



Theoretical study of high performance hydrocarbon-based ion-exchange membranes



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ABSTRACT

To obtain a basic insight for developing hydrocarbon based polymer membranes that have high proton conductivity, we designed new molecules by introducing the sulfonyl group (SO₂) into various positions of benzene sulfonic acid and analyze their deprotonation reaction. We evaluated the activation and stabilization energies of deprotonation reactions of these model molecules with three water molecules. The energies were highly dependent on the positions of the sulfonyl group. For the case of a sulfonyl group introduced between the carbon and sulfur atom of the sulfonic group (SO₃H), the activation energy decreased and the stabilization energy increased. These changes were attributed to the charge distribution around the oxygen atoms averaged owing to the high electronegativity of the sulfonyl group. Our results suggest that introducing highly electronegative functional groups can improve the performance of hydrocarbon-based membranes, without the need for fluorine atoms.

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1. Introduction

Polymer electrolyte fuel cells (PEFCs) are a promising technology for use as an energy source in electric vehicles owing to their low operating temperatures and low weight [1–3]. However, wider spread use of these systems requires higher performance and lower costs. A schematic image of a typical PEFC is shown in Fig. 1. In this type of fuel cell, electrochemical reactions occur in a membrane electrode assembly (MEA), which consists of gas diffusion layers, microporous layers, catalyst layers, and a polymer electrolyte membrane (PEM). Hydrogen gas provided from the anode side is split into protons and electrons on a platinum surface, which acts as a catalyst. Electrons and protons move to the surface of a platinum in the cathode side through an external circuit and the PEM, respectively. These components react with oxygen and water is generated. Perfluorosulfonic acid type materials, such as Nafion, are typically used for the PEM [1,4]. Owing to the presence of the sulfonic group, these membranes are strongly acidic and have high ion conductivity, thus making them suitable for use in fuel cells. However, fluorine-based membranes are difficult to fabricate and expensive. Moreover, such membranes decompose at high temperatures. To address these problems, hydrocarbon-based membranes have received some attention, as these may be

easier to fabricate than fluorine-based membranes [5–8]. However, hydrocarbon-based membranes have low proton conductivity at low humidity [9]. This characteristic is attributed to the flexibility and acidity of the side chain [10–20]. Thus, to improve hydrocarbon-based membranes, we compared the chemical properties of fluorine-based membranes and those of hydrocarbon-based membranes. We focused on deprotonation reactions of the short side chain Nafion model (SSC) and benzene sulfonate acid (BSA) as a model for a hydrocarbon based membrane in low water content cases [21,22]. For both molecules, at a water content greater than 3, static deprotonated states can be obtained. Moreover, we clarified that the activation energies of the deprotonation reaction decrease with increasing water content. Compared with SSC, the activation energy of BSA is larger than that of SSC, and the stabilization energy of BSA is smaller than that of SSC. These results show that fluorine atoms affect not only the stabilization energy, but also the activation energy. Therefore, to develop hydrocarbon-based membranes that have high proton conductivity, even at low water content, it is necessary to decrease the activation energy and increase the stabilization energy to the same level as that of fluorine-based membranes. Thus, to realize a non-fluorine-based membrane with a small activation energy and large stabilization energy, in this study we designed molecular models based on BSA and evaluated their activation and stabilization energies through electronic structure calculations. We introduced an electron withdrawing sulfonyl group (SO₂) into BSA, and investi-

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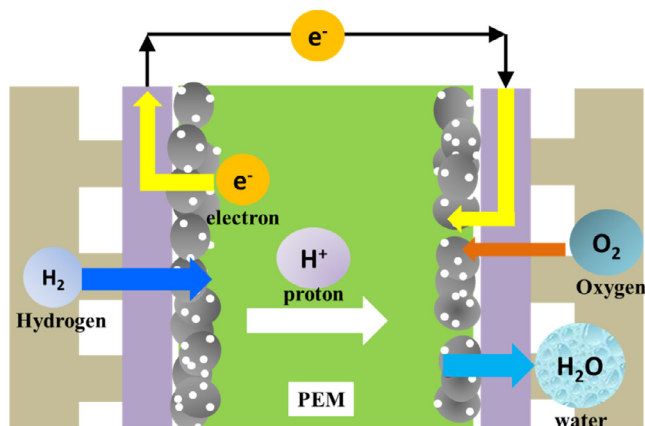


Fig. 1. Schematic model of PEFC.

gated changes of activation and stabilization energies. Furthermore, changing the position of the SO_2 group allowed us to evaluate how the placement of the group affected the energy. To clarify the differences of the activation and stabilization energies, we analyzed the charge distribution of the function groups in detail.

2. Computational details

In Fig. 2, the molecular structures of the base model and four models are shown. We suppose to improve polymers with sulfonic styrene acid structure like a Sulfonated polyether ether ketone (S-PEEK) and thus employ BSA molecule as the base model shown in Fig. 2(a). Fig. 2(b)–(d) have SO_2H at the ortho, meta, and para positions (relative to the sulfonic group), respectively. Fig. 2(e) shows a model in which SO_2 is introduced between a carbon atom and a sulfonate atom. In this study, we denote our model compounds as *o*-hydrosulfonyl benzene sulfonic acid (*o*-HSBSA), *m*-hydrosulfonyl benzene sulfonic acid (*m*-HSBSA), *p*-hydrosulfonyl benzene sulfonic acid (*p*-HSBSA), and benzene sulfonyl sulfonic acid (BSSA), respectively. To control the number of electrons in these model compounds, SO_2H is used rather than SO_2 . BSSA has the same structure in which one OH of the dithionic acid is changed to a phenyl group. The dithionic acid cannot be isolated, and thus BSSA, which has the same structure as a dithionic acid, is likely to be unstable [23]. Thus, in this study, we focused only on the effect of the electron-withdrawing groups on the deprotonation phenomena and the position dependence of the groups on the reaction. We do not focus on the thermal stability of the molecules.

In this study, we considered the chemical reactions of model molecules and three water molecules, i.e., a water content of 3. The reason for using this water content is that we cannot obtain stable anionic structures when the water content is lower than 3 for molecules containing sulfonic groups in previous studies [21]. To obtain stable structures for the reactants and products, we performed geometry optimization and confirmed that the obtained structures are on the minimum point of a potential energy surface by vibration analysis. Moreover, in our transition state calculations, we performed geometry optimization and vibration analysis to obtain a saddle point structure, and confirmed that the obtained imaginary frequency mode corresponded to the deprotonation reaction. We defined the energy difference between the energy of the reactant and the energy of the transition state as the activation energy. We also defined the energy difference between the reactant and the energy of the product as the stabilization energy. The basis set superposition error was corrected by the counterpoise method. The charge distribution was analyzed by Natural

Bond Orbital (NBO) [24]. All calculations were performed based on density functional theory, and B3LYP was used as the exchange–correlation functional [25], with 6-311+G** as a basis set function. Gaussian09 [26] was used for all calculations and VESTA [27] was used for modeling and visualizing the results.

3. Results and discussion

In Fig. 3, the activation energy of the deprotonation reaction in each model is shown. For the case of the *x*-HSBSA models (Fig. 2 (b)–(d)), we found a tendency that the activation energy increases when the position of SO_2H is closer to the sulfonic group and the activation energies are lower than that of BSA (Fig. 2(a)). However, the differences among these models were small, and the activation energy was about 3 kcal/mol. In the case of BSSA (Fig. 2(e)), the activation energy was 0.3 kcal/mol, which is lower than that of SSC, a model for Nafion, 0.7 kcal/mol [21]. The error in the energy calculated by our method in this study was almost 2 kcal/mol [28], thus a comparison between BSSA and SSC is difficult. However, we can say that the energy barrier of the deprotonation reaction is similar for both models. The deprotonation reaction of the sulfonic group is the proton transfer from the sulfonic group to the negatively charged oxygen atoms in water molecules and did not include bond rearrangements. Owing to the relatively high electronegativity of the oxygen atoms, the electrons of the sulfonic group are localized on the oxygen atoms. If electrons are highly localized on oxygen atoms, this can be considered to make a repulsive force between the oxygen atoms of the water molecule and the sulfonic group larger. Consequently, the activation energy of the protonation increases. Hence, we consider that the dominant factor of the activation energy is the ability of a water molecule to approach the proton, which is determined by the charge distribution in the region near the sulfonic group. To clarify the reason for the SO_2 position dependence of the activation energy, we focused on the NBO charges of the oxygen and hydrogen atoms of the sulfonic group in the model molecules. The NBO charges of oxygen and hydrogen atoms of the sulfonic group are shown in Table 1. The charge on hydrogen atoms for all models showed almost the same values. This result indicates that the NBO charge of the H atom does not affect the activation energy of the deprotonation reaction. Next, we focused on the NBO charges of the oxygen atoms of the sulfonic group. In each oxygen atom, the differences of the NBO charge among the models were small, but comparing the sum of the NBO charge of the three oxygen atoms, the total for BSSA was -2.55 , and those for the other models were -2.63 and -2.64 . This result means that the electrons of BSSA is less localized around oxygen atoms of SO_3^- compared with other models. The activation energy of BSSA was also lower than those of other models, thus, this result suggests a correlation between the charge distribution of the oxygen atoms and the activation energy. The sum of the charge of SO_3^- in BSSA is -0.59 , which is larger than other model. This is due to the less charge of the sulfur atom of SO_3^- . This result means that electron distribution of SO_3^- of BSSA is more flatten.

Fig. 4 shows the stabilization energy of the deprotonation reaction in each model. The stabilization energy is defined by the energy difference from the energy of the product to that of the reactant. The stabilization energy of *o*-HSBSA (Fig. 2(b)) was -0.6 kcal/mol, and those of *m*-HSBSA (Fig. 2(c)) and *p*-HSBSA (Fig. 2(d)) were both -1.1 kcal/mol. These energies were higher than that of BSA which is 0.55 kcal/mol and are less than that of SSC which is -3.7 kcal/mol. However, the stabilization energy of BSSA was -2.8 kcal/mol. This energy is lower than that of SCC, but higher than those of the other model molecules. The differences between the models is likely to be caused by the charge dis-

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