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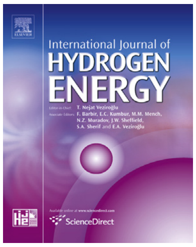

Hydroxide ion transfer in anion exchange membrane: A density functional theory study

Guoqing Yang, Juanyuan Hao**, Jie Cheng, Ning Zhang, Gaohong He, Fengxiang Zhang, Ce Hao*

State Key Laboratory of Fine Chemicals, Dalian University of Technology, Panjin 124221, People's Republic of China

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ABSTRACT

A theoretical investigation of hydroxide ion transport mechanism in quaternary ammonium functionalized polystyrene (QAPS) anion exchange membrane (AEM) was studied by density functional theory (DFT). The results showed that there were two steps for OH^- transferring through QAPS-AEM. The first step was the movement of OH^- in water channel, which was induced by frequently forming and breaking of hydrogen bonds (H-bonds) between H_2O and OH^-. The second step was that OH^- transferred across the quaternary ammonium (QA) groups by following the rotation about C–C single bond, which was the rate-determining step for OH^- transferring in QAPS-AEM. We presented that the ionic groups on the side chain of polymer with smaller space steric should provide higher ion conductivity due to their lower rotation energy barriers.

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Introduction

Fuel cells, the conversion technologies of chemical energy from fuel and oxidant into electrical energy cleanly and efficiently, have been undergoing revolutionary developments and expected to be one of the most promising environmentally-friendly power sources for widely application such as transportation and stationary [1,2]. Among many kinds of fuel cells, anion exchange membrane fuel cells (AEMFCs) have obtained the increasing attention primarily, in recent years, because of a better kinetic characteristics for the oxygen reduction reaction (ORR), and therefore non-noble metals such as Co and Ni could be used as catalyst, simpler water management and reduced the degree of corrosion [3–6]. Despite the mentioned advantages, AEMFCs have a few challenges such as low anion conductivity and poor chemical stability at high pH on anion exchange membrane (AEM) which is the hard-core of AEMFC, especially the low anion conductivity limits the practical applications (vehicular, stationary, portable) [4,7–9]. As for this issue, many encouraging progresses have been achieved in recent years to increase the anion conductivity of AEMs, in the following several aspects, synthesizing novel structure including backbone and the side chains, increasing the ion exchange capacity (IEC) and adjusting cross-linking degree [10–13]. However, not enough research literatures exist on the relationship between hydroxide ions transport mechanism in AEM and the polymer

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* Corresponding author.
** Corresponding author.
E-mail addresses: jyhao@dlut.edu.cn (J. Hao), haoce@dlut.edu.cn (C. Hao).

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structures [8]. For that reason, researchers couldn't primarily design the superior anion exchange groups and the polymer structure with high ionic conductivity.

To our knowledge, there have been no reports about an explicit hydroxide ions transport mechanism in AEM [14–20]. Until now, the hydroxide ions transport mechanisms in AEM were proposed analogous to the transport of protons in proton exchange membrane (PEM) [21], in a certain extent (*ECS* meeting abstracts: http://ma.ecsdl.org/content/MA2014/01/15/667.short). For hydroxide ions transport mechanisms in AEMs, the main research technology was molecular dynamics (MD) simulation. Lin Zhuang and his coworkers [22] presented the self-cross-linking and self-aggregating design methods to increase the IEC and boost the ionic conductivity by MD method. Boris V. Merinov [23] reported that ammonium groups were mostly located along walls of the water channel and the mobile OH^- were distributed inside of the channels. In the hydrated membranes, Hiromitsu Takaba [24] suggested that OH^- transport in AEMs would follow Grotthus mechanisms coupled with Vehicle mechanisms, but it was quite different from the proton transport mechanism. Recently, Chen et al. [25] developed a new multiscale reactive molecular dynamics model for hydroxide in aqueous solution and reported that a continuous overlapping region produced by side chains and it facilitated the OH^- transport with Vehicular and Grotthuss mechanisms. However, those studies only showed the effects of water content and ionic groups on OH^- diffusion coefficients, while they couldn't give a detailed investigation in the relationship between the process of hydroxide ions moving and the weak interaction such as H-bonds. To compensate the limitation of MD in calculation accuracy, recently, density functional theory (DFT) was successfully used to choose the proper segment to describe the characteristics of AEM due to its high degree of accuracy to describe the structures in the atomistic and molecular scale [26]. However, there were still no comprehensive theoretical studies about OH^- transport mechanism in AEM based on DFT [8,27].

In the present study, the DFT calculation was applied to investigate the hydroxide ions transport mechanism in AEM based on quaternary ammonium functionalized polystyrene (QAPS-OH) which coupled with OH^-. The key roles of H-bonds in water channel and the lowest energy barrier route of OH^- traversing the quaternary ammonium (QA) groups were analyzed in detail. This fundamental study of OH^- transport mechanism in AEM would provide guideline for increasing hydroxide ion conductivity and discovering novel AEMs.

Computational details

All calculations in this paper were performed with the first-principles method based on DFT by using the Gaussian 09 suite of programs [28]. The geometries optimization and vibrational frequencies analysis of the QAPS-OH models were calculated using DFT with the hybrid exchange-correlation functional B3LYP and 6-311++G(d,p) basis sets used for Nafion and 1,2,3-triazole-triazolium calculation [17,29]. All charges were represented using the Mulliken charges analysis. The precision of convergence is 10^{-6}. A scaling factor of 0.961 was utilized to calculate the IR spectra (NIST Computational Chemistry Comparison and Benchmark Database NIST Standard Reference Database Number 101 Release 15b, August 2011, Editor: Russell D. Johnson III. http://cccbdb.nist.gov/). Solvation effects were taken into account by means of the Polarizable Continuum Model (PCM) and water solution. The reaction potential energy barriers were obtained by comparing the sum of electronic energies of the reactants (a) (E_a) or products (b) (E_b) with the corresponding energies of the transition states (TS) (E_{TS}). The binding energies of hydroxide ion to oligomeric fragment were calculated using the equation: $E_{binding} = E_{frag+OH}$-$E_{frag}$-$E_{OH} + E_{BSSE}$, where $E_{frag+OH}$, E_{frag}, E_{OH} and E_{BSSE} were the total electronic energies of QAPS-OH, the QAPS fragment, the single hydroxide ion, and the effects of basis set superposition error (BSSE), respectively.

Results and discussions

Selection of calculation model

Several AEMs adopting polystyrene as backbone or quaternary ammonium as ionic groups have received much attention for electrolyte membrane in recent years, because of their good physical stability and relatively high chemical stability [13,30–33]. Therefore, we selected the QAPS-AEM as the study object, whose backbone and side chains are polystyrene and QA groups, respectively. To simplify the computational processes, we selected a repeated structure fragment to represent the polymer. Fig. 1a shows the geometric configuration of the selected fragment. In order to confirm the reasonability of our model, we compared its calculated infrared spectra (IR) with experimental ones firstly. The IR spectra of the model were calculated based on the optimized geometry with 6-311++G(d,p) basis sets (the red line in Fig. 1b). The band of 3200 cm^{-1} is assigned to stretching vibrations of aromatic C–H in benzene; the band of 2900 cm^{-1} is due to the symmetric stretching vibration of C–H in $N(CH_3)_3$ and the peak of 1498 cm^{-1} is due to the C–H bending vibrations in $N(CH_3)_3$. The another two peaks of 1527 cm^{-1} and 840 cm^{-1} are assigned to aromatic C=C stretching and C–H bending vibrations, respectively. The calculated IR spectra agrees very well with the experimental values [30] (the green line in Fig. 1b). Therefore, we could get the conclusion that the calculation model was reasonable and reliable for exploring OH^- transport mechanism in QAPS-OH AEM.

The process of hydroxide ion transferring

The polymer structure of AEM constituted by backbones and side chains. Based on the reported results that the ionic transport channel was crucial to the mobility of OH^- in AEMs [4,8], we draw the conclusion that, comparing with the backbone, the functional groups and water molecules among two adjacent side chains played more important roles in OH^- transport process. A detailed analysis was implemented on the process of a hydroxide ion moved through the AEM, then we presented that there were two steps in this process. One step was the transport process when hydroxide ions were between two functional groups, in other word, hydroxide ions

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