by starting from reactant 4A.
polymer main chain once the degradation reaction has been initiated.

3.3.1. Polymer main chain end group initiation

For the case of \(-\text{CF}_2\text{H}\) and \(-\text{COOH}\) end groups, the initiation is the same as in the concentrated OH\(^-\) environment shown above and described in Figs. 2 and 4. The mechanism for degradation initiation of the R–CF\(_2\) end group is different because the mechanism described in Fig. 3 involves multiple OH radicals. Therefore, an alternative initiation mechanism for the R–CF–CF\(_2\) end group is proposed as follows, involving only one OH radical, which would correspond to an environment with a low OH radical concentration:

Degradation initiated at R–CF–CF\(_2\) under the fuel cell conditions: R–CF\(_2\)–CF\(_2\)–CF\(_2\)–O\(^-\) + H\(_2\) \rightarrow R–CF\(_2\)–CF\(_2\)–CF\(_2\)–OH + H\(_2\) \rightarrow R–CF\(_2\)–CF\(_2\)–CF\(_2\)–CFOH + H\(_2\) \rightarrow R–CF\(_2\)–CF\(_2\)–CF\(_2\)–CFO\(^-\) + H\(_2\)O + O\(_2\) \rightarrow R–CF\(_2\)–CF\(_2\)–CF\(_2\) + O \rightarrow \text{CFCF}_2\text{OH} + H\(_2\)O.

The barriers and energetics are described in Fig. 6. Reaction 6B has the highest barrier of 0.74 eV.

In a fuel cell environment, H\(^+\), formed from the reaction between H\(_2\) and OH\(^-\), can also attack the polymer main chain to cause degradation initiation, but it was found that the barriers are higher with H\(^+\) than with OH\(^-\). We will describe degradation of the main chain by H\(^+\) in a later section.

3.3.2. Propagating polymer main chain degradation

In the fuel cell environment, there is a limited amount of OH radicals. Since the OH radical is involved in the initiation step, the propagation of the polymer main chain degradation will involve more plentiful species, such as O\(_2\) and H\(_2\).

Chain propagation under the fuel cell conditions: R–CF\(_2\)–CF\(_2\)–O\(^-\) + O\(_2\) + H\(_2\) \rightarrow R–CF\(_2\)–CF\(_2\)–O\(^-\) + O\(_2\) \rightarrow R–CF\(_2\)–CF\(_2\)–CFO\(^-\) + H\(_2\)O \rightarrow R–CF\(_2\)–CF\(_2\)–CFO\(^-\) + H\(_2\)O \rightarrow R–CF\(_2\)–CF\(_2\) + O \rightarrow \text{CFCF}_2\text{OH} + H\(_2\)O.

The related energetics and barriers are shown in Fig. 7. The reactions can be reproduced with the final R–CF\(_2\) product, continuously propagating along the polymer main chain. Reaction 7B has the highest barrier of 0.59 eV. We find that degradation propagation of the main chain has relatively low barrier for both environments, but it is more difficult in the fuel cell conditions than under concentrated OH\(^-\) conditions. The present mechanism under the fuel cell conditions requires gas crossover where either H\(_2\) crosses over to the cathode or O\(_2\) crosses over to the anode across the membrane [25].

3.3.3. Side chain degradation

Rather than attacking the sulfonic acid group directly, the OH\(^-\) can react with H\(_2\) to form H\(^+\) (\(\Delta E = -0.59\) eV, barrier = 0.04 eV) [18]. The H\(^+\) can react with F attached on tertiary carbon to form HF (\(\Delta E = -1.05\) eV, barrier = 1.00 eV) or the sulfonic acid group to form HSO\(_3\)\(^-\) (\(\Delta E = -0.91\) eV, no barrier) [18]. The product HSO\(_3\)\(^-\) can form H\(_2\)SO\(_4\) or SO\(_3\), which was found by mass spectroscopy near the cathode of a fuel cell [3]. It is interesting to note that the same experiments did not find H\(_2\)SO\(_4\) or SO\(_3\), which was found in Fenton degradation experiments [16]. Thus, we see that the experiments support our result that in a fuel cell, the sulfonic acid degrades to SO\(_3\)^{-}2, while in Fenton reagent, the sulfonic acid degrades to SO\(_4\)^{2-}.

3.4. Degradation under fuel cell conditions without crossover at the cathode

At the cathode without crossover, there is no H\(^+\) as a reactant because of the lack of H\(_2\). Main chain degradation initiation and propagation can still occur but at higher reaction barriers. For the end groups, the degradation initiation is the same as shown in Figs. 2 and 4, except for the R–CF–CF\(_2\), which we propose the following mechanism (Fig. 8): R–CF\(_2\)–CF–CF\(_2\)–OH + O\(_2\) + H\(_2\)O \rightarrow R–CF\(_2\)–CF–CF\(_2\)–CFO\(^-\) + H\(_2\)O \rightarrow R–CF\(_2\)–CF–CF\(_2\)–CFO\(^-\) + H\(_2\)O \rightarrow R–CF\(_2\)–CF–CF\(_2\) + O \rightarrow \text{CF}–\text{CF}_2\text{OH} + \text{HOOH}.

Fig. 6. Initiation mechanism for degradation in the fuel cell environment of the R–CF–CF\(_2\) end group. In the fuel cell environment, the OH attacks and breaks the double bond followed by O\(_2\) gas attacking the radical and subsequent reaction with H\(_2\) gas. The rate-determining step is 6B with a barrier of 0.74 eV (B3LYP). The difference between this mechanism and the Fenton environment mechanism in Fig. 3 is that it is limited to only one OH\(^-\) reactant.
We find that the step reaction shown in Fig. 8A, has the highest barrier of 1.20 eV among the whole process. The main chain radical, R–CFQCF2, can undergo continued degradation as follows.

Chain propagation under fuel cell conditions without crossover at the cathode: $\text{R}–\text{CF}_2–\text{CF}_2–\text{O}_2 + \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{R}–\text{CF}_2–\text{CF}_2–\text{O}_2 – \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{R}–\text{CF}_2–\text{CF}_2–\text{OO} + \text{OH} + \text{OH} + \text{H}_2\text{O} \rightarrow \text{R}–\text{CF}_2–\text{CF}_2–\text{OH} + \text{OH} + \text{OH} + \text{H}_2\text{O}.

We find that the reaction (R–CF2–CF2–O2 + H2O → R–CF2–CF2–OO + H2O → R–CF2–CF2–OH + OH + H2O) has a calculated reaction enthalpy of 0.97 eV as shown in Fig. 9A, making it the rate-determining reaction. Note that, for this reaction, the reaction enthalpy (0.97 eV) is higher than the reaction barrier (0.92 eV). This is due to ZPE and solvation corrections, and there is indeed a true transition state for this reaction as shown in the supplemental information. From the comparison of these results and the results with crossover, we find that the barrier for main chain degradation is higher when there is no H2 crossover gas with chain propagation barrier of 0.97 versus 0.59 eV. For the degradation of the side chain, we know that without H2, the barrier to break the sulfonic acid group is 0.96 eV [18], whereas the reaction is completely barrierless with H2. Therefore, without H2 gas at the cathode from crossover, Nafton degradation is more difficult.

### 3.5. Degradation under fuel cell conditions without crossover at the anode

Radicals that degrade Nafton can be generated directly at the anode from Pt and H2 [17]. Nafton degradation can also occur in particular dry conditions when HOOH travels to the anode from the cathode [41], forming OH radicals on the Pt catalyst [18].

The theoretical solvated binding energy of H2 on Pt is 2.83 eV [38]. We determined the barrier for the removal of H2 from the Pt (111) surface. The solvated barrier was found to be 3.69 eV, as shown in Fig. 10A. This result indicates that making H2 from Nafton is quite difficult at the anode. We propose an alternative mechanism to generate H2 that involves the generation of H2 directly from H2 on the Pt anode in the following Pt (111) surface catalyzed reaction: Pt (111) + H2 → Pt –H (111) + H2. The transition state and
barrier of this reaction are shown in Fig. 10B and the solvated barrier for H⁺ generation is 2.27 eV.

Compared to the barrier to generate OH⁻ from Pt–OOH (0.76 eV) and Pt–HOOH (0.53 eV) [18], this barrier is much higher. We find that the Pt surface does catalyze the generation of H⁺ from H₂, but forming radicals in this fashion is more difficult than forming radicals at the cathode. The H radical can subsequently attack the different main chain end groups with the mechanisms as follows:

Degradation initiated at R–CF₂H under fuel cell conditions without crossover at the anode (Fig. 11A): R–CF₂H + H⁺ → R–CF₂ + H₂.

![Figure 10](image1.png)

Fig. 10. Mechanisms to generate H⁺ from H₂ at the anode. The energetics of the solvated and gas phases is described by regular and italic numbers, respectively. The mechanism in 10A shows how H, adsorbed on the Pt catalyst, can break off directly from the surface with a barrier of 3.69 eV. As an alternative mechanism, H₂ can form Had + Hd with a lower barrier of 2.27 eV as shown in Fig. 10B. The high barriers show the energetic difficulty of generating a radical at the anode from H₂ and Pt.

![Figure 11](image2.png)

Fig. 11. Initiation and propagation mechanisms in the fuel cell environment of the R–CF₂H end group at the anode without O₂ crossover. The initiation starts with H radical formed at the anode attacking the –CF₂H end group to form –CF₂ and H₂ with a barrier of 0.31 eV (B3LYP). Degradation propagation can continuously occur with the breaking of the C–C bond to form CF₂ = CF₂, which is the rate-determining step with a barrier of 1.41 eV (B3LYP).
Degradation initiated at R–CF2=CF2 in fuel cell conditions without crossover at the anode (Fig. 12): 
\[ \text{R–CF2=CF2}\rightarrow\text{H}^{+}\rightarrow\text{R–CF2–CFH–CF2}^{\#}\rightarrow\text{R–CF2}^{\#}+\text{CH}=\text{CF2}. \]

Degradation initiated at R–CF2–COOH in fuel cell conditions without crossover at the anode (Fig. 13): 
\[ \text{R–CF2–COOH}\rightarrow\text{H}^{+}\rightarrow\text{R–CF2–CH(OH)O}^{\#}\rightarrow\text{R–CF2}^{\#}+\text{O}=\text{CH}(\text{OH}). \]

The transition states for the three end groups, R–CF2H, R–CF, and R–CF2–COOH are 0.31, 1.24, and 0.62 eV, respectively. All of the main chain initiation barriers are higher with H+ than with OH−. After initiation, the main chain can continue to degrade with the following mechanism, which is more difficult without O2.

Chain propagation under fuel cell conditions without crossover (Fig. 11B): 
\[ \text{R–CF2–CF2}^{\#}\rightarrow\text{R–CF2}^{\#}+\text{CF2}=\text{CF2}. \]

This reaction has a reaction enthalpy of 1.36 eV and reaction barrier of 1.41 eV, as shown in Fig. 11B, and occurs continuously along the main chain. Another possible reaction is for R–CF2 to react with water: 
\[ \text{R–CF2}^{\#}+\text{H}_2\text{O}\rightarrow\text{R–CF2OH}+\text{H}^{+}. \]

However, this reaction has a higher energy barrier of 1.86 eV and is less likely. Thus, we see that the main chain degradation is more difficult at the fuel cell anode without O2 crossover, when compared to degradation at the cathode without H2 crossover.

As mentioned above, the barrier to attack the side chain with H+ is lower than with OH− [18]. However, the barrier to generate this H+ at the anode is quite high, 2.27 eV. Thus, it might be possible for H+ to be generated at the anode and attack the Nafion membrane [17], but the concentration of H+ would be low. Energetically, it is more favorable for H2 to crossover and react with OH− to form H+.

Table 1 summarizes the highest barrier for main chain degradation for different end groups and environments. We also include the barriers for OH and H radicals to attack the protonated and unprotonated side chain end group, R–SO3H and R–SO3. When comparing the B3LYP and M06 results, the B3LYP level of DFT seems to be accurate enough with a difference in calculated energy of around 0.1 eV, except in the cases where the barriers were quite large (>1.2 eV). We find that polymer main chain degradation is favorable in concentrated OH− environments with a barrier as low as 0.09 eV. On the other hand, the side chain degradation is more difficult and has an initiation barrier of 0.96 eV.

Under the fuel cell conditions, because there is less OH radicals, the barrier for the degradation of the polymer main chain is much higher, 0.59 eV, if gas crossover occurs. The barrier for side chain degradation will be lower because of the presence of H+, which makes reactions to remove the sulfonic acid group barrierless. This explains why mostly side chain group products are observed in degradation experiments conducted in a fuel cell-like environment [3,13,26]. Under the fuel cell conditions without crossover, it was shown that both main and side chain degradations are more difficult with barriers as high as 1.41 eV for the main chain and 0.96 eV for the side chain.

Based on the various scenarios studied, the most energetically favorable degradation mechanism in PEMFC occurs when H2 gas from the anode reacts with OH− from the cathode to form H+ (0.04 eV barrier). This H+ then attacks the Nafion side chain sulfonic acid groups resulting in reaction products H2SO3 or SO2 (barrierless) [3]. The only significant barrier in this mechanism is the formation of OH−, which has been shown to be formed from HOOH and Pt with a barrier of 0.59 eV [18]. The alternative mechanism to generate H+ directly from H2 and Pt was calculated to be more difficult with a higher barrier of 2.49 eV.

In order to make this proposed mechanism more difficult at the molecular level, replacing Pt with alternative catalysts that do not favor the formation of OH− from HOOH is a possible strategy to improve Nafion durability. Catalysts that have lower OH binding [42] will make the reaction HOOH→OH−+OHrad more difficult by increasing this 0.53 eV barrier. Care must be made that the new catalyst does not lead to higher HOOH generation, which will lead to higher OH− production. For example, Au which has a lower OH binding.
binding energy produces more HOOH during the ORR [43] than Pt, although it is not always the case that the OH binding energy and HOOH production are correlated.

4. Conclusions

Using DFT, we have studied the degradation of the Nafion main chain in concentrated OH− and fuel cell environments: 

**Concentrated OH**− conditions: During concentrated OH− experiments such as Fenton or HOOH vapor tests, the environment contains high concentrations of OH radicals and water, but no O2 and H2 gas.

**Polymer main chain**: We find the highest barrier in the degradation process for different end groups are 0.31, 0.22 and 0.09 eV for R−COOH, R−CF−CF2 and R−CF2H, respectively. Such a low barrier suggests that the main chain degradation is not difficult at high OH radical concentrations.

**Polymer side chain**: In comparison, the barrier for degradation of the side chain is 0.96 eV.

**Fuel cell conditions**: During PEM fuel cell operations, water, O2 and H2 gas are present in the environment. There is only trace concentration of peroxy radicals. Therefore, we limit the degradation mechanism to contain only one OH radical reactant.

**Polymer main chain**: We find the rate-determining barrier for different end groups to be 0.59, 0.74 and 0.59 eV for R−COOH, R−CF−CF2 and R−CF2H, respectively.

**Polymer side chain**: In comparison, there is no barrier to degrade the sulfonic acid group.

**Fuel cell conditions without crossover at cathode**: Without crossover, there is no H2 to participate in the reaction.

**Polymer main chain**: We find the rate-determining barrier for different end groups to be 0.97, 1.19 and 0.97 eV for R−COOH, R−CF−CF2 and R−CF2H, respectively.

**Polymer side chain**: In comparison, the barrier for degradation of the side chain is 0.96 eV.

**Fuel cell conditions without crossover at anode**: Without crossover, there is no O2 or HOOH to participate in the reaction.

**Polymer main chain**: We find the rate-determining barrier to be 1.41 eV for all end group cases.

**Polymer side chain**: In comparison, there is no barrier to degrade the sulfonic acid group with H+, although it is very difficult to generate the H+ at the anode with a barrier of 2.27 eV.

A significant finding from our theoretical study is that the mode of degradation (main chain or side chain) is dependent on the environment. We find that in concentrated OH− environment, the barrier for degradation to occur on the main chain is 0.09 eV, while attacking the side chain has a barrier of 0.96 eV. This is in contrast to a fuel cell environment, where the barrier for degradation to occur at the main chain is 0.59 eV, while attacking the side chain has no barrier. As discussed previously [26], the fuel cell environment is more complicated than a concentrated OH− environment because of the presence of both OH− and H+. In addition, we showed that the high concentration of OH− can skew the degradation experiments to favor main chain degradation over side chain degradation. Therefore, to accurately study Nafion degradation, the concentrations of HOOH, H2, and O2 need to emulate that of a fuel cell.

Our comparison study of Nafion degradation at the anode versus the cathode showed that degradation is more difficult without gas crossover for both main chain and side chain degradation. At the cathode, main chain degradation can still occur without H2, but the mechanism is more difficult with a higher barrier for main chain propagation of 0.97 eV versus 0.59 eV. Side chain degradation is also more difficult without H+.

At the anode, the main chain and side chain degradation begins with H+. Our calculations show that the generation of H+ from H2 and Pt has a high barrier of 2.27 eV. This H+ can attack both the main chain and the side chain, and we showed that the barrier to attack the main chain without O2 from the cathode is 1.41 eV.

We find that the rate limiting degradation barrier increases in a fuel cell both on the main chain (from 0.59 eV to 0.97 eV) and the side chain (from 0 to 0.96 eV), if crossover is eliminated at the cathode. We predict that the reduction of H2 gas crossover will reduce the rate of degradation reactions. This can be accomplished with membranes that are less vulnerable to H2 crossover. Another strategy to reduce Nafion degradation would be to find catalysts

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**Table 1**

DFT predicted reaction barriers (eV) for Nafion degradation of different end groups in the main chain and side chain for four environments.

<table>
<thead>
<tr>
<th>Environment</th>
<th>Main chain end group</th>
<th>Side chain end group</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R−CF2H</td>
<td>R−CF=CF2</td>
</tr>
<tr>
<td>Concentrated OH−</td>
<td>0.02 Fig. 2 (0.06)</td>
<td>0.22 Fig. 3d (0.24)</td>
</tr>
<tr>
<td></td>
<td>0.09 Fig. 5b−i (0.18)</td>
<td>0.09 Fig. 5b−i (0.18)</td>
</tr>
<tr>
<td>Fuel cell (With H2/O2 crossover)</td>
<td>0.02 Fig. 2 (0.06)</td>
<td>0.74 Fig. 6b (0.071)</td>
</tr>
<tr>
<td></td>
<td>0.59 Fig. 7b (0.57)</td>
<td>0.59 Fig. 7b (0.57)</td>
</tr>
<tr>
<td>Fuel cell (No crossover, cathode)</td>
<td>0.02 Fig. 2 (0.06)</td>
<td>1.20 Fig. 8a (1.15)</td>
</tr>
<tr>
<td></td>
<td>0.97 Fig. 8b (0.97)</td>
<td>0.97 Fig. 8b (0.97)</td>
</tr>
<tr>
<td>Fuel cell (No crossover, anode)</td>
<td>0.31 Fig. 11a (1.55)</td>
<td>1.24 Fig. 12b (1.58)</td>
</tr>
<tr>
<td></td>
<td>1.41 Fig. 11b (1.55)</td>
<td>1.41 Fig. 11b (1.55)</td>
</tr>
</tbody>
</table>

* Energies are calculated using B3LYP and M06 (in parentheses) functionals. Under concentrated OH− conditions, degradation of the polymer main chain has a barrier as low as 0.09 eV, while degradation of the side chain has a higher barrier of 0.81 or 0.96 eV. In the fuel cell environment, degradation of the side chain is barrierless, while the barrier for the main chain degradation is 0.39 eV. Under the fuel cell conditions at the cathode, there is no H2 crossover, the barriers are significantly higher for both main and side chain degradations. Under the fuel cell conditions at the anode, where there is no O2, the barriers are significantly higher for the main chain degradation and the reaction is barrierless for the side chain degradation.

b The reaction to generate a radical at the anode from H2 has much higher barrier versus the reaction to generate a radical at the cathode from HOOH (2.27 eV versus 0.53 eV).
that have a lower OH\textsuperscript{−} binding energy than Pt. This would make the barrier to generate OH\textsuperscript{−} from HOOH and Pt more difficult, limiting the generation of radicals that causes Nafion degradation.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.memsci.2013.02.060.

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