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

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ABSTRACT

Degradation of the Nafion electrolyte in Proton Exchange Membrane Fuel Cells (PEMFCs) limits the lifetime, motivating development of materials that resist degradation. The mechanism for degradation of Nafion under fuel cell conditions remains uncertain. Studies of Nafion degradation in concentrated OH$^{\bullet}$ 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 Nafion degradation under both concentrated OH$^{\bullet}$ and fuel cell conditions. These studies confirm that under concentrated OH$^{\bullet}$ conditions Nafion degrades when peroxide radicals attack end groups ($-COOH$, $-CF\!=\!CF_2$, $-CF_2H$); followed by degradation of Nafion along the polymer main chain, as proposed previously. However we find that under fuel cell conditions, Nafion degradation occurs along the polymer side chain starting with H$^{\bullet}$ attacking the side chain groups such as the sulfonic acid, $-SO_3^{-}$. We find that it is easier for OH$^{\bullet}$ to attack the main chain than H$^{\bullet}$, while vice versa, it is easier for H$^{\bullet}$ radical to attack the side chain than OH$^{\bullet}$.

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1. Introduction

Nafion is a critical component of state-of-the-art Proton Exchange Membrane Fuel Cells (PEMFCs). Currently lifetime of Nafion based PEMFCs is limited to ~2000 h [1,2], well short of the 5000–10,000 h operational requirement needed for successful automotive applications. In order to improve the durability of Nafion, a number of studies have been performed to determine the mechanism of its degradation [1,3–17]. In our recent paper [18], we showed that Nafion degradation occurs when OH radicals attack the Nafion side chain. These OH radicals are generated on the Pt (111) surface during fuel cell operation from HOOH and OOH$_{ad}$ with calculated barriers of 0.53 and 0.76 eV, respectively. Our work also provides a potential energy map describing how HOOH and OOH$_{ad}$ can be generated as side reactions during the ORR. This energy map is useful in explaining why certain experimental conditions (such as high H$_2$ concentration) can lead to higher concentrations of HOOH, which in turn generates more OH radicals as shown in experiment [13]. We then showed that these OH radicals can attack vulnerable sites on the Nafion side chain, in particular the sulfonic acid group. Nafion

degradation is also initiated in the reaction of the OH radical with H$_2$ 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 H$_2$SO$_3$, 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$^{\bullet}$ or H$^{\bullet}$ reactant, which is a free energy barrier for the reaction to occur.

Another possible location of Nafion 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–CF$_2$═CF$_2$, R–CF$_2$H) 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 Nafion, and are used to simulate OH radicals in PEMFCs [5,15,16]. Treating Nafion with elemental fluorine to eliminate polymer main chain end groups [20,21] showed dramatic improvements in Nafion 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 Nafion degradation [5]. Another high concentration ex-situ experiment is H$_2$O$_2$ vapor tests [22–24]. In addition to accelerating degradation with a high concentration of OH radicals, this

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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 differs 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$^{\bullet}$ experiments is the presence of O_2 and H_2 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 H_2 to the cathode and O_2 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 6–311 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 ($\Delta[E]$) 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 $5 \times 5 \times 0$. 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$^{\bullet}$ conditions versus fuel cell conditions

To distinguish between experiments under concentrated OH$^{\bullet}$ [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$^{\bullet}$ environment, allows multiple OH radicals as reagents as found in Fenton reagents [5,15] and H_2O_2 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 H_2 and O_2 gases as reagents in the fuel cell environment,
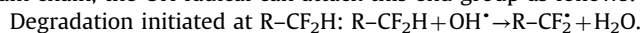
because they are present as fuel and can diffuse into the membrane during crossover processes in a fuel cell. Crossover of the O_2 to the anode [25] and H_2 to the cathode are known to be accelerated during start/stop operation [39]. To contrast the role of crossover, we designed a third environment, which has low OH radical concentration, high O_2 concentration but no H_2 available to simulate the cathode side without crossover. The fourth simulates Nafion degradation occurring at the anode without O_2 crossover. In this environment, there is high H_2 concentration which leads to H radical but no O_2 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$^{\bullet}$ 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–CF$_2$H, R–CF=CF$_2$, and R–COOH, which appear as results of the manufacturing process [5]. The initiation process of the polymer main chain degradation leaves R$^{\bullet}$ 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.

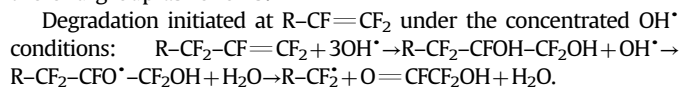#### 3.2.1. R–CF$_2$H polymer main chain end group initiation
When the end group is R–CF$_2$H or if there is a C–H bond in the main chain, the OH radical can attack this end group as follows:
Degradation initiated at R–CF$_2$H: R–CF$_2$H+OH$^{\bullet}$→R–CF$_2^{\bullet}$+H$_2$O.
The transition state and energetics are described in Fig. 2 with a barrier of 0.02 eV for the initiation of the polymer degradation at a –CF$_2$H end group. The potential energy of the reactant/transition/product states are reported in the supplemental information.

3.2.2. R–CF=CF$_2$ polymer main chain end group initiation
When the end group is R–CF=CF$_2$, the OH radical can attack the end group as follows:
Degradation initiated at R–CF=CF$_2$ under the concentrated OH$^{\bullet}$ conditions: R–CF$_2$–CF=CF$_2$+3OH$^{\bullet}$→R–CF$_2$–CFOH–CF$_2$OH+OH$^{\bullet}$→R–CF$_2$–CFO$^{\bullet}$–CF$_2$OH+H$_2$O→R–CF$_2^{\bullet}$+O=CFCF$_2$OH+H$_2$O.
The transition states 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:
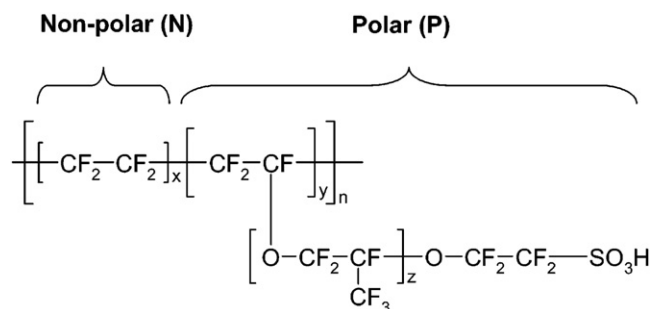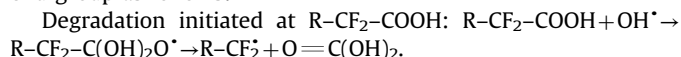Degradation initiated at R–CF$_2$–COOH: R–CF$_2$–COOH+OH$^{\bullet}$→R–CF$_2$–C(OH)$_2$O$^{\bullet}$→R–CF$_2^{\bullet}$+O=C(OH)$_2$.

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.