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Theoretical studies on the degradation of hydrocarbon copolymer ionomers used in fuel cells



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ABSTRACT

Details on the degradation mechanism of hydrocarbon ionomers for polymer electrolyte membrane fuel cells (PEFCs) have been investigated using density functional theory (DFT). Two model compounds of a hydrocarbon ionomer were selected to investigate the nature of the degradation, where the compounds selected represented the general features of available hydrocarbon polymer electrolyte membranes (PEMs). The results show that two degradation reactions are energetically favorable, indicating two possible weak sites in the hydrocarbon PEMs susceptible to OH or H radical attack. One site has an aryl sulfonated bond and a sulfonate group, and the other site has an aryl ether bond. The alkane chains in the PEMs were calculated to be relatively stable against radical attack. In addition, we found that in contrast to the degradation of perfluorinated PEMs, hydrocarbon PEMs are relatively robust against H radical attack.

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1. Introduction

PEMs play an important role in separating electrodes, by transporting protons in the membrane and in forming membrane electrode assemblies as an ionomer in PEFCs. Good stability and high proton conductivity at low water contents are desired properties for PEMs. According to the generic industry standard, a lifetime durability of 40,000 h and an uninterrupted service life of 8000 h at > 80% power are desirable for PEFCs in stationary applications. These figures can be compared with the 20,000 and 6000 operating hours required for buses and cars, respectively [1,2]. Chemical degradation caused by oxidative species produced as a result of chemical reactions in cycling operating fuel cells poses a serious obstacle to the stability of PEMs [3]. Thus, connected with the above stability issues, the details on oxidative species and their formation mechanisms have been extensively studied in PEFCs. For example, hydrogen peroxide, OH radicals, H radicals, and OOH radicals are believed to be prevalent in solution [4–6]. In particular, OH radicals and H radicals are believed to play a major role in membrane

degradation reactions. Generally, two possible generation mechanisms are discussed in the literature. One is attributed to the crossover of O₂ from the cathode to the anode through the membrane and incomplete reaction with H₂ on the surface of the anode catalyst, and the other is a result of the reaction of H₂O₂ (which is an intermediate of the two-electron reduction of O₂ at the cathode) with trace metal. The latter is considered as a main source of OH radical formation in the fuel cell with a hydrocarbon-based membrane [3,7–14]. An understanding of the mechanism of degradation is obviously the first step required for improving the chemical stability of PEMs.

Perfluorinated membranes, such as Nafion, are currently widely used in PEFCs, even though they also suffer from chemical degradation caused by oxidative species, and many studies have been reported on their degradation mechanisms [15–19]. Yu et al. proposed that OH radicals can attack the S–C bond in Nafion to form H₂SO₄ and carbon radicals, with an energy barrier height of 0.96 eV, while H radicals can attack the C–F bond to form HF and carbon radicals based on quantum mechanical calculations [17]. Yu et al. also reported on the degradation mechanisms of Nafion with different end groups (–COOH, –CF=CF₂, and –CF₂H) employed in different fuel cells operating conditions [18]. A recent study by Ghassemzadeh et al. indicated that OH radicals could attack the α–O–C bond in the side chain of Nafion, and H radicals could possibly

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attack the tertiary carbon C–F bond on both the main and side chains of Nafion [19].

On the other hand, there have been persistent efforts to find viable alternatives for Nafion. In particular, the aromatic polymer family has attracted much attention because of its promising properties, such as low production cost and environmental friendliness. Therefore, various types of hydrocarbon PEMs employing aromatic polymers have been reported so far [20–24], and the durability of these hydrocarbon PEMs has also been investigated extensively [25,7,13,26–28,12]. Hübner et al. employed electron paramagnetic resonance (EPR) techniques to identify degraded membrane fractions caused by OH radicals using eight model sulfonated aromatic compounds [25]. Panchenko proposed various degradation mechanisms for model sulfonated poly(ether ether ketone) (SPEEK) compounds and polyethersulfone (PSU) based on DFT calculations, where the mechanism indicated that the phenyl ring was attacked by OH radicals and oxygen molecules, leading to the loss of the sulfonic acid group [12]. Perrot et al. investigated the degradation of a model compound of sulfonated aryl ether ketones (SPAEEK) using nuclear magnetic resonance (NMR), infrared (IR), and mass spectroscopy and demonstrated that the oxidation of the phenolic groups resulted in chain scission after OH radical attack on the aromatic ring [28]. Despite these efforts, a clear and comprehensive understanding of the degradation mechanisms of hydrocarbon PEMs is still lacking because of the complicated nature of the degradation pathway.

Recently, Rikukawa's group reported on novel hydrophilic–hydrophobic block copolymer ionomers [29] based on polyphenylenes using a new method, catalyst transfer polycondensation, which was proposed by Yokoyama et al. and Sheina et al. [30,31]. This copolymer exhibits high proton conductivity at low hydration by precisely controlling the diblock lengths and composition of the polymer. As shown in Fig. 1(a), this hydrocarbon copolymer consists of a main chain of polyphenyl rings and two different side chains with hydrophobic and hydrophilic groups and several other functional groups (phenyl rings, alkane chains, ether groups, and sulfonate groups). This type of main chain is often used in hydrocarbon PEMs. In addition, its side chain is similar to that of other hydrocarbon PEMs, such as SPEEK and sulfonated polyether sulfone (SPES) compounds. In this work, we took this new copolymer as an example of hydrocarbon PEMs and investigated its possible degradation mechanisms by applying DFT calculations.

The remainder of this paper is organized as follows. The computational details are described in Section 2. Various possible degradation mechanisms initiated by OH or H radicals on the side and main chains are presented in Section 3, and a summary is given in Section 4.

2. Computational details

Two model compounds of the novel hydrocarbon copolymer ionomer, denoted as M1 and M2, were selected to study the degradation reactions. Fig. 1(b) shows the structure of M1, which is a model compound with a hydrophilic domain on the side chain and

a key sulfonate group for proton donation. It also includes common functional groups used in hydrocarbon PEMs, such as a phenyl ring, an alkane chain, and an ether group. Fig. 1(c) shows the molecular structure of M2, modeling a main chain consisting of phenyl rings. In M2, the methoxy groups were used as a substituent site for the side chain of the copolymer. All the geometries of the stationary points on the potential energy surfaces were optimized at the B3LYP/6-31+G (d) and B3LYP/6-311++G(2d, 2p) levels of theory [32,33]. Since PEMs are hydrated by water in PEFCs, the effect of the solvent was taken into account using the polarizable continuum model (PCM) [34–36]. The resulting structures obtained at the gas phase B3LYP/6-311++G(2d, 2p) level of theory were then optimized further, including any solvent effects. The vibrational frequencies were calculated to confirm that the transition states had only one imaginary frequency and that the local minima had no imaginary frequency. The reaction enthalpies were obtained in the gas phase and in water at room temperature. The zero point energies (ZPEs) of all the optimized structures were also calculated at the corresponding levels of theory mentioned above and were included in the calculation of the relative energies. All the calculations in this work were carried out using the Gaussian09 software package [37].

3. Results and discussion

In this section, we will discuss the degradation reactions of the membranes in terms of the side- and main-chain degradation. For the model compound with a side chain, M1, shown in Fig. 1(b), all of its noted atom sites (C1–C9) could be attacked by oxidative species. For the model compound with a main chain, M2, shown in Fig. 1(c), we note that atoms C1, C2, and C3 were considered to be possible sites that could react with oxidative species. For both models, possible degradation mechanisms occurring at these sites were proposed and are discussed in this section based on our DFT calculations. Concerning the oxidative species involved in the above degradation reactions, we mainly focused on OH and H radicals, but sometimes included O₂, based on data from previous studies [17,18,12]. Considering that only trace amounts of oxidative species are present in PEFCs, one OH radical and one H radical were introduced in our computations. These radicals mostly work as an initiator of reactions, and introduce radicals into the membrane. Unless otherwise noted, all the energies mentioned in the following text were obtained at the B3LYP (PCM)/6-311++G(2d, 2p) level of theory, including the ZPE corrections, as described in Section 2. The terms R and R' are used to represent the inactive fragments in the relevant figures.

3.1. Side chain degradation by OH radicals

3.1.1. OH radical attack on the sulfonate group

It can be seen in Fig. 1(b) that C1 is a carbon atom in a phenyl ring bonded directly to the sulfonate group. The stability of the C–S bond is very important for the performance of PEMs because OH radical attack on this bond can result in the loss of the sulfonate group, causing the membrane to cease being a proton conductor.

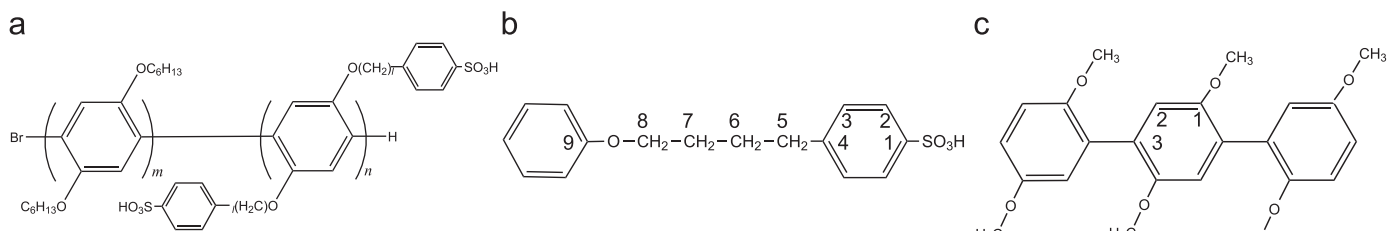


Fig. 1. The chemical structures of (a) the copolymer and its model representations, (b) M1 (side chain), and (c) M2 (main chain).

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