A theoretical study of how C2-substitution affects alkaline stability in imidazolium-based anion exchange membranes

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Abstract

We use density functional theory and investigate the effect on C2-substitution in imidazolium-based anion exchange membranes (AEMs). Here, a C2-unsubstituted 1-ethyl-3-(4-isopropylbenzyl) imidazolium cation (EIIM), a 1-ethyl-2-methyl-3-(4-isopropylbenzyl) imidazolium cation (EMIIM), a 1-ethyl-2-isopropyl-3-(4-isopropylbenzyl) imidazolium cation (EIIIM) and a 1-ethyl-2-phenyl-3-(4-isopropylbenzyl) imidazolium cation (EPhIIm) are prepared. In our previous paper, we suggested that C2-unsubstituted EIIM was quite sensitive to a deprotonation reaction because it was thermodynamically downhill. In the present work, we calculate the alkaline stability of the C2-substituted imidazolium cations and clarify which part is most affected by the C2-substitution. First, in order to investigate the effect on the steric hindrance by each substituent, potential energy curves are described. The effect appears explicitly in the C2-substituted imidazolium cations. Second, the minimum energy paths along the ring-opening and deprotonation reactions are calculated. Finally, we conclude that the alkaline stability is in the order of EMIIM > EIIIM > EPhIIm > EIIM. Furthermore, the order of

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the alkaline stability is consistent with that of the experiment performed by Lin *et al.*

Keywords: Density functional theory, C2-substitution, Imidazole, Steric hindrance, Alkaline stability

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1. Introduction

Proton exchange membrane fuel cells (PEMFCs) have been focused as one of the most promising environment-friendly energy sources. They have the great potential to apply to automobiles and domestic electric power supply due to their high power density, high energy conversion efficiencies and low operation temperature. Nafion perfluorosulfonic acid membranes which are most popular as proton exchange membranes show high alkaline stability, high ionic conductivity and long durability.[1] However, PEMFCs need noble metal catalysts such as platinum for acid environment, resulting in high cost and the cost prevents PEMFCs from being commercialized. Therefore, there is a high expectation for anion exchange membrane fuel cells (AEMFCs) where OH^- or other anions pass through anion exchange membranes (AEMs) instead of protons.

The detail mechanism of AEMFCs with typical hydrogen fuel is the following.

AEMFCs can use non-precious metal such as nickel[2] and cobalt[3] to catalysts for alkaline environment and overcome the tender point of PEMFCs in the aspect of the cost. However, AEMFCs also have some problems. The most serious issue is alkaline stability of AEMs and they are very sensitive to OH^- attack. In particular, OH^- anions lead to faster degradation of AEMs in the absence of water at elevated temperature. Hence, the lifetime of the AEMs

gets very short and AEMFCs are still inadequate to spread widely to societies. There are many kinds of AEMs such as quaternary ammonium (QA)[4], guanidinium[5], pyridinium[6] and imidazolium[7] cations. Although QA cations are most common among anion exchange groups, their alkaline stability is poor
 25 due to some degradation pathways (S_N2 and Hoffmann elimination).[8, 9] Thus, various cations based on AEMs have been investigated both experimentally and theoretically.

Recently, it has been reported that imidazolium cations raise the durability to OH^- attack due to the presence of the π -conjugated imidazole ring compared with quaternary ammonium cations.[10] The main degradation reaction
 30 in imidazolium-based AEMs is called ring-opening reaction, which is a kind of nucleophilic substitution reaction. OH^- anions attack the C between the two N atoms of the imidazole ring (α -C) under alkaline condition and then the imidazole ring is broken. AEMs degraded by OH^- attack lose the ability in ion
 35 conductivity. Lin *et al.* revealed that the alkaline stability of C2-substituted imidazolium cations substituted by methyl, isopropyl and phenyl groups is significantly enhanced compared with C2-unsubstituted imidazolium cations due to the effect on the steric hindrance by their substituents.[11] Steric hindrance plays a critical role in physically protecting imidazolium cations against OH^-
 40 attack. Hence, C2-substitution is an important factor to enhance the alkaline stability of AEMs. In addition to the alkaline stability, the ionic conductivity also has been investigated.[12, 13] However, the condition of ideal substituents which satisfies both of them is still unclear and the present situation cannot help depending on trial and error.

45 In our previous paper, the alkaline stability of a C2-unsubstituted imidazolium cation was numerically investigated.[14] The results showed that although the C2-substituted imidazolium cation has the resistance to the ring-opening reaction, it was quite sensitive to a deprotonation reaction due to thermodynamically downhill. Hence, we concluded that the deprotonation reaction
 50 was an initial degradation reaction before the ring-opening reaction and it was much more dominant rather than the ring-opening reaction.

Based on density functional theory (DET), in the present analysis, we theoretically investigate the effect on C2-substitution and the alkaline stability in C2-substituted imidazolium cations. In order to compare our results with that of the experiment performed by Lin *et al.*, One C2-unsubstituted and three C2-substituted imidazolium cations substituted by methyl, isopropyl and phenyl groups are prepared and their alkaline stability is compared to each other. In particular, we focus on how the energy barriers for the two degradation pathways of the ring-opening and deprotonation reactions change by each substituent.

2. Computational Method

We use Gaussian 09 (G09)[15] to optimize structures and calculate the energies for the initial state (IS), transition state (TS) and final state (FS) 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 B3LYP method, 6-311++G(2d,p) basis set, and polarizable continuum solvation model (PCM) implemented in G09. In addition, we use the natural bond orbital population scheme for molecular orbital analysis and atomic charge calculations. A temperature of 80 °C is used 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 defined as $G = H - TS$, where H , T and S are enthalpy, temperature and entropy, respectively.

G is calculated by adding the following terms to E : 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 energy E reported by G09 includes the electronic energy of the solute and the interactions with the dielectric medium. The energy change ΔE and ΔG^0 are defined as, $\Delta E = E(C) - (E(A) + E(B))$ and $\Delta G^0 = G^0(C) - (G^0(A) + G^0(B))$. Additionally, the energy barrier $\Delta E^\ddagger$

and $\Delta G^{\neq,0}$ are defined as, $\Delta E^{\neq} = E([AB]^{\neq}) - (E(A) + E(B))$ and $\Delta G^{\neq,0} = G^0([AB]^{\neq}) - (G^0(A) + G^0(B))$. $[AB]^{\neq}$ is the exact TS (the saddle point on the potential energy surface) and it is obtained from this approximate point by using the Berny optimization algorithm as implemented in G09.

85 3. Results and Discussion

Referring the paper of Lin *et al.*, we use the same C2-substituents as their experiment and evaluate the alkaline stability. First, four geometries are optimized as shown in Fig. 1. Figure 1(A) is a C2-unsubstituted 1-ethyl-3-(4-isopropylbenzyl) imidazolium cation (EIIM). Figures 1 (B), (C) and (D) are
90 1-ethyl-2-methyl-3-(4-isopropylbenzyl) imidazolium cation (EMIIM), a 1-ethyl-2-isopropyl-3-(4-isopropylbenzyl) imidazolium cation (EIIIM) and a 1-ethyl-2-phenyl-3-(4-isopropylbenzyl) imidazolium cation (EPhIIM), respectively. Second, we describe potential energy curves (PECs) and investigate the effect on the steric hindrance in the C2-substituted imidazolium cations. Finally, the
95 minimum energy paths along the ring-opening and deprotonation reactions are calculated and it is found that the C2-substitution can significantly enhance the alkaline stability of the deprotonation reaction.

In order to investigate the effect on the steric hindrance quantitatively, PECs of each imidazolium cation are shown in Fig. 2. Here, the reference ($\Delta E = 0$) is
100 the sum of the energy of the separated reactants. If necessary, we describe the PECs by a method; we assume that an OH^- anion approaches to the α -C and then the ring-opening reaction occurs. Thus, we fix the distance between the α -C and the O of the OH^- anion d and calculate the potential energy as a function of d , changing d from 3.5 to 1.5 Å with every 0.1 Å. Figure 2 indicates that in
105 the case of EIIM, the approach of an OH^- anion makes the potential energy continue to decrease monotonically due to the attractive interaction between the H bonding to the α -C and the O of the OH^- anion, which eventually results in the deprotonation reaction at $d = 2.6$ Å as shown in Fig. 3. Hence, the alkaline stability of EIIM is by far the lowest. On the other hand, the effect on the steric

hindrance appears obviously in EMIIM, EIIIM and EPhIIM due to the repulsive interaction between the OH^- anion and every substituent. The highest points of EMIIM, EPhIIM and EIIIM are 0.21, 0.27 and 0.29 eV, respectively. The larger the size of the substituent is, the larger the effect on the steric hindrance also tends to become. This is because the isopropyl and phenyl groups consist of a larger number of atoms than the methyl group and the repulsive interaction between electrons becomes stronger. The π -electrons generated by the benzene ring in EPhIIM are weakly-bounded to the nucleus and it is easy to move freely. Thus, when an OH^- anion approaches to the α -C, the π -electrons intend to avoid the OH^- anion and then the potential energy in EPhIIM gets a little smaller than that in EIIIM. Hence, EIIIM has the largest effect on the steric hindrance among the C2-substituted imidazolium cations. Consequently, the effect on the steric hindrance is in the order of EIIIM > EPhIIM > EMIIM > EIIM. From the analyses of the PECs, EIIM is exceedingly vulnerable to attack from the OH^- anion and all of the following calculations are performed in only the C2-substituted imidazolium cations.

Using the C2-substituted imidazolium cations, we calculate the minimum energy paths along the ring-opening reaction. The reference ($\Delta G = 0$) is also the sum of the Gibbs free energy of the separated reactants in common with $\Delta E = 0$. Figure 4 demonstrates that all of the energy paths are very similar. The energy barriers in EMIIM, EIIIM and EPhIIM are 1.53, 1.50 and 1.48 eV, respectively as shown in Table 1. They are almost comparable to each other and the differences can be negligible. This result shows that the C2-substitution plays the role of the steric hindrance and hinders the OH^- attack only when an OH^- anion approaches to the α -C of an imidazole ring. Once the ring-opening reaction begins to occur, the differences between the substituents do not depend on the energy barriers. Although the differences between the energy barriers are quite little, the alkaline stability is in the order of EMIIM > EIIIM > EPhIIM. Furthermore, the step (E) to (G) corresponds to the situation of the approach of an OH^- anion as shown in Fig. 2. The highest steps (F) of EMIIM, EPhIIM and EIIIM are 0.21, 0.25 and 0.31 eV, respectively in terms of ΔE and those are

closely consistent with the highest points of Fig. 2. Nucleophilic substitution
 reaction is affected by the lowest unoccupied molecular orbital (LUMO) energy
 of a compound and the lower the LUMO energy is, the easier the nucleophilic
 attack becomes.[16] In the case of imidazolium cations, the lower LUMO energy
 145 of the compound makes OH^- attack easier and the durability of the ring-opening
 reaction decreases. Figure 5 shows that the LUMO energy of EMIIM, EIIIM and
 EPhIIM are -1.029, -1.080 and -1.439 eV, respectively. EMIIM has the highest
 LUMO energy because the hyper-conjugation between the π -conjugated imida-
 zole ring and the σ bond of the methyl group increases the electron density at
 150 the imidazolium cation.[17] Hence, EMIIM can make OH^- attack most difficult.
 On the other hand, EPhIIM has the lowest LUMO energy because the electron-
 withdrawing effect by the phenyl group decreases the electron density at the
 imidazolium cation.[18] The order of the LUMO energy in the C2-substituted
 imidazolium cations is completely consistent with that of the energy barriers of
 155 the ring-opening reaction.

As well as the ring-opening reaction, we also calculate the minimum energy
 paths along the deprotonation reaction. Figure 6 demonstrates that the dif-
 ferences between the substituents depend on the energy barriers sensitively in
 contrast to the ring-opening reaction. Table 2 shows that the energy barriers
 160 in EMIIM, EIIIM and EPhIIM are 3.83, 3.47 and 2.15 eV, respectively and all
 of them are very high. The energy changes of EMIIM and EIIIM are 0.43 and
 0.50 eV, respectively, indicating that the ISs are most stable. Although the
 energy change of EPhIIM is -0.05 eV, the reaction is highly reversible. Hence,
 C2-substitution can hinder the deprotonation reaction and enhance the alkaline
 165 stability dramatically. The deprotonation reaction is triggered by OH^- attack
 to the C bonding to the α -C (β -C). Table 3 shows the electron density dis-
 tribution at the α -C and β -C. The electron density distribution at the β -C in
 EMIIM, EIIIM and EPhIIM is -0.634, -0.278 and -0.141, respectively and there
 are considerable differences. In particular, the electron density distribution at
 170 the β -C of EMIIM is much higher than the other cations because the β -C has
 three H atoms and it can attract most electrons from the H atoms due to the dif-

	ΔE (eV)	ΔG^0 (eV)	$\Delta E^\ddagger$ (eV)	$\Delta G^{\ddagger,0}$ (eV)
EMIIM	-1.05	-0.49	1.10	1.53
EIIIM	-1.14	-0.67	0.98	1.50
EPhIIM	-1.06	-0.49	0.93	1.48

Table 1: Calculated energy changes and energy barriers in the ring-opening reaction. There are little differences between the energy barriers. Energy is given by eV.

ference between the electronegativities of C and H, which results in the highest energy barrier. The β -C of EIIIM has one H atom and the electron density distribution is lower than that of EMIIM. Thus, the repulsive interaction between
175 electrons gets weaker and then the energy barrier is lower than that of EMIIM. However, the β -C of EPhIIM has no H atoms and cannot attract electrons from H atoms. As the result, the electron density distribution at the β -C decreases and the energy barrier is lowest. Hence, the alkaline stability of the deprotonation reaction is in the order of EMIIM > EIIIM > EPhIIM. Incidentally,
180 Table 3 also shows that the electron density distribution at the α -C is almost equivalent. This is because the number and the element of the atoms bonding to the α -C are common regardless of the differences between the substituents. To be specific, all of the α -C have one C and two N atoms. Thus, the energy barriers of the ring-opening reaction are almost independent of the differences
185 between the substituents as shown in Table 1. Consequently, C2-substitution makes a most effective influence on the electron density distribution at the β -C. Therefore, the C2-substitution exerts a most important effect to hinder the deprotonation reaction and eventually the alkaline stability can be enhanced considerably compared with that of C2-unsubstitution.

190 4. Conclusion

Based on DFT method, it is numerically investigated how C2-substitution affects the alkaline stability in imidazolium cations. First of all, we prepare four imidazolium cations and PECs are described. They indicate that the effect

	ΔE (eV)	ΔG^0 (eV)	$\Delta E^\ddagger$ (eV)	$\Delta G^{\ddagger,0}$ (eV)
EMIIM	0.08	0.43	3.46	3.83
EIIM	-0.33	0.50	3.22	3.47
EPhIIM	-0.46	-0.05	1.56	2.15

Table 2: Calculated energy changes and energy barriers in the deprotonation reaction. In contrast to the ring-opening reaction, the differences between the substituents depend on the energy barriers. Energy is given by eV.

electron density distribution	α -C	β -C
EMIIM	0.506	-0.634
EIIM	0.516	-0.278
EPhIIM	0.488	-0.141

Table 3: Electron density distribution at the α -C and β -C in EMIIM, EIIM and EPhIIM.

on the steric hindrance appears explicitly in the C2-substituted imidazolium
195 cations as several experimental groups point out. Next, the minimum energy
paths along the ring-opening and deprotonation reactions are calculated. The
energy barriers of the ring-opening reaction are almost comparable to each other.
Hence, they are independent of the differences between the substituents. How-
ever, the energy barriers of the deprotonation reaction depend on the differences
200 between the substituents because the differences seriously affect the electron
density distribution at the β -C.

Considering the comprehensive evaluation of the PECs and the energy paths
along both the ring-opening and deprotonation reactions, the alkaline stability
is in the order of EMIIM > EIIM > EPhIIM > EIIM because EMIIM can
205 hinder the deprotonation reaction most effectively among the C2-substituted
imidazolium cations due to the highest electron density distribution at the β -C.
The order is consistent with that of the experiment by Lin *et al.* We conclude
that the most important effect of C2-substitution is to increase the electron
density at the β -C and hinder the deprotonation reaction. Therefore, the methyl

210 group which has three H atoms can be most promising as the substituent of
imidazolium cations.

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FIGURES

Figure 1: Calculated optimized geometries in imidazolium cations. (A) EIIM (C2-unsubstituted). (B) EMIIM. (C) EIIIM. (D) EPhIIM. (B), (C) and (D) are substituted by methyl, isopropyl and phenyl groups. Yellow, blue and magenta spheres are C, H and N, respectively.

Figure 2: Calculated PECs. Effect on the steric hindrance appears except for EIIM. d is fixed and changed from 3.5 to 1.5 Å with every 0.1 Å. Energy is given by eV.

Figure 3: Calculated optimized geometry at $d = 2.6$ Å in EIIM. EIIM is degraded at $d = 2.6$ Å due to the deprotonation reaction. A red sphere is O. The black arrow shows d .

Figure 4: Calculated optimized geometries of EMIIM and minimum energy paths along the ring-opening reaction. (E) IS. (F) TS₁. (G) intermediate state (IMS₁). (H) TS₂. (I) IMS₂. (J) TS₃. (K) FS. Energy is given by eV.

Figure 5: LUMO energy and isosurface of the C2-substituted imidazolium cations. The order of the LUMO energy corresponds to that of the energy barriers in the ring-opening reaction. Energy is given by eV.

Figure 6: Calculated optimized geometries of EMIIM and minimum energy paths along the deprotonation reaction. (L) IS. (M) TS. (N) FS. Energy is given by eV.