An Initial Degradation Reaction before Ring-Opening in Imidazolium-Based Anion Exchange Membranes: A DFT Study

Ryo Tsuchitani
Department of Applied Physics, Osaka University, Suita, Osaka 565-0871, Japan

Hiroshi Nakanishi and Hideaki Kasai*
Department of Applied Physics, Osaka University, Suita, Osaka 565-0871, Japan, and Center for Atomic and Molecular Technologies, Osaka University, Suita, Osaka 565-0871, Japan
(Received 19 November 2013; Accepted 19 December 2013; Published 28 December 2013)

Based on density functional theory, we report an initial degradation reaction before a ring-opening reaction which is a traditional degradation reaction in imidazolium-based anion exchange membranes (AEMs) and has been reported by several experimental groups. In the present work, a 1-ethyl-3-(4-vinylbenzyl) imidazolium (EVIm) monomer is focused as a part of imidazolium-based AEMs. Firstly, a hydroxide anion is put to the EVIm monomer and the geometry is optimized. Secondly, the minimum reaction path along the ring-opening reaction is calculated and it is concluded that the EVIm monomer is resistant to the ring-opening reaction because of the high energy barrier. Further, when the hydroxide anion is put near the EVIm monomer, the C-H bond at the C2 position of imidazole ring is elongated. As the result, the feasibility of a dehydrogenation reaction where the hydrogen bonding to the C2 position desorbs is suggested. Finally, in order to compare the energy barrier to that of the ring-opening reaction, the minimum reaction path along the dehydrogenation reaction is calculated. From these analyses, we propose that the dehydrogenation reaction precedes the ring-opening reaction and it is also much more dominant rather than the ring-opening reaction in the EVIm monomer.


Keywords: Density functional calculations; Ion-solid interactions; Aromatics

I. INTRODUCTION

Polymer electrolyte fuel cells have the potential to become one of the most promising energy sources which can provide clean and efficient energy [1, 2]. Proton exchange membrane fuel cells (PEMFCs) have been paid more attention due to their high power density, high energy conversion and low operating temperature. However, PEMFCs need noble metal catalysts such as platinum for acid environment, resulting in high cost and it prevents PEMFCs from being commercialized. Furthermore, Nafion-type membranes which are often used in PEMFCs [3] are also expensive and harmful to environment with regard to recycling and disposal of fluorinated polymers.

In contrast to PEMFCs, anion exchange membrane fuel cells (AEMFCs) can use non-precious metal such as nickel and cobalt as catalysts for alkaline environment [4, 5] and they can overcome the weak point of PEMFCs. However, the most serious issues of membranes are alkaline stability and ion conductivity because AEMs are greatly sensitive to attack of anions. These drawbacks lead to decrease of the lifetime of AEMFCs and eventually hinder the commercialization.

The most traditional anion exchange membranes (AEMs) are quaternary ammonium cationic groups. [6–13] However, they are easy to be damaged by hydroxide attack. The major degradation pathways of quaternary ammonium cationic groups are nucleophilic substitution (SN2) and β-hydrogen (Hofmann or E2) elimination. Furthermore, in the process of fabrication of quaternary ammonium-based AEMs, carcinogenic substance is often generated. Therefore, it is necessary to look for alternatives to quaternary ammonium cations.

Recently, in order to improve alkaline stability and ion conductivity of quaternary ammonium cationic groups, other cationic groups, e.g. guanidinium [14, 15], phosphonium [16, 17] and imidazolium [18–29] based AEMs have been investigated. In particular, imidazolium-based AEMs have been reported to show resistance to the SN2 substitution and β-hydrogen elimination reactions and improve the alkaline stability because of the presence of π-conjugated imidazole ring. [30] However, another degradation reaction is also observed in imidazolium-based AEMs. The degradation reaction is called ring-opening reaction and it is a nucleophilic substitution reaction where hydroxide anions attack the C2 position of the imidazole ring and the ring breaks eventually.

Ye et al. clarified the detail mechanism of the ring-opening reaction by the analysis of the 1H NMR spectra. [30] However, evidence of other degradation reactions was not detected from the analysis. Therefore, the majority of degradation pathways in imidazolium-based AEMs still remains unclear and they are needed to study the ring-opening reaction both experimentally and theoretically in detail in order to clarify the mechanism and improve alkaline stability.

Based on the density functional theory (DFT), in the present analysis, we investigate the mechanism of the ring-opening reaction in imidazolium-based AEMs. Using a 1-ethyl-3-(4-vinylbenzyl) imidazolium (EVIm) monomer as a part of imidazolium-based AEMs, we calculate a minimum energy path along the ring-opening reaction and a dehydrogenation reaction and compare their energy barriers. From these calculations, we suggest that the degrag-
dation reaction is more dominant than the ring-opening reaction in the EVIm monomer.

II. COMPUTATIONAL METHOD

We use Gaussian 09 (G09) [31] to optimize and calculate energies for the reactant and transition state structures. For a model reaction \( A + B \rightarrow C \), we optimize the geometries of species \( A, B, \) and \( C \) in a dielectric medium of \( \varepsilon = 80 \) (corresponding to water). During the calculations, we use the DFT B3LYP22 method, 6-311++G(2d,p) basis set, and polarizable continuum solvation model (PCM) implemented in G09 because when hydroxide anions pass through an AEM, \( H_2O \) molecules also follow the hydroxide anions due to the attractive interaction of hydrogen bond between the oxygen of the hydroxide anions and the hydrogen of the \( H_2O \) molecules. Hence, applying the PCM method makes our calculations more realistic. Moreover, we use a temperature of 80°C in all calculations because the operating temperature of AEMFCs is around 80°C and imidazolium-based AEMs are also degraded at elevated temperature. We then compute the force constants based on the optimized structure, resulting in the vibrational frequencies and gibbs free energies \( G \).

\( G \) is calculated by adding the following terms to \( E_{SCF} \): cavity formation energy, van der Waals interactions, translational free energy, quantum mechanical rotational and vibrational free energies, and zero point energy, all as reported by G09 software. The self-consistent field (SCF) energy \( E_{SCF} \) reported by G09 includes the electronic energy of the solute and the interactions with the dielectric medium. The energy change \( \Delta G^0 \) and the energy barrier \( \Delta G^{#.0} \) are defined as, \( \Delta G^0 = G^0(C) - G^0([AB]) \) and \( \Delta G^{#.0} = G^0([AB]^#) - G^0([AB]) \). [AB]^# is the exact transition state (the saddle point on the potential energy surface) and obtained from this approximate point by using the Berny optimization algorithm as implemented in G09.

III. RESULTS AND DISCUSSION

First, an EVIm monomer is prepared as a part of imidazolium-based AEMs and optimized in order to investigate the mechanism of a ring-opening reaction as shown in Fig. 1. Second, a minimum reaction path along the ring-opening reaction is calculated and it is confirmed that the energy barrier is high. Finally, a minimum reaction path along a dehydrogenation reaction is also calculated and the energy barrier is compared with that of the ring-opening reaction.

Figure 2 shows the minimum energy path and the geometries along the ring-opening reaction. The energy barrier \( \Delta G^{#.0} \) and the energy change \( \Delta G^0 \) are 1.35 eV and −0.75 eV, respectively. The value of the energy barrier is generally very high. Hence, the EVIm monomer is resistant to the ring-opening reaction. In addition, compared the initial state (A) in Fig. 2 to the geometry in the absence of the hydroxide anion in Fig. 1, the C–H bond at the C2 position is elongated from 1.08 Å to 1.15 Å. This indicates that the C–H bond is likely getting weak due to the attractive interaction between the hydrogen bonding to the C2 position and the oxygen of the hydroxide anion. Consequently, the feasibility of the dehydrogenation reaction where the hydrogen bonding to the C2 position desorbs and reacts with the hydroxide anion, which results in the formation of \( H_2O \) is suggested. In order to compare the energy barrier of the dehydrogenation reaction with that of the ring-opening reaction, a minimum energy path along the dehydrogenation reaction is also calculated in Fig. 3. Figure 3 shows the reaction path and the geometries along the dehydrogenation reaction. The initial state (F) is the same geometry as the initial state (A) in Fig. 2. The optimized geometry seems to favor the dehydrogenation reaction because the hydroxide anion is located just near the hydrogen bonding to the C2 position. Actually, we tried several calculations in order to find the different geometry of the initial state for the ring-opening reaction by changing the initial position of the hydroxide anion. However, their results led to the same geometry as shown in Figs. 2 (A) and 3 (F). This indicates that the attractive interaction between the hydroxide anion and the hydrogen bonding to the C2 position is very strong and the geometry is more stable than any other geometry. The energy barrier \( \Delta G^{#.0} \) is nonexistent and the energy change \( \Delta G^0 \) is −0.38 eV. Hence, the minimum energy path indicates that the dehydrogenation reaction is thermodynamically downhill.

Thus, we conclude that when the hydroxide anion approaches to the C2 position in the EVIm monomer, the dehydrogenation reaction precedes the ring-opening reaction because the dehydrogenation reaction occurs at \( d_{C-O} = 2.62 \) Å in Fig. 3(G) while the ring-opening reaction occurs at \( d_{C-O} = 1.33 \) Å in Fig. 2(B), where \( d_{C-O} \) is the distance of the C–O bond. Additionally, the dehydrogenation reaction is thermodynamically downhill in contrast to the high energy barrier of the ring-opening re-

http://www.sssj.org/ejssnt (J-Stage: http://www.jstage.jst.go.jp/browse/ejssnt/) 139
FIG. 2: Calculated minimum energy path and geometries along the ring-opening reaction. (A) initial state. (B) one transition state. (C) intermediate state. (D) the other transition state. (E) final state. Energy is calculated at 80°C and it is given in eV. A red sphere is oxygen. The solid and dot arrows show the distance of the C-H bond and the distance of the C-O bond, respectively.

action. Therefore, the dehydrogenation reaction is much more dominant rather than the ring-opening reaction.

IV. CONCLUSION

In this paper, we used DFT and investigated the mechanism of the ring-opening reaction in an EVIm monomer which is a part of imidazolium-based AEMs. The energy barrier for the ring-opening reaction is 1.35 eV and the value is generally very high, which means that the EVIm monomer is quite tolerant toward the ring-opening reaction. When the hydroxide anion is put near the EVIm monomer, the C–H bond at the C2 position is somewhat elongated and it indicates that the bond becomes weak due to the attractive interaction between the hydrogen bonding to the C2 position and the oxygen of the hydroxide anion. Thus, the minimum energy path along a dehydrogenation reaction of the hydrogen bonding to the C2 position is calculated in order to compare the energy barrier with that of the ring-opening reaction. The dehydrogenation reaction has no energy barrier and it is thermodynamically downhill. Furthermore, the dehydrogenation reaction occurs before the ring-opening reaction because $d_{C-O}$ of the transition state in the dehydrogenation reaction is 2.62 Å in contrast to 1.33 Å in the ring-opening reaction. Hence, the dehydrogenation reaction is an initial degradation reaction before the ring-opening reaction and it is much more dominant rather than the ring-opening reaction in the EVIm monomer. Therefore, we suggest that the dehydrogenation reaction is one of the dominant degradation reactions and it probably occurs in actual imidazolium-based AEMs including EVIm monomers.

Acknowledgments

This work is supported in part by: MEXT Grant-in-Aid for Scientific Research on Innovative Areas Program (2203-22104008) and Scientific Research programs (A) (24246013); JST ALCA Program “Development of Novel Metal-Air Secondary Battery Based on Fast Ox-
ide Ion Conductor Nano Thickness Film” and Strategic Japan-Croatia Research Cooperative Program on Materials Sciences Program “Theoretical Modeling and Simulations of the Structural, Electronic, and Dynamical Properties of Surfaces and Nanostructures in Materials Science Research.” Some numerical calculations in this work were carried out on SR16000 at YITP in Kyoto University.


http://www.sssj.org/ejssnt (J-Stage: http://www.jstage.jst.go.jp/browse/ejssnt/)