Effects of hydration level, temperature, side chain and backbone flexibility of the polymer on the proton transfer in short-side-chain perfluorosulfonic acid membranes at low humidity conditions

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ABSTRACT

Ab initio molecular dynamics (MD) simulations are done to elucidate the electronic structure properties of a short-side-chain perfluorosulfonic acid (SSC PFSA) membrane at low humidity conditions. The artificial neural network (ANN) approach along with statistical methods is then employed to model and analyze these properties. The ANN method substantially speeds up the *ab initio* electronic structure calculations and has superior accuracy in mimicking the results of such calculations. The aim of this study is to understand the effects of hydration level, temperature, side chain flexibility of the SSC PFSA membranes, and backbone flexibility of the SSC PFSA membranes on the proton transfer in these membranes. Statistical analysis of results using analysis of means (ANOM) and analysis of variance (ANOVA) methods shows that no proton transfer from the SSC PFSA to the neighboring water molecules occurs at considerably low hydration levels. However, an increase in the probability of proton transfer is observed when the SSC PFSA membrane is sufficiently saturated. This process is more favorable at low temperatures. Moreover, the flexibility of either the side chains or the backbone of the SSC PFSA membrane has a great influence on the proton transfer phenomenon in such a way that allowing them to move freely causes an increase in the affinity of the SSC PFSA membrane to share its protons with water molecules. Further investigation is performed concerning the combined effect of the independent parameters (i.e., hydration level, temperature, side chain flexibility of the SSC PFSA membrane, and backbone flexibility of the SSC PFSA membrane) on the proton transfer process and the results are reported in detail.

1. Introduction

As concerns grow about damage to the environment of our planet, the availability of conventional fuels, and the political viability of nuclear power, alternative fuels for energy supplies need to be examined. It is believed that the energy produced by renewable-based approaches will extensively be employed as replacements for the currently used energy resources in the near future. One promising approach to be considered is use of hydrogen as a significant element in our energy future. Major advantages of using hydrogen include the following: firstly, it is a clean source of energy; secondly, it can be used for seasonal storage of energy; thirdly, it can easily be transported, and finally, it can be employed to produce electrical as well as thermal forms of energy [1].

Proton exchange membrane (also known as polymer electrolyte membrane) fuel cells (PEMFCs) represent a critical step in the proposed hydrogen-based energy [2]. They use hydrogen fuel and oxygen from the air to produce electricity. The main part of a PEMFC is the proton exchange membrane (PEM) that separates reactant gases and conducts protons. The most widely used PEM is Nafion®, which was developed by DuPont Inc. [3] and consists of a polytetrafluoroethylene backbone and double ether perfluoro side chains terminating in a sulfonic acid group. Nafion is characterized by high proton conductivity (i.e., 0.13 S cm^{-1} at 75 °C and 100% relative humidity) [4], chemical stability, and longevity of more than 60,000 h in a fuel cell environment [5]. However, the hydration requirement of conventional PEMs such as nafion results in problematically low operating temperatures limited by the boiling point of water (i.e., $T \leq 100$ °C at 1 atm.). Since PEMFCs can potentially save considerable energy and are secure within a hydrogen-based economy along with improvements in air quality, significant effort has been made to design and synthesize improved high performance materials used in PEMFCs such as membranes and catalysts [6]. In this regard, development of PEMs that can operate under simultaneous conditions of 100 °C and low humidity and therefore without pressurization of the system while exclusively transporting protons is widely considered to be an important research and development requirement for fuel cell technology [7].

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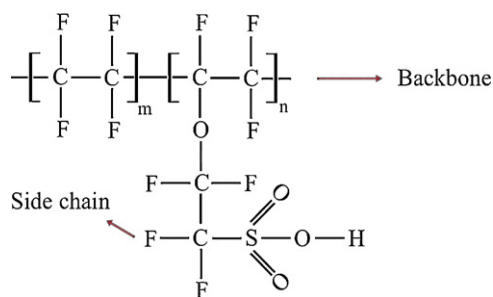 E-mail addresses: ahadian@imr.edu, samad_ahadian@yahoo.com (S. Ahadian).

Fig. 1. Chemical structure of the monomer of the SSC PFSA membrane.

One strategy for modifying the current PEMs is to change the chemistry of the backbone, side chains, and even the protogenic groups of membranes. It has been found that the length of the side chain has an impact on the membrane properties [8–10] as tested by short-side-chain perfluorosulfonic acid (SSC PFSA) membranes, which were firstly synthesized by the Dow Chemical Company [11]. The chemical structure of the SSC PFSA monomer is shown in Fig. 1. Typical values of m and n are 7 and 1, respectively. This material did not find much application in fuel cells and was not even further characterized due to difficulty in the synthesis of such a membrane. However, recently, this membrane has become the subject of great attention because of a simpler synthesis procedure proposed by Solexis [12]. The current investigation is a theoretical study on the proton conduction in a SSC PFSA membrane at low humidity conditions.

Due to difficulties concerning the experimental measurements in PEMFCs, modeling approaches such as atomistic simulation methods have been a powerful and valuable tool for improving the efficiency of PEMFCs [13,14]. Atomistic simulation methods are well suited to study important phenomena, which occur at the nanoscale level during the operation of a PEMFC such as transport mechanisms of ions, and water, morphological and structural changes of the PEMs. They can help to fill the existing knowledge gap between experimental observations and corresponding phenomena at nanoscale, to interpret the experimental data, and to predict and consequently rationally design new PEMs with higher efficiency. Recent reviews on the fundamentals and applications of molecular modeling methods in this field have been published by Kreuer et al. [15], Elliott and Paddison [16], Eikerling et al. [17], and Devanathan [2]. In the present investigation, we focus on first principles based electronic structure calculations to study proton transfer in a SSC PFSA membrane at low humidity conditions.

The fundamental problem of electronic structure calculations using *ab initio* quantum physics methods is that they become computationally intractable when the number of atoms and electrons in the underlying system becomes large. In order to tackle this problem, an artificial neural network (ANN) approach is employed to provide rapid and accurate interpolation of the *ab initio* database. Following this, statistical methods, i.e., analysis of means (ANOM) and analysis of variance (ANOVA), are used to interpret the results of ANN predictions. It is obvious that in practice many factors affect the proton transfer phenomenon in the SSC PFSA membranes. Knowing the quantitative effect of each parameter is very important. This task can be done using ANOM and ANOVA methods. More importantly, such determination is extremely difficult while we deal with a considerable number of variables, which are simultaneously changing. Statistical methods used in this investigation could also help us to provide such useful information. As a case study, the effect of four parameters, namely, number of water molecules, temperature, side chain flexibility of the SSC PFSA membrane, and backbone flexibility of the SSC PFSA membrane on binding energy per water molecule and energy gap between the highest occupied

molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is assessed. These electronic structure properties, i.e., binding energy per water molecule and HOMO–LUMO energy gap are measures of the proton transfer in the PFSA membranes.

The binding energy per water molecule is computed by the following equation:

$$\text{Binding energy per water molecule} = \frac{E_T - E_{\text{SSC PFSA}} - nE_{\text{H}_2\text{O}}}{n} \quad (1)$$

where E_T is the total energy of the system, $E_{\text{SSC PFSA}}$ is the total energy of the SSC PFSA membrane, $E_{\text{H}_2\text{O}}$ stands for the total energy of a single water molecule, and n denotes the number of water molecules. The binding energy defined above is indeed the negative of *vertical fragmentation energy*, firstly suggested by Konôpka et al. [18], which for a system A–B is defined as

$$E_{\text{A–B}}^{\text{frag}} = E(\text{A}) + E(\text{B}) - E(\text{A–B}) \quad (2)$$

where $E_{\text{A–B}}^{\text{frag}}$ is the vertical fragmentation energy, $E(\text{A})$ is the total energy of the segment A, $E(\text{B})$ stands for the total energy of the fragment B, and $E(\text{A–B})$ denotes the total energy of the whole system. Notice that no structural relaxation of fragments A and B are allowed and that these fragments are simply frozen according to an instantaneous configuration (as generated by static optimization or as sampled from a molecular dynamics (MD) simulation at finite temperature) [19]. This quantity (i.e., $E_{\text{A–B}}^{\text{frag}}$) is a measure of bond strength between the fragments A and B [20]. Consequently, the calculated binding energy per water molecule here is a measure of the bond strength between the SSC PFSA membrane and water molecules. On the other hand, the self-dissociation of the proton in sulfonic acids such as SSC PFSA membranes is a function of the strength of the Lowry–BrØnsted acid or conjugate base (Here, SSC PFSA membrane (i.e., R-SO$_3^-$) and hydronium ion (i.e., H$_3$O$^+$) are Lowry–BrØnsted acid and conjugate base, respectively) [21] such that the stronger the acid or its conjugate base, the more convenient the proton transfer from the SSC PFSA membrane to water molecules. Therefore, the binding energy per water molecule has an adverse relationship with the rate of the proton transfer reaction.

The HOMO–LUMO energy gap is also a measure of chemical stability of the system, which is also equivalent to the strength of the Lowry–BrØnsted acid (i.e., R-SO$_3^-$) or of the base (i.e., H$_3$O$^+$). Likewise, the stronger the acidity of the SSC PFSA membrane or basicity of water molecules, the more convenient the proton transfer from the SSC PFSA membrane to the water molecules. In general, as a chemical reaction progresses towards a transition state, electron density is transferred from the HOMO to the LUMO. The HOMO–LUMO energy gap attains a minimum value at the transition state and the system then proceeds towards another ground state, where the gap increases once again. Thus, for HOMO–LUMO driven reactions, the gap should behave in a predictable manner, being a minimum at the transition state and larger at the products and reactants [22,23].

The rest of this paper is delineated as follows. First, the computational details including the model associated with density functional theory (DFT) calculations, ANN approach, and statistical methods are presented. Following this, we would report and discuss the obtained results. Finally, we summarize our findings.

2. Computational details

2.1. Model and ab initio molecular dynamics simulation

The model used is a fragment of the SSC PFSA membrane. A hydrated SSC PFSA membrane model with three water molecules is illustrated in Fig. 2. As can be seen, the SSC PFSA membrane model comprised a backbone and two side chains. Electronic structure