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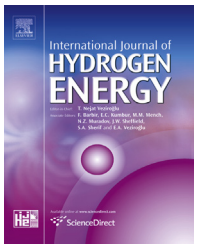

Theoretical methodology for calculating water uptake and ionic exchange capacity parameters of ionic exchange membranes with applications in fuel cells

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ABSTRACT

The water uptake (WU) and ionic exchange capacity (IEC) are important parameters for proton exchange membranes (PEMs), WU represents their total water content, while IEC is the measure of the ability of the membrane to facilitate movement of H_30^+ ions, located in the aqueous environment, through the $-SO_3^-$ sulfonyl groups anchored in their structure. IEC is also the measure of relative concentration of acid groups within polymer electrolyte membrane. According to the vehicle mechanism of proton transport, an appropriate amount of water content and a suitable value of IEC in PEMs are necessary for achieving high proton conductivity. In this work, studies based on density functional theory (DFT), molecular mechanics (MM) and dynamics molecular (DS) were realized in order to develop a theoretical methodology to obtain these parameters. Our proposal considers the ionomer, the solvation medium and the interactions between the ionomer and water molecules. The methodology is applied to structures of sulfonated poly(ether-imide) (SPEI) with $(-SO_3H)_n$ (n = 1, … 6) groups. These structures were built and optimized aiming to obtain above properties as a function of the number of sulfonyl groups. The comparative study demonstrates the SPEI with four sulfonyl groups is the polymer having better properties for successful operation in Fuel Cell.

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Nomenclature

Acronyms	*meaning*
WU	water uptake
IEC	ionic exchange capacity
PEM	proton exchange membrane
DFT	density functional theory
MM	molecular mechanics
MD	molecular dynamic
SPEI	sulfonated polymer ether imide
PEMFCs	proton exchange membrane fuel cells
GGA	generalized gradient approximation
PW91	Perdue and Wang 1991
DNP	double numerical plus polarization
MS	materials studio
NPT	number of molecules, pressure and temperature constants
NVT	number of molecules, volume and temperature constants

Introduction

Polyelectrolyte membranes have been extensively investigated lately due to their potential applications in different types of electrochemical devices such as ion conducting membranes in fuel cells [1]. Since years ago, polymer electrolyte membrane fuel cells (PEMFCs) are regarded to be new devices for clean and efficient power generation in the twenty-first century because of features such as high efficiency, high energy density, and environmental friendliness [2]. The perfluorinated sulfonic acid membrane, which is known as DuPont™ Nafion®, has been used for years as electrolyte in PEMFC. However, despite great successes with this membrane, it presents many disadvantages during the operation mechanism of the PEMFC [3], and besides they are expensive.

Hydrogen and fuel cells technology is facing three main challenges related to new polymeric materials for membranes: reducing the high cost of production, increasing durability and chemical and mechanical stability at temperatures above 100 °C, and improving proton conductivity at temperatures above 120 °C.

Nowadays, many efforts are being directed towards developing new non-DuPont™ Nafion® electrolyte polymers, possessing excellent overall properties in order to build proton exchange membranes for fuel cell [4]. However, most of the efforts have been focused on the experimental developments, thereby neglecting the development of theoretical methods. A theoretical methodology is necessary, since it could significantly contribute to guide the experimental work, which would reduce the experimental time and resource savings. Some of the main problems that the ionic membranes, for use in PEM cells, have presented are the low proton conductivity at low relative humidity and the low mechanical properties at high temperatures and humidities. Ion conduction is a thermally activated process and its magnitude varies dramatically from one material to the other. The type of electrolyte, which may be either liquid or solid, determines the temperature at which the fuel cell may be operated.

Proton conductivity is the property more important for proton exchange membranes and is usually the first characteristic considered when evaluating membranes for potential fuel cell use. The performance of a membrane is dependent on proton conductivity, which in turn often depends on its water content. High proton conductivity is supported by high level of water uptake; at the same time, it is also a sign of low-dimensional stability as water influences the polymer microstructure and mechanical properties.

The main limitation to obtain a polymeric material with a high value of conductivity at high temperatures is to maintain the polymeric membrane hydrated, since, in operating conditions of the fuel cell, the temperature increases above 100 °C, so that the liquid evaporates consequently resulting in the reduction of hydration [5–17]. Two of the parameters which determine and predict the proton conductivity of the membrane are water uptake (WU) and ion exchange capacity (IEC). The rapid increase in computing resources and the progress in software offer new possibilities to rapidly gain new information from molecular modeling and simulation of the conductivity phenomena.

In the present approach, studies based on Density Functional Theory (DFT), Molecular Mechanics (MM) and Molecular Dynamics (MD) Simulations were realized in order to develop a theoretical methodology to obtain water uptake and ionic exchange capacity parameters. The methodology was applied to structures of sulfonated poly(ether-imide) (SPEI) with $(-SO_3H)_n$ (n = 1, … 6) groups. Poly(ether imide)s modified by sulfonation are particularly interesting as PEMs because the sulfonide groups $(-SO_3H)_n$ show good water retention and excellent adhesive ability with polymides and inorganic materials [18–22]. These structures were built and optimized aiming to obtain above properties as a function of the number of sulfonyl groups.

Methodology and computational details

Repeat unit structure of poly(ether imide) (Ultem-type), Fig. 1, was used in this work in order to build molecular computer models of sulfonated poly(ether imide), PEI–$(SO_3H)_n$, $n = 1, 2, 3, 4, 5, 6$. Once the structures were built, it is necessary to carry out the geometry optimization or energy minimization since after they have been sketched, they are often in high energy configurations. Starting dynamics simulations from such unoptimized structures can lead to simulations of systems at temperatures much higher than room temperature. In this work three aspects were considered to select a geometry optimization method and quality level of the results: system size, convergence threshold and basis set used. In this study, the calculations were carried out using functional GGA PW91 and DFT semi-core pseudopotentials as approximation for treatment of core electrons [23,24]. This treatment replaces core electrons by a single effective potential, reducing the computational cost; the DNP (Double Numerical plus polarization) atomic orbital basis set was used in the calculation. In order to obtain structural, vibrational, reactivity, selectivity