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Molecular modeling and simulation of ion-conductivity in chitosan membranes

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Abstract

The objective of this work is to provide some elements for developing a theoretical methodology aimed to describe the ion conductivity mechanism of chitosan membrane and to obtain its magnitude. Atomistic molecular modeling has been utilized to construct an ionic-conducting polymer–electrolyte system consisting of chitosan, H_2O molecules and H_3O^+, OH^-, SO_4^{2-} ions, inside of the simulation cell. The COMPASS force field was used. The simulation allows describing the ionic conductivity mechanism along the polymer matrix. The theoretical results obtained are compared with previously reported experimental data for chitosan membranes. The present methodology can be considered as a first step towards understanding these complex problems of technological interest.

Keywords: Ion-conductivity; Polyelectrolyte; Chitosan membrane

1. Introduction

Chitosan is a polyelectrolyte derived from chitin, the second biopolymer most abundant in the nature only after the cellulose, through a deacetylation process. Chitin is well known to consist of 2-acetamido-2-deoxy-β-D-glucose groups by a β (1–4) linkage. Thus, chitosan is the *N*-deacetylated derivate of chitin, although this *N*-deacetylation is almost never complete [1]. The chitosan macromolecule has unique properties [2] as a consequence of the presence of both amino and hydroxyl groups in their structure, as shown in Fig. 1.

The comprehension of both ionic conduction mechanism and ionic conductivities of the hydrated chitosan membranes are very important in developing alkaline polymer electrolyte or acidic polymer electrolyte fuel cells. Hither to, there has been a minimal amount of experimental work conducted to address ionic conductivity in chitosan polyelectrolyte membranes. To our knowledge, there is no theoretical effort dealing with this issue. Within the framework of experimental domain, Wan et al. [3] have reported measurements of the intrinsic ionic conductivity on chitosan membranes with various degrees of deacetylation and different molecular weights. The values that they have found were as high as 10^{-4} S cm^{-1} after hydration for 1 h. On the other hand, Soontarapa et al. [4] have prepared four types of chitosan membranes for investigating their electrochemical properties. The membranes were unscrosslinked, 1 and 2% crosslinked, and acid-doped membranes. The conductivity at 100% of relative humidity under H_2 atmosphere was measured within a temperature range of 40–80 °C. It was found that the conductivity of the 2% doped membrane with 1% H_2SO_4 was a half of that of Nafion® 117 at all temperatures. However, theoretical work for the chitosan membranes is null practically.

Polyelectrolyte membranes have been extensively investigated lately due to their potential applications in different types of electrochemical devices such as solid non-corrosive electrolytes [5]. As ion conducting membranes in fuel cells [6], electrolyte polymers have been used over the past three decades. For the case of application in fuel cells, a primary goal is to find polymer materials with ion conductivities within the range of mS/cm at temperatures up to 100 °C. Electrolytes containing different ions such as

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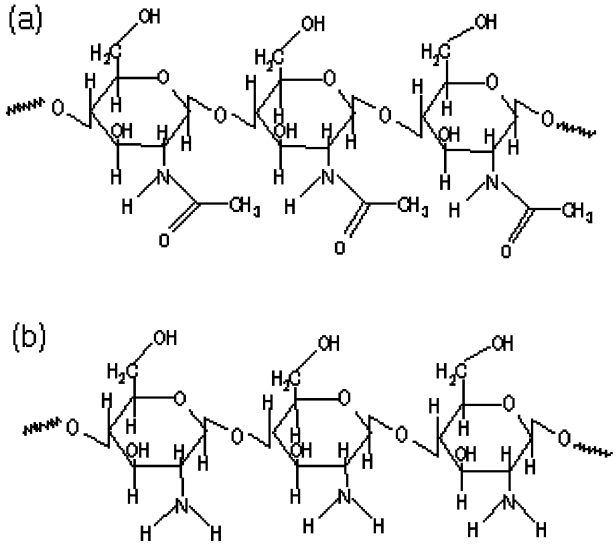

Fig. 1. Segments of (a) chitin and (b) chitosan.

sulfonic, hydronium, hydroxide, oxide and carbonate ions as charge carriers are known, and are the basis for the many categories of fuel cells under development today [7].

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. The main limitation to obtain a polymeric material with a high value of conductivity at high temperatures is necessary to maintain the polymeric membrane hydrated, since their ionic conductivity increases linearly with the water content, the membrane reaches the maximum conductivity when it is completely hydrated. Nevertheless, the obtained results to date are quite promising. Polymers classes for this type of applications such as poly(ethylene oxide), poly(vinylalcohol), poly-(acrylamide), poly(vinylpyrrolidone), poly(ethyleneimine), various poly(aminosilicates), and poly(benzimidazole) have been examined in combination with sulfuric, phosphoric and various halide acids [8].

Due to its capacity of water retention, the chitosan has recently emerged as a new alternative to obtain membranes with high ionic conductivity at moderate temperatures, >90 °C, for fuel cells operation. Chitosan membrane loses its water content around 110 °C [9]. Another important advantage of this polymer is that their behavior can be changed significantly by modifying the hydroxyl and amine groups or the residual acetamide groups by NH_3, CH_2OH, PO_3H, or SO_3H ones, with suitable chemical methods [10], so that ionic conductivity of the chitosan membrane can be improved. Chitosan also has a high potential for development into sophisticated functional polymers quite different from those of synthetic polymers since it has both free amino groups and hydroxyl groups on its backbone, which are easily modified by many organic reactions [11,12] As copolymer, chitosan is readily converted to fibers, films, coatings, and beads as well as powders and solutions further enhancing its usefulness [13].

The conduction mechanism in chitosan membranes is partly unknown at present and the experimental work has not, despite many efforts, been able to resolve all the atomistic-level details. To our best knowledge, there are few works devoted to theoretical prediction of the ionic conduction mechanism of polyelectrolyte, among them stand out the realized by Ennari et al. [14–16]. 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 study, molecular dynamics (MD) atomistic simulations of an ion-conducting system, consisting of two chain-polymeric (each one with 12 amino groups protonated-chitosan monomers), one hydronium ion, one hydroxide ion, 200 water molecules and 12 sulfate ions, was constructed to study the ionic conductivity of both hydronium and hydroxide ions. This system could be constructed of the following way: when a chitosan film is formed after the evaporation of acetic acid, the amino groups are protonated. Besides, a sodium sulfate solution produces the dissociation of both SO_4^{2-} and Na^+ ions. If the sulfates are added to protonated chitosan membrane and the sodium ions are removed, then the system used in this work is constituted.

The MD was realized by using COMPASS forcefield [17], which is the first ab initio forcefield that has been parameterized and validated using condensed-phase properties, in addition to various ab initio and empirical data for isolated molecules. Consequently, this forcefield enables accurate prediction of structural, conformational, vibrational, ionic conductivity and thermo physical properties for a broad range of molecules in isolation and in condensed phases.

The present work looks to find a general methodology that could be applied to any polymer electrolyte membrane, besides it could turn out to be a reliable, economical and useful tool to the design and synthesis process of this type of membranes which are used in many technological applications.

2. Methodology

The methodology used in this work was based on a procedure previously reported by Ennari et al. for studying proton-conducting polymer electrolyte system consisting of poly(ethylene oxide) sulfonic acid anion [11–13]. In this work, the amorphous builder module of Accelrys was used to construct polymeric membrane/small molecule penetrant system. The minimization and molecular dynamics simulations were carried out using discover molecular simulation program. In order to obtain both the ionic conduction mechanism and the ionic conductivities of the hydrated