Solid State Ionics 274 (2015) 94–99

Contents lists available at ScienceDirect

Solid State Ionics

journal homepage: www.elsevier.com/locate/ssi

Quantum chemical analysis of the deprotonation of sulfonic acid in a hydrocarbon membrane model at low hydration levels

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A R T I C L E   I N F O

Article history:
Received 3 September 2014
Received in revised form 6 February 2015
Accepted 4 March 2015
Available online 24 March 2015

Keywords:
Polymer electrolyte fuel cells
Transition state
First principle calculation
Activation energy
Hydrogen bond

A B S T R A C T

We conducted a quantum chemical analysis of the deprotonation reaction of the sulfonic group (SO_3H) in a model of a hydrocarbon (HC) membrane, which has been proposed as a new proton conductor for polymer electrolyte membranes (PEMs) of polymer electrolyte fuel cells (PEFCs). By comparison with perfluorosulfonic acid (PFSA) species, activation energies are higher at all hydration levels. When deprotonation occurs in the PFSA at hydration level three, the activation energy in the model HC is still higher than the thermal energy of the PEFC operation temperature and therefore it is difficult or impossible to overcome it. Moreover, at hydration level three, the deprotonated state is not stable, in contrast to PFSA, and deprotonation of SO_3H and protonation of the sulfonate (SO_3^-) should occur with the same probability. Because the activation energy is high and the deprotonation state is unstable, it is difficult to deprotonate the SO_3H of the model HC to SO_3^- at hydration level three. Moreover, a bond-order analysis shows that SO_3^- is more strongly connected to H_3O^+ than it is for PFSA. These appear to be the main causes of the remarkably reduced proton conductivity in HC membranes at low hydration levels.

1. Introduction

Polymer electrolyte fuel cells (PEFCs) have attracted great attention as new high-current-density power sources for home use, automobiles, and other vehicles because of their portability. Some products have already been commercially developed and sold. However, several aspects of their function are unclear, such as the dynamics of molecules inside the PEFC, water behavior in the microenvironment of the cell, and their degradation process. To construct high-performance cells at a low cost for the entire system, it is necessary to clarify aspects of the PEFC components by performing basic research from various viewpoints. The principle of power generation using PEFC is the reversal of water electrolysis. Hydrogen molecules supplied from an anode are dissociated into electrons and protons (H^+) on a catalyst such as Pt. The produced electrons and H^+ are transported to the Pt catalyst on the cathode through an external circuit and polymer electrolyte membrane (PEM), respectively. Oxygen gas is supplied at the cathode and water is generated on the Pt catalyst. At this time, power is generated simultaneously with the water. If H^+ can reach the catalyst layer of the cathode via PEM easily, the efficiency of power generation is good. Therefore, a PEM that transports H^+ efficiently is required. Various PEMs are available, including those at the stage of research and development, and can roughly be divided into perfluorosulfonic acid (PFSA) species and hydrocarbon (HC) species. A typical PFSA ionomer is Nafion. This polymer consists of a hydrophobic tetrafluoro backbone, ether, and sulfonic group (SO_3H). Various kinds of PFSA polymers are known, depending on the length of the fluorocarbon backbone. A common feature of PFSAs is high proton conductivity even at a low hydration level.

Recently, HC PEMs have attracted attention because of their relatively low cost of synthesis and heat-resistant properties. HCs consist of various groups, including phenyls, ether, and SO_3H, e.g., sulfonated polyether ether ketone (S-PEEK). In contrast to PFSAs, proton conductivity in HCs decreases dramatically with decreasing levels of hydration [1–3]. Some typical PFSAs and HC are shown in Fig. 1.

In general, H^+ exists as H_3O^+ connected to water molecules. In a PEM, water molecules contribute to H^+ conduction in two ways. First, forming a solvation shell around deprotonated SO_3H or sulfonate (SO_3^-) groups, the produced solvation shell prevents a strong connection between H_3O^+ and SO_3H. Second, the water molecule acts as a channel for protons hopping along the hydrogen bond between water molecules and H_3O^+. As mentioned above, PFSAs show good proton conductivity even at low hydration levels. By contrast, proton conductivity in current HCs at low hydration levels is very low [1,3]. This decrease of proton conductivity in HCs at low hydration levels is often explained by the low flexibility and low hydrophobicity of the polymer backbone by comparison with PFSA membranes [1–14]. Because of those properties, it is difficult for water molecules to form water clusters in the membrane. Therefore, proton conductivity decreases dramatically at low hydration levels. By contrast, there is another view that the acidity of the membrane, i.e., the ease of the deprotonation reaction, is

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http://dx.doi.org/10.1016/j.ssi.2015.03.005
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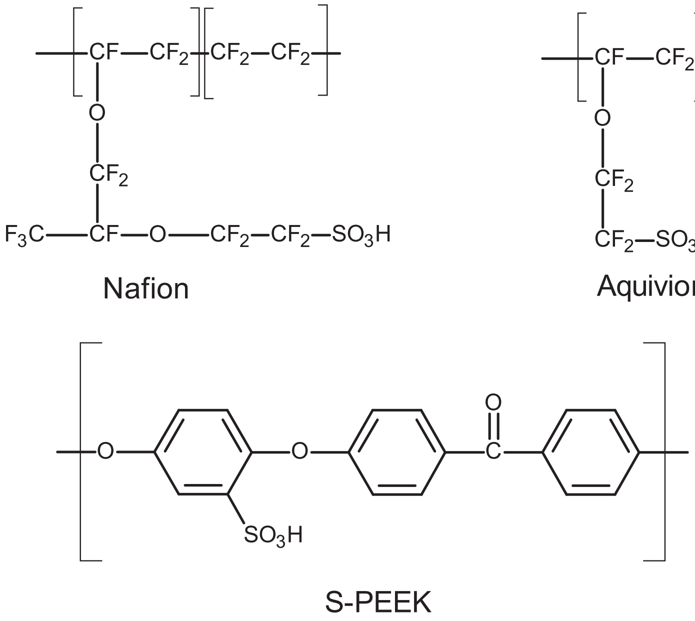

Fig. 1. Typical PEMs.

also affected by proton conductivity [2,15]. As shown in Fig. 1, both HCs and PFSAs have SO_3H generally, but the SO_3H of HCs is considered to be difficult to deprotonate by comparison with the SO_3H of PFSAs because of the differences in acidity. For this reason, there are few SO_3^- that have negative charges at lower hydration levels and therefore it is difficult to form larger solvation shells.

The most stable geometries are reported in model HCs and PFSA at low hydration levels. According to Wang et al., the SO_3H of $CF_3O(CF_2)_2SO_3H$, a short chain PFSA (scPFSA) as a model PFSA, is deprotonated such that its geometry consists of SO_3^-, H_3O^+, and water molecules, and is in its most stable state at a hydration level of three or more [16]. Paddison and Clark et al. reported that the deprotonated state of *p*-toluene sulfonic acid (*p*-TSA), a model HC, is more stable than the protonated state by 0.1 kcal/mol at a hydration level of three [17,18]. Considering a case in which *p*-TSA becomes more complicated, the characteristics of S-PEEK (modS-PEEK) obtained by substituting the methyl (CH_3) group of *p*-TSA with 2,5-dimethoxy phenyl ($CH_3OC_6H_3OCH_3$) were analyzed as a model HC by two groups, Idupulapati et al. [19] and Clark et al. [18]. Idupulapati et al. reported that protonated geometries are more stable at hydration levels of one to three [19], but Clark et al. reported that the more stable geometry at hydration level three is deprotonated [18]. However, the activation energy (ΔEa) and energy difference before and after deprotonation of SO_3H (ΔH) are not reported in these investigations. Recently, we revealed the properties of the deprotonation reaction of SO_3H of scPFSA at a low hydration level [20]. scPFSA are stabilized by deprotonation at hydration level three through very low ΔEa. We also showed a possibility that produced H_3O^+ is bound around the SO_3^- at this hydration level. However, the ΔEas of various HCs are still unknown. The properties of HCs at low hydration levels cannot be understood perfectly without estimating their ΔEas, which hinders the molecular design of PEMs with greater performance than currently reported materials. Acidity is evaluated by p*Ka* in experimental measurements, but p*Ka* is described only by ΔH, and does not provide an estimate of ΔEa. In addition, p*Ka* is defined as a value in the solvent. In contrast to solutions in which the ratio of water molecules to SO_3^- is large, the ratio of water molecules to SO_3^- is extremely low in PEM. There is no guarantee that the acidity of the membrane can be evaluated by p*Ka*, which is a characteristic of protons in solution.

In this study, ΔEa and ΔH for the deprotonation reaction in a model HC were determined using a quantum chemical procedure previously applied to scPFSA [20]. Static quantum chemical calculations are difficult to apply to dynamic processes, e.g., molecular diffusion. However, to date this procedure is the best method for analysis of the chemical properties or the situation of a molecule in a specific condition. In this report, we describe deprotonated HC membranes, especially the properties of a model HC that have been deprotonated at low hydration levels. This study is expected to contribute knowledge that will enable the future design and synthesis of monomers for PEMs that can conduct protons efficiently at low hydration levels. The purpose of this study is to clarify the chemical properties of fundamental HC PEMs. Then, we analyzed the model molecule of the S-PEEK which is the most fundamental among all HC PEMs.

The calculation procedure and preparation of the initial geometry are discussed in the Computational detail section. The obtained results are discussed in the Results and discussion section. The Conclusion section concludes with our discussion.

2. Computational detail

The simplest and essential model molecule for HCs is benzene sulfonic acid ($C_6H_5SO_3H$; BSA). Both Paddison [17] and Clark et al. [18] used *p*-TSA as their model HC. Idupulapati et al. [19] and Clark et al. [18] used modS-PEEK as their model HC. The p*Ka*s of BSA and *p*-TSA are similar [21]. Clark et al. reported similar stable geometries for *p*-TSA and modS-PEEK at each hydration level [18]. For these reasons, it is thought that the difference between 2,5-dimethoxy phenyl ($CH_3OC_6H_3OCH_3$), methyl (CH_3), and hydrogen does not greatly affect the deprotonation reaction. Therefore, BSA, as the simplest model molecule was adopted in this study. The target hydration levels one to three were used for the prediction of ΔEa, ΔH, geometrical properties or so on, as previously used for the study of scPFSA [20]. The relative configuration between SO_3H and water molecules in reactant, transition state, and product for each hydration level was set in the same manner as for the analysis of scPFSA [20]. Paddison has already reported the stable geometries for his model HC, *p*-TSA [17]. According to his study, relative configurations of SO_3H/SO_3^- and liquid molecules at all hydration levels were almost the same as those determined by Wang et al. for scPFSA [16]. Therefore, it is considered to be no problem to assume a reactant, transition state, and product similar to those used in the analysis of scPFSA. In this study, all atoms were allowed to relax.