INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2016) 1–10

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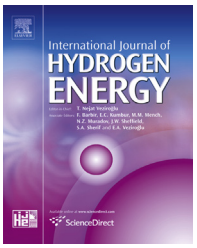

Molecular dynamics simulation study of a polynorbornene-based polymer: A prediction of proton exchange membrane design and performance

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ARTICLE INFO

Article history:
Received 28 January 2016
Received in revised form
25 May 2016
Accepted 29 May 2016
Available online xxx

Keywords:
Sulfonated polynorbornene
Molecular dynamics simulations
Mean square displacement
Radial distribution function
Proton conductivity
Proton exchange membranes

ABSTRACT

A novel polymer material based on polynorbornenes prepared via ring-opening metathesis polymerization (ROMP) was intended to be used as proton exchange membranes. In order to study the microstructure and forecast their macro properties, molecular dynamics simulations were used to lucubrate the transport behavior of hydrated sulfonated polynorbornene-based (SPNB) proton exchange membrane at different temperatures. Simulation results have shown that SPNB membranes swell upon hydration and become phase segregated into hydrophobic and hydrophilic domains with sulfonic acid groups located at their interface. By evaluating the radial distribution function (RDF), it was observed that with increasing number of water molecules caused by the rising temperatures, which leading to more water molecules solvate the sulfur atoms and hydronium ions, the average sulfur-hydronium ion separation distance increased and larger water clusters formed. The results of the mean square displacements (MSDs) showed that the proton conductivity of the membrane with the designed structure was 0.056 S/cm which can meet the application requirements of the proton exchange membranes. Moreover, the simulated proton conductivities qualitatively followed the experimental data at 298 K, 323 K and 348 K, respectively. The molecular dynamics simulation can provide predictive performance of this designed polymer structure before its preparation, which is of guidance significance to the preparation of proton exchange membranes.

Introduction

Proton exchange membrane fuel cells (PEMFCs) have attracted much attention as promising electrochemical energy converters, due to their high-efficiency and low/zero emissions [1–3]. PEMFC technology has already provided sufficient performance and durability to be competitive with alternative technologies [4–6]. The proton exchange membrane (PEM), which serves as the medium for transporting protons from the fuel cell anode to cathode while simultaneously preventing fuel/oxidant crossover, is a critical component in determining PEMFC performance [7,8]. Currently, perfluorosulfonic acid membranes such as Nafion, are the most commonly used

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http://dx.doi.org/10.1016/j.ijhydene.2016.05.254
0360-3199/

Nomenclature

PEMFCs	Proton exchange membrane fuel cells
PEM	Proton exchange membrane
ROMP	Ring-Opening Metathesis Polymerization
IEC	Ion Exchange Capacity
MD	Molecular Dynamics
RDF	Radial Distribution Function
MSD	Mean Square Displacement
SPNB	Sulfonated Polynorbornene
SPPO	Sulfonated Poly (2,6-dimethyl-1,4-phenylene oxide)
SPEEK	Sulfonated poly (ether ether ketone)
$g_{(A-B)}(r)$	The probability distribution of B atoms at a distance r from A atom
D	The diffusion coefficient of hydronium ions.
N	Total number of particles
N_B	Number of B particles in the system
n_B	Number of atoms B located at the distance r in a shell of thickness r from atom A
V	Total volume of the system
k	Boltzmann constant
σ	The proton conductivity of hydronium ions
$r_j(t)$, $r_j(0)$	Positions at time t and at the beginning of dynamic calculations, respectively.

PEMs and have served as the benchmarks for assessing membrane performance because of their excellent chemical and electrochemical stability and outstanding proton conductivity [9]. However, Nafion has some shortcomings, such as high cost and high fuel permeability [10]. So the development of novel PEM materials, especially low-cost non-fluorinated polymers, has received extensive attention [11,12]. Meanwhile, polynorbornenes prepared via ring-opening metathesis polymerization (ROMP) have become the research focus on functional polymer materials. They have the following properties. Firstly, as a living polymerization technique, ROMP is an effective route to synthesize polymers with controlled size and well-defined structures, especially in comparison to vinyl addition polymerization [13,14]. Moreover, with the rapid development of Grubbs catalyst, it is convenient to obtain target polymer with high molecular weight via ROMP at room temperature and atmospheric pressure. Secondly, due to the high degree of strain in the norbornene ring, the ROMP of norbornene derivatives can be easily initiated [15]. Moreover, the backbone of the polynorbornenes with the single bond, double bond and five-member cycle configuration alternately existing could achieve better mechanical properties than that of the aromatic polymers. Consequently, polynorbornenes prepared via ROMP have increasingly become a focus of our research of proton exchange membranes. Up to now, Zhao et al. [16] and Li et al. [17] had described a primary research on this aspect. Zhao et al. [16] reported the synthesis of PEMs based on polynorbornenes functionalized with pendant difluoroalkyl sulfonic acids. However, these membranes showed less than ideal proton conductivities (0.012–0.049 S/cm) at room temperature. Li et al. [17] generated the new type of sulfonated cyclo-olefin based polymers by employing the ROMP Ru catalyst. To increase the mechanical strength and decrease the swelling ratio of proton exchange membranes, cross-linking during the radical polymerization procedure was generated. But the ion exchange capacity (IEC) and proton conductivities of these membranes remained low. Based on these studies, we designed a new structure based on polynorbornenes and it would be able to be used as PEMs and show good comprehensive performance.

However, the function feature size of the PEM is forced on the level of nano-size, so it is important to analyze the structure of the PEMs from a microscopic perspective to help understand the mechanism and forecast macro-performance. Currently, researches on PEMs are no longer confined to the preparation and modification, but extended to molecular dynamics (MD) simulation. Bahlakeh et al. [18–20], employed MD simulation to investigate the effect of degree of sulfonation (DS) on structural and dynamical characteristics of sulfonated poly (ether ether ketone) (SPEEK) and sulfonated poly (2,6-dimethyl-1,4-phenylene oxide) (SPPO) membranes at different temperatures. They used radial distribution functions (RDF) for different atomic (sulfur, oxygen atoms of water and hydronium ions) pairs to study the microscopic structure of the membranes and calculated the diffusion coefficients to obtain the theoretical proton conductivity, simulation results have shown that the simulated ionic conductivities were 0.002 S/cm, 0.0037 S/cm, 0.005 S/cm, 0.009 S/cm, 0.0051 S/cm and 0.011 S/cm, while the experimental values were 0.011 S/cm, 0.0123 S/cm, 0.0155 S/cm, 0.0178 S/cm, 0.0189 S/cm and 0.022 S/cm, respectively. The simulation results were about one third to one fourth of previously reported experimental values. But the simulated ionic conductivities qualitatively followed the experimental data. Chen et al. [21,22], constructed a molecular dynamic calculation model for the Nafion 117 membranes on Materials Studio (MS) material simulation platform to study its microstructure and transport property. The predicted diffusion coefficient of both water molecules and hydrogen ions increase with the water content, which agree well with the variation trend of experimental data. Kyung et al. [23] set up the molecular models for hydrated Nafion 117 and perform molecular simulations for various temperatures and monomer numbers to analyze the motion of water molecules and hydronium ions. The results showed that the distribution of water molecules in the Nafion membrane was quite close to that of hexagonal ices but quite deviated from that of pure water molecules. At the temperature of 353 K, the self-diffusion coefficient values are 2.14×10^{-7} cm^2/s for one monomer and 1×10^{-7} cm^2/s for five monomers and they are in the range of the experimental estimates of 1.8×10^{-6} cm^2/s–5×10^{-8} cm^2/s. All these researches were based on the known macro-performance of the prepared membranes, then narrow down the gap between simulation results and experimental data by adjusting the parameters and algorithms of MD simulation. These progresses provided a basis for forecasting the performance of the non-prepared membranes with specific structures.

In this paper, we employed MD simulation to investigate whether the designed structure of the polynorbornene-based

Please cite this article in press as: Li X, et al., Molecular dynamics simulation study of a polynorbornene-based polymer: A prediction of proton exchange membrane design and performance, International Journal of Hydrogen Energy (2016), http://dx.doi.org/10.1016/j.ijhydene.2016.05.254