

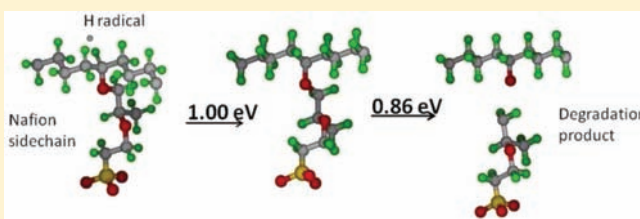
Mechanism for Degradation of Nafion in PEM Fuel Cells from Quantum Mechanics Calculations

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ABSTRACT: We report results of quantum mechanics (QM) mechanistic studies of Nafion membrane degradation in a polymer electrolyte membrane (PEM) fuel cell. Experiments suggest that Nafion degradation is caused by generation of trace radical species (such as OH[•], H[•]) only when in the presence of H₂, O₂, and Pt. We use density functional theory (DFT) to construct the potential energy surfaces for various plausible reactions involving intermediates that might be formed when Nafion is exposed to H₂ (or H⁺) and O₂ in the presence of the Pt catalyst. We find a barrier of 0.53 eV for OH radical formation from HOOH chemisorbed on Pt(111) and of 0.76 eV from chemisorbed OOH_{3,d}, suggesting that OH might be present during the ORR, particularly when the fuel cell is turned on and off. Based on the QM, we propose two chemical mechanisms for OH radical attack on the Nafion polymer: (1) OH attack on the S–C bond to form H₂SO₄ plus a carbon radical (barrier: 0.96 eV) followed by decomposition of the carbon radical to form an epoxide (barrier: 1.40 eV). (2) OH attack on H₂ crossover gas to form hydrogen radical (barrier: 0.04 eV), which subsequently attacks a C–F bond to form HF plus carbon radicals (barrier as low as 1.00 eV). This carbon radical can then decompose to form a ketone plus a carbon radical with a barrier of 0.86 eV. The products (HF, OCF₂, SCF₂) of these proposed mechanisms have all been observed by F NMR in the fuel cell exit gases along with the decrease in pH expected from our mechanism.



1. INTRODUCTION

Proton exchange membrane fuel cells (PEMFCs) convert hydrogen to electricity efficiently, with water as its main waste product. Their small size and low operating temperature (~ 70 – 85 °C) make PEMFCs ideal for automotive applications if Nafion membranes could meet the 5000–10 000 h operational requirement. The general consensus is that hydrogen peroxide and radicals are involved in the chemical degradation of Nafion.^{1–14} The presence of such radicals has been detected directly through spin-trapping ESR methods^{10,12,14} in a fuel cell environment. However, there are several distinctly different interpretations of these experiments on how the radicals are generated and what mechanism is responsible for the Nafion chemical degradation. Because hydroxyl radicals are introduced by Fenton's reagents, many experiments have been conducted to show that Nafion does degrade in the presence of Fenton's reagents.^{1,5,7} Because appreciable quantities of Fenton's reagents are not observed under normal fuel cell operating conditions, it has been suggested^{8,9} that Pt nanoparticles break off from the cathode/anode catalyst during operation and form Fenton-like reagents with HOOH once they are in the membrane. However, experiments show that chemical degradation of Nafion can occur without nanoparticles breaking off,^{1–3,6} leading to the conclusion that hydroxyl radicals must be generated even when the Fenton-like reagents are not presented.

Nafion has excellent thermal and mechanical stability due to its fluoropolymer structure (Figure 1). But there is evidence that Nafion chemically degrades through OH radical attack at defects

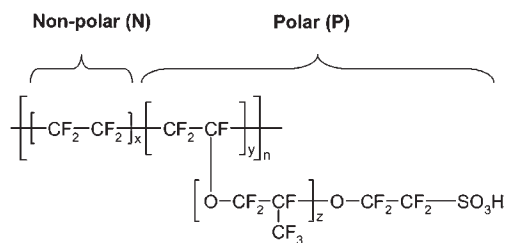


Figure 1. Chemical structure of Nafion. Nafion 117 has an average composition of $x = 6.5$, $y = 1$, $z = 1$. N indicates the nonpolar monomeric units while P indicates the polar monomeric units.

such as C–H and C=C that might result from the manufacturing process.^{4,7} An often-cited defect vulnerable to such attack is the main chain carboxylic acid group that appears unintentionally from the initiators during the polymerization process.^{1,5,6}

Many mitigation strategies have been proposed to reduce Nafion degradation in PEMFCs including the following: (1) decreasing Fenton contaminants; (2) chemically degrading OH radicals that are formed during operation; (3) chemical stabilization of defect sites; (4) membrane reinforcement during cycling.¹⁵

It would be useful to obtain a good understanding of the degradation mechanism, so that the focus could be on the most

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Table 1. DFT-Predicted Reaction Energetics Involved in the Formation of OH Radical on a Pt Surface^a

reaction step barrier (eV)	ΔE (gas)	E_{TS} (gas)	ΔE (solv)	E_{TS} (solv)
$H_{ad} + OOH_{ad} \rightarrow HOOH_{ad}$ (Figure 2A)	0.23	0.53	-0.09	0.26
$HOOH_{ad} \rightarrow OH_{ad} + OH^*$ (Figure 2B)	0.76	0.77	0.35	0.53
$OOH_{ad} \rightarrow O_{ad} + OH^*$ (Figure 2C)	0.91	0.97	0.42	0.76
$HOOH_{ad} \rightarrow 2OH_{ad}$ (Figure 2D)	-1.31	0.45	-1.88	0.12

^a The energy of the reaction, ΔE , and barrier, E_{TS} , for the reactions are shown for both gas phase and solvation phase. The corresponding structures of the reaction are shown in Figure 2.

relevant strategies. For example, the strategy of reducing Fenton contaminants may be ineffective, if Fenton's reagents are not the source of the OH radical. Also, the strategy to chemically stabilize defect sites may not be effective, if the sites inherent to Nafion are vulnerable to radical attack.

Recently, Ghassemzadeh et al.⁶ used F NMR to show that *Nafion degradation occurs only when Pt catalyst, H₂ and O₂ are all present, but not otherwise*. Their work emulated conditions for fuel cell operation at cathode and anode, when either H₂ or O₂ may cross over to the other electrode. After 120 h of operation, the F NMR showed significant loss (~10%) of OCF₂ and SCF₂ side-chain groups. This and some other studies^{2,3} suggest that the degradation can occur at relatively mild open circuit conditions, where there is no dissolution of Pt catalyst into Nafion. In addition, Ghassemzadeh⁶ observed significant degradation at the side chains and proposed mechanisms by which Nafion can degrade through nondefect side-chain sites.

Here, we investigate mechanisms underlying the chemical degradation of Nafion under open-circuit conditions using first-principles quantum mechanics (QM) as outlined in section 2. Section 3 reports results of calculating the energetics of various possible degradation mechanisms.

2. COMPUTATIONAL METHODS

We used the SeqQuest¹⁶ code for the Perdew, Burke, and Ernzerhof¹⁷ (PBE) flavor of density functional theory (DFT) with a double- ζ plus polarization basis set of contracted Gaussian functions optimized for periodic calculations. Our calculations used a periodic slab of Pt with six closest packed layers. The density grid was six points per angstrom, while the reciprocal space grid was $5 \times 5 \times 0$. We also predicted the effects due to solvation using a periodic Poisson-Boltzmann solver^{18,19} to obtain the free energy of solute-solvent interaction.

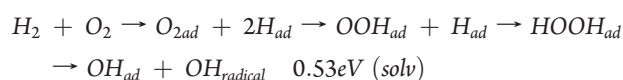
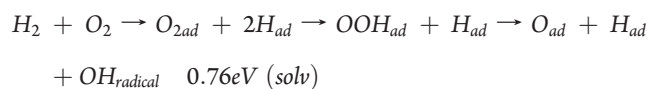
Nonperiodic QM calculations were carried out using the B3LYP^{20,21} hybrid DFT functional with the Jaguar code.²² Here we used the 6-311 g**²³ basis set. All geometries were optimized using the analytic Hessian to determine that the local minima have no negative curvatures (imaginary frequencies), whereas the transition state structures led to exactly one negative curvature. The vibrational frequencies from the analytic Hessian were used to calculate the zero-point energy corrections at 0 K, which was added to the Jaguar implicit solvation correction and the QM energy ($\Delta[E]$) to obtain the enthalpy at 0 K.

3. RESULTS AND DISCUSSION

Formation of OH Radicals. On the basis of the QM (including solvation), we previously determined the mechanism for the oxygen reduction reaction (ORR) between the (H₃O)⁺ migrating through the Nafion from the anode to the cathode and O₂ at the cathode to form H₂O on the Pt (111) surface.^{24,25} The catalyst plays a crucial role in facilitating reactions that generate

OH radicals chemisorbed on the catalyst. The current work used similar DFT calculations to determine the energetics of HOOH and OH radical formation on the Pt (111) surface (see Table 1 and corresponding structures in Figure 2). We find that on Pt in solution the barrier to form the OH radical from HOOH is 0.53 eV while the barrier to form OH from OOH is 0.76 eV. Without the Pt catalyst, the barrier to form the OH radical from HOOH is 2.66 eV. This barrier is dramatically reduced on the Pt (111) surface, because Pt binds more strongly to both product species (O and OH) than to the reactant species (OOH and HOOH).

Our results demonstrate that OH radicals can be formed when H₂ and O₂ gases react on a Pt surface in a PEMFC as result of H₂ gas crossover to the cathode^{10,13} or from O₂ gas crossover to the anode.^{12,14} Figure 3 shows the potential energy landscape of reactions involving H₂ (or H⁺), O₂, and the Pt (111) surface in the membrane during ORR. Note that H₂ gas and H⁺ have the same energy in the context of the standard hydrogen electrode.²⁶ Figure 3 includes data for the barriers for the OH formation, OOH formation, OOH dissociation, O₂ dissociation, and HOH formation published previously.²⁵ We find that the following mechanisms for forming OH radicals have reasonably low energetic barriers:



if crossover of H₂ from the anode and O₂ from the cathode are present.

The Ghassemzadeh experiments⁶ showed that Nafion *degradation is not observed* when Nafion is exposed to H₂ and O₂ gases but without Pt. This agrees with our conclusion that the Pt catalyst surface plays a key role in OH radical formation and, therefore, Nafion degradation. Figure 3 shows that formation of OH radicals occurs only if O_{2ad} forms OOH_{ad} by reaction with H_{ad} (the upper blue path) rather than the O_{2ad} dissociating to 2O_{ad} (the lower orange path). This barrier for the O₂ dissociation is lower than that for the OOH formation, 0.25 vs 0.37 eV. Thus, the energetically most favorable pathway does not lead to OH radical formation. However, under conditions where the Pt surface is highly saturated with adsorbates, O₂ dissociation may be inhibited because it requires two empty 3-fold fcc sites to dissociate by forming two adsorbed oxygens.²⁵ When the Pt surface is completely saturated with both H_{ad} and O_{2ad}, the O₂ dissociation is limited by available surface space. In contrast, the OOH formation mechanism, which may lead to OH radical formation, is more favored when the surface is saturated with a concentrated amount of H and a dilute amount of O₂. Figure 4 illustrates this concept showing how O_{2ad} \rightarrow 2O_{ad} can proceed at

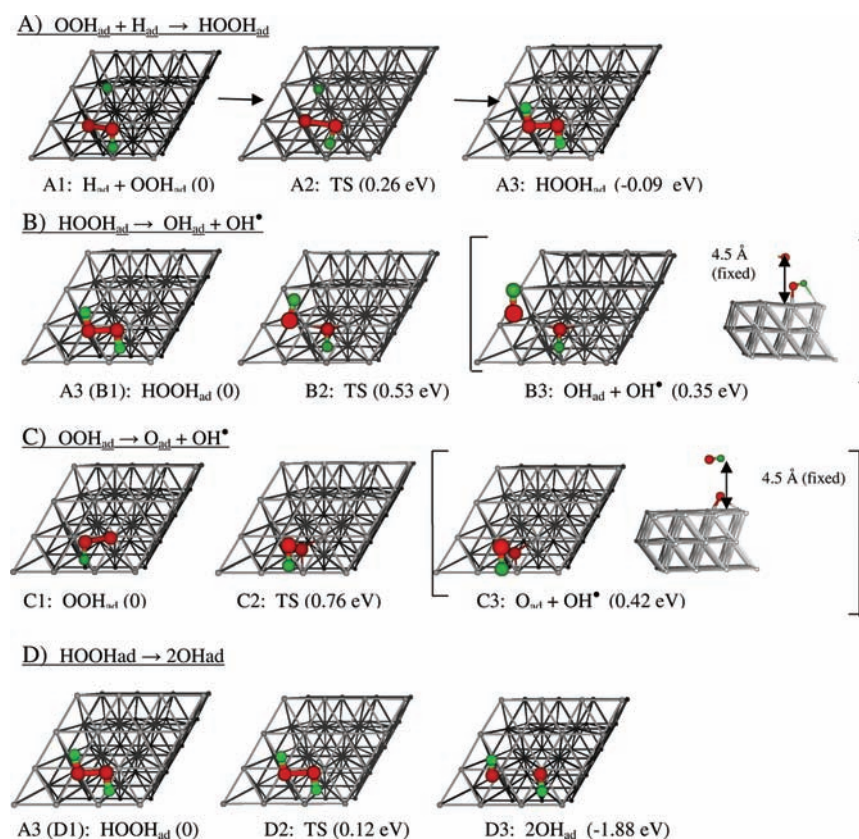


Figure 2. Nudged elastic band (NEB) reaction paths of HOOH formation and OH radical formation from DFT, corresponding to solvent energies in Table 1. Calculated energy results for 2×2 cells (4×4 cells in figure shown for clarity).

low coverage but is hindered when the surface is saturated with adsorbed H. Figure 4 also shows that $\text{O}_{2\text{ad}} + \text{H}_{\text{ad}} \rightarrow \text{OOH}_{\text{ad}}$ is not impeded by high coverage of adsorbed H. Indeed, the Ghassemzadeh experiments⁶ show that Nafion degradation is greater for gas mixtures that are H_2 -rich (90% H_2 , 2% O_2 , 8% Ar) than for O_2 -rich (20% O_2 , 2% H_2 , 78% Ar), which agrees with our proposed mechanisms.

Degradation of Nafion from OH Radicals. After OH radicals are formed on the Pt surface, they can chemically degrade Nafion. Various mechanisms have been proposed on how OH radicals attack Nafion. Some mechanisms focus on defect sites, created in small quantities due to inherent flaws in the manufacturing process.^{3–7} In this case, eliminating these defect sites would be an effective strategy in preventing Nafion degradation. However, our analysis suggests that Nafion degradation can occur even if no defects are in the Nafion membrane. Thus, it is inherent in the chemical structure of Nafion.

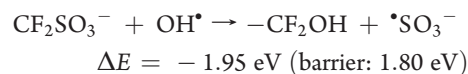
To determine whether OH radicals can attack defect-free Nafion, we focus on the sulfonic acid groups. The C–F bonds in Nafion chains are very strong, but the C–S bond can be attacked by OH radicals. Ghazzamedeh et al. proposed the mechanism in Figure 5 to explain Nafion side-chain degradation in the presence of OH radicals.⁶ We calculated the enthalpies of this mechanism but found very high barriers for two steps in this mechanism, making it unlikely at the normal 80 °C operating temperature: (1) The sulfonate radical breaking off from the side chain to form SO_3 was calculated to be +2.19 eV (Figure 5B). (2) The barrier to form an aldehyde and HF from an alcohol is 1.94 eV (Figure 5D).

Kumar²⁷ proposed a similar degradation mechanism and calculated its energetics using DFT (Gaussian 03). They found

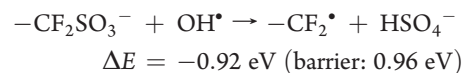
that three of the steps in the mechanism have barrier values between 1.52 and 1.91 eV. Both of these proposed mechanisms involve high barriers and require multiple OH radicals, making them implausible.

We propose a new Nafion side-chain degradation mechanism that leads to low barriers and which require only one OH radical to initiate degradation of the Nafion side chain. Because the sulfonic acid side-chain group is a very strong acid ($\text{p}K_{\text{a}} = -2.8$), we calculated the barrier of breaking the side-chain group deprotonated ($-\text{CF}_2\text{SO}_3^-$) rather than protonated ($-\text{CF}_2\text{SO}_3\text{H}$). We find ((Figure 6A) two mechanisms by which the OH radical can break the C–S bond.

(1) C-Attack. OH attack on the C:

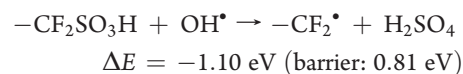


(2) S-Attack. OH attack on the S atom:



Alternatively, the OH radical can attack the minority species, a protonated sulfonic acid group in a similar fashion:

(3) Neutral sulfonate attack:



We expect attack on the sulfur of the deprotonated sulfonic acid group (+0.96 eV) to be the dominant first step in

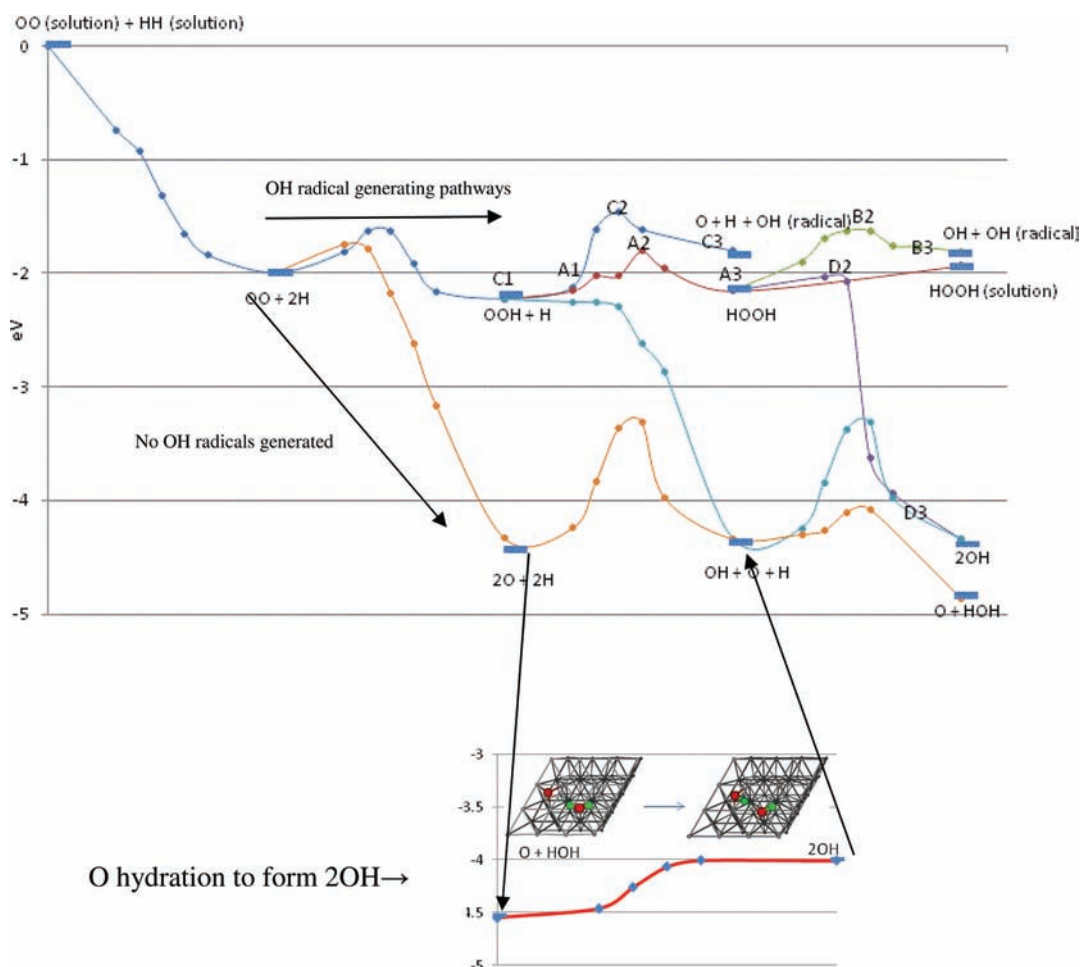


Figure 3. Potential energy map of H_2 (or H^+) and O_2 reacting in solvent phase. The labels A1 to C4 represent coordinate geometries shown in Figure 2 of our new reaction mechanisms. The other energies were calculated previously.²⁵ To form OH in the ORR, the reaction $\text{O}_{\text{ad}} + \text{HOH}_{\text{ad}} \rightarrow 2\text{OH}_{\text{ad}}$ (barrier = 0.50 eV)²⁵ was previously proposed as an alternative to direct OH formation from O_{ad} and H_{ad} .

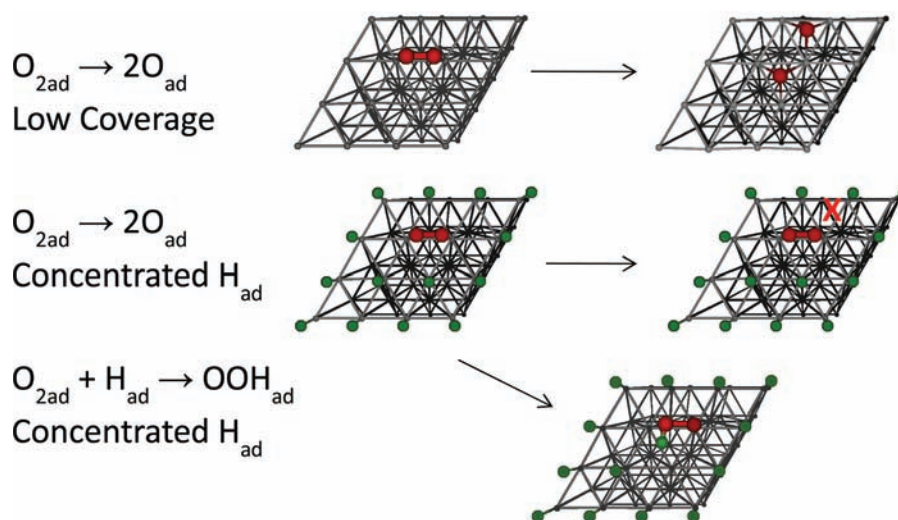
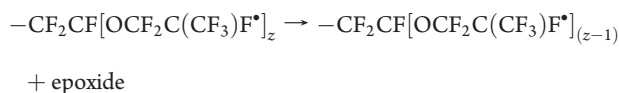


Figure 4. Illustration of the effect of high concentration of H_2 on the surface reactions of O_2 . In a surface covered with H_{ad} , $\text{O}_{2\text{ad}} \rightarrow 2\text{O}_{\text{ad}}$ is hindered. However $\text{H}_{\text{ad}} + \text{O}_{2\text{ad}} \rightarrow \text{OOH}_{\text{ad}}$ is not. This explains why, in experiments with a high concentration of H_2 gas, Nafion degradation occurs at a higher rate.

degradation by OH radicals. The first initial step of breaking the C–S bond (Figure 6A) leads to formation of an epoxide that

breaks off from the side chain (Figure 6B) (barrier = 1.40 eV). This epoxide unzipping reaction can propagate along the side

chain until the side chain is completely devoid of ether groups via (Figure 6B):



The epoxides formed by this mechanism can react with water to form tetrafluoroethylene glycol, $\text{HOCF}_2\text{CF}_2\text{OH}$ (Figure 6C), Which is seen in exit water by NMR (vide infra).

An alternative second process for decomposition after S-attack is tetrafluoroethylene to dissociate from the side chain via:

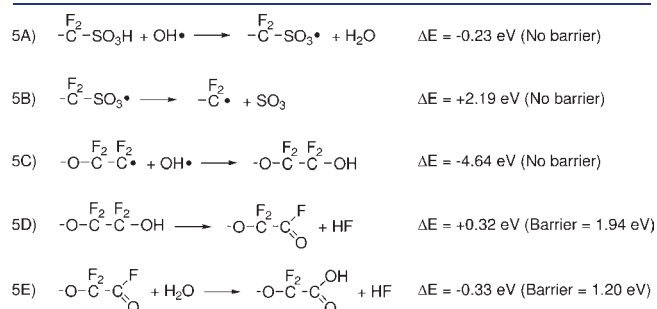
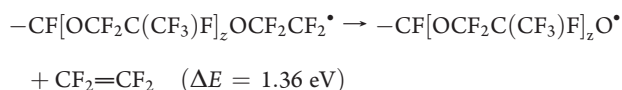


Figure 5. Mechanism of degradation of Nafion sulfonic acid group proposed by Ghassemzadeh et al.⁶ Energetics are from our DFT calculations. We consider steps 5B and 5D to be unlikely at normal fuel conditions.

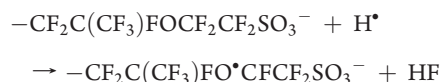
The perfluoroethene can subsequently react with water to form HCF_2CFOH ($\Delta E = -1.82 \text{ eV}$).

This S-attack mechanism leads to removal of both OCF_2 and SCF_2 groups from Nafion (both have been identified by F NMR⁶). This explains why $\sim 10\%$ reduction of these groups from the Nafion occurs after 120 h exposure to H_2 , O_2 , and Pt catalyst. Products of this reaction are H_2SO_4 and tetrafluoroethylene glycol (or tetrafluoroethyl alcohol), which agree well with exit water analysis from experiment,⁶ which show the greatly reduced pH expected from sulfuric acid formation, and which observe F NMR signals of OCF_2 corresponding to the tetrafluoroethylene glycol.

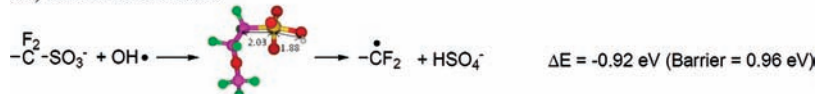
Degradation of Nafion from H Radicals. Ghassemzadeh⁶ observed experimentally HF in the exit stream of a fuel cell in which Nafion undergoes degradation, but HF is not a product of the mechanism described in the previous section. Next, we propose a second Nafion side-chain degradation mechanism with low overall barrier that explains the formation of HF.

This reaction mechanism is shown in Figure 7. It begins with OH radicals reacting with H_2 crossover gas to form H radical (Figure 7A) (0.04 eV barrier). These H radicals then react with the C–F bond directly to form HF. It is favorable for H radical to react with fluorines bonded to secondary or tertiary carbons with barriers and enthalpies listed below:

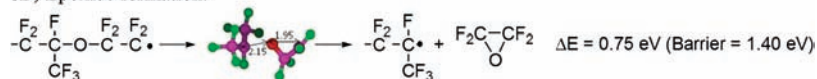
Fluorine on secondary carbon: $\Delta E = -1.00 \text{ eV}$ (barrier: 1.23 eV)



6A) Radical Substitution:



6B) Epoxide formation:



6C) Epoxide Hydrolysis:

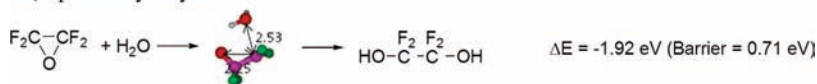
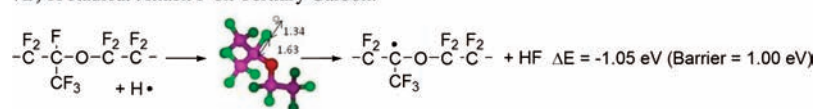


Figure 6. Proposed degradation mechanism involving OH radical attacking the Nafion sulfonic acid group.

7A) H Radical Formation:



7B) H Radical Attack F on Tertiary Carbon:



7C) Ketone Formation:

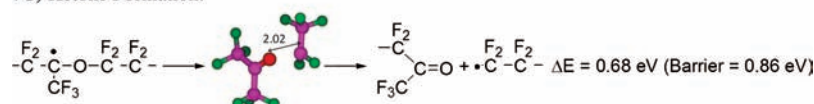
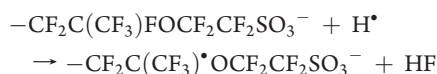


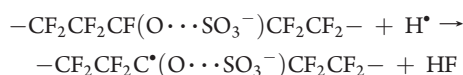
Figure 7. Proposed degradation mechanism involving H radical attacking Nafion side chain.

Fluorine on tertiary carbon: $\Delta E = -1.05$ eV (barrier: 1.00 eV) (Figure 7B)



The easiest C–F bond to break is at the F on tertiary carbon bonded to two carbons and one oxygen. This is found in two locations: (1) on the side-chain carbon bonded to the $\text{OCF}_2\text{CF}_2\text{SO}_3^-$ group (described above); (2) the backbone carbon that connects to the side chain.

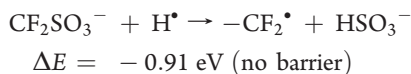
H radical reaction with fluorine on backbone carbon (Figure 7B).



Following formation of the carbon radical and HF, the ether C–O bond can break to form a ketone and a carbon radical as shown in Figure 7C. This mechanism removes both OCF_2 and SCF_2 groups from Nafion, and these groups will end up in the exit stream, as observed with F NMR.⁶

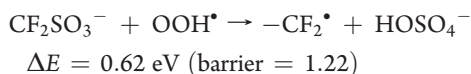
Our proposed mechanism depends on having a modest concentration of H_2 gas in the same region where there is OH, since the H radicals are generated when H_2 gas reacts with OH radicals. Indeed Ghassemzadeh⁶ showed that the rate of the Nafion degradation increases when the gas mixture (containing H_2 , O_2 , and Ar) is highly concentrated in H_2 rather than O_2 . Thus, our mechanism explains the experimental⁶ observation that greater degradation occurs when there is increased H_2 in the system.

In addition to H_{rad} reacting with the Nafion chain to form HF, it is also favorable for H_{rad} to react with the sulfonate group:



The radical product of this reaction can continue to decompose the Nafion side chain as in Figure 6B,C. This reaction with H radical has similar exothermicity as the one involving OH radical (-0.91 vs -0.92 eV) but has no barrier. The new product HSO_3^- could be expected to produce H_2SO_3 and SO_2 , both of which were observed² in mass spectroscopy of the fuel cell cathode exit gas. This supports the role of H radicals in the degradation of Nafion.

Degradation of Nafion from OOH Radicals. The H radical discussed above would react with dioxygen to produce OOH^\bullet ($\Delta E = -2.24$ eV, no barrier) which can also lead to degradation of Nafion, as suggested previously.^{4–6,9} Thus, OOH^\bullet can attack the C–S bond



similar to that for OH^\bullet . However, for OOH , the exothermicity is reduced by 1.54 eV and the barrier 0.26 eV higher.

4. CONCLUSION

We show three mechanisms by which OH radical species formed on a Pt surface can cause degradation of a defect-free Nafion polymer.

- S-attack by OH radical: the OH radical reacts with the carbon–sulfur bond of the Nafion side chain to form H_2SO_4 (lowering the pH) while generating radicals that decompose to OCF_2 .

- C-attack: the OH radical attacks crossover H_2 , leading to H radical that in turn reacts with the Nafion side chains to form HF plus OCF_2 and SCF_2 groups.
- S-attack by H radical: the H radical from OH reacting with crossover H_2 , attacking the sulfonate group, forming H_2SO_3 and leading to subsequent degradation similar to the S-attack mechanism.

All the products of these three mechanisms have been observed with F NMR and mass spectroscopy in the exit gases in fuel cell experiments as well as the decrease in pH. We consider that the excellent agreement with the experimental observation provides a strong validation of our mechanisms for degradation of defect-free Nafion.

Previously, some workers have assumed that degradation of Nafion in a fuel cell is dominated by radicals attacking defects in the Nafion structure. For example, Choudhury assumed that degradation occurs at defects in the Nafion and listed stabilization of polymer defects as a mitigation strategy to address this.¹⁵ Another suggestion was that undesired Fenton's reagents are formed from Pt nanoparticles breaking off from the catalyst surface^{8,9} and that elimination of Fenton's reagents will reduce degradation.¹⁵ We showed in this paper that neither strategy should be completely effective because OH radicals generated by reactions associated with ORR on the Pt catalyst can attack a defect-free Nafion side chain.

We suggest that one promising strategy to reduce Nafion degradation would be to modify the catalysts to disfavor formation of the peroxides that lead to OH formation during on–off cycling. Also, one might consider polymers that are more resistant to radical attack. For example, we found that H radical attacks fluorine on a tertiary carbon with a barrier of 1.00 eV, while the barrier for attacking fluorine on a secondary carbon is 1.23 eV. Thus, maybe the Nafion side chain can be modified to eliminate fluorine on tertiary carbons altogether by replacing such F with CF_3 . This will increase the barrier to form HF by 0.23 eV, slowing Nafion degradation. Additionally, our analysis shows that Nafion degradation will be greater on long side-chain Nafion that has two F on tertiary carbon (Figure 1 with $z = 1$) compared to short side-chain Nafion that have only one (Figure 1 with $z = 0$). Indeed, this is consistent with recent experiments.²⁸

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