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

Ryo Tsuchitani [a], Hiroshi Nakanishi [a], Hideyuki Shishitani [b], Susumu Yamaguchi [b], Hirohisa Tanaka [b], Hideaki Kasai [a,c,d,*]

[a] Department of Applied Physics, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan
[b] R & D Division, Daihatsu Motor Co., Ltd., 3000 Yamanoue, Ryuo, Gamo, Shiga 520-2593, Japan
[c] Center for Atomic and Molecular Technologies, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan
[d] Center for Continuing Professional Development, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan

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

## 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.

$$\text{Anode}: H_2 + 2OH^- \rightarrow 2H_2O + 2e^- \tag{1}$$

$$\text{Cathode}: 1/2O_2 + H_2O + 2e^- \rightarrow 2OH^- \tag{2}$$

$$\text{Overall}: H_2 + 1/2O_2 \rightarrow H_2O \tag{3}$$

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 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 $\pi$-conjugated imidazole ring compared with quaternary ammonium cations [10]. The main degradation reaction in imidazolium-based AEMs is called ring-opening reaction, which is a kind of nucleophilic substitution reaction. $OH^-$

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* Corresponding author at: Department of Applied Physics, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan.
*E-mail address:* kasai@dyn.ap.eng.osaka-u.ac.jp (H. Kasai).

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anions attack the C between the two N atoms of the imidazole ring ($\alpha$-C) under alkaline condition and then the imidazole ring is broken. AEMs degraded by $OH^-$ attack lose the ability in ion 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 $OH^-$ 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.

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 was an initial degradation reaction before the ring-opening reaction and it was much more dominant rather than the ring-opening reaction.

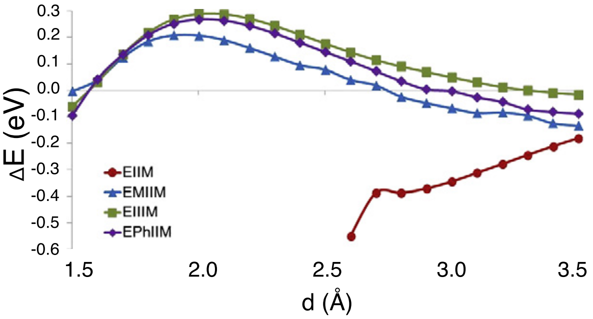

**Fig. 2.** Calculated PECs. Effect on the steric hindrance appears except for EIIM. *d* is fixed and changed from 3.5 to 1.5 Å with every 0.1 Å. Energy is given by eV.

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.

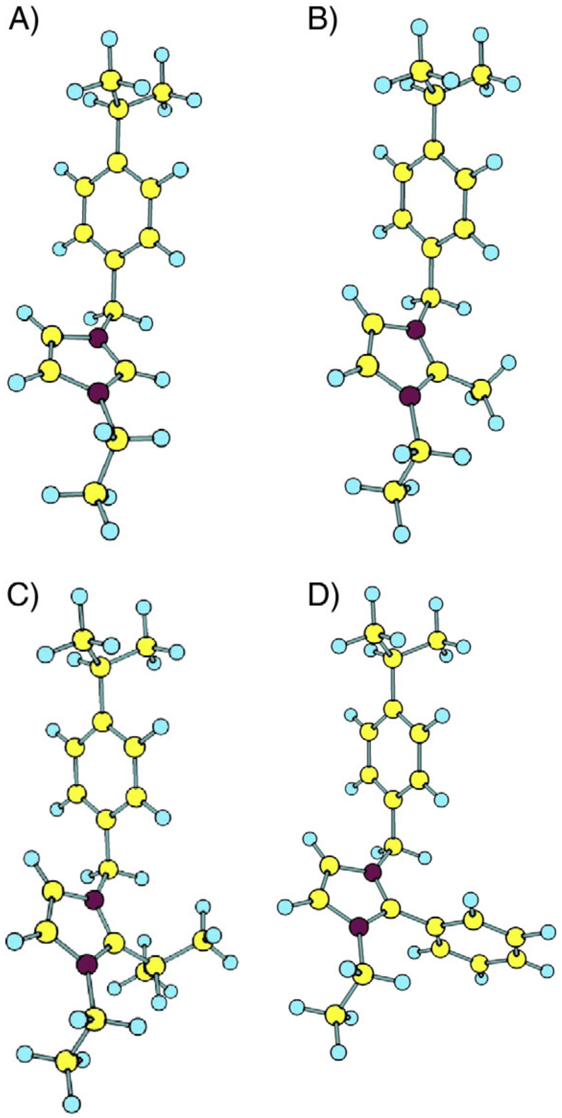

**Fig. 1.** Calculated optimized geometries in imidazolium cations. (A) EIIM (C2-unsubstituted). (B) EMIIM. (C) EIIIM. (D) EPhIIM. (B), (C) and (D) are substituted by methyl, isopropyl and phenyl groups. Yellow, blue and magenta spheres are C, H and N, respectively.

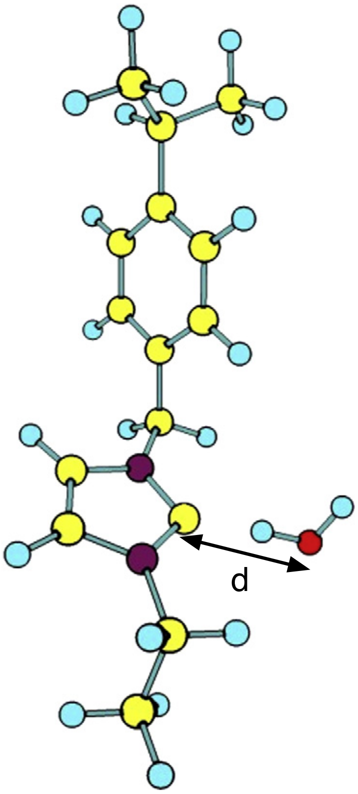

**Fig. 3.** Calculated optimized geometry at $d = 2.6$ Å in EIIM. EIIM is degraded at $d = 2.6$ Å due to the deprotonation reaction. A red sphere is O. The black arrow shows *d*.