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Ionic conductivity in a chitosan membrane for a PEM fuel cell using molecular dynamics simulation

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ABSTRACT

A classical molecular dynamics simulation using a COMPASS force field was applied to systems contained chitosan, hydronium ions, various amounts of water: 10, 20, 30 or 40% water. The simulation predicted the diffusion coefficient, the ion conductivity, the coordination between particles. The system containing 40% water is most suitable as a conducting material because it has the highest ion conductivity value (7.14×10^{-2} S/cm). Such a material was studied in a temperature range of 298–360 K, the conductivity results followed Arrhenius behavior. A study at 70, 80, 90° of deacetylation (DDA) at a constant of 40% water content showed the same trend in conductivity behavior. The coordination was considered in evaluating the location of particles in order to understand the transport mechanism of the ions. Conductivity is appropriate in the systems in which the Eigen ion, water cluster are formed.

1. Introduction

Fuel cells are now prime candidates for new energy sources because of their environmentally friendly generation. There are many types of fuel cell, depending on their operations. Among them, a proton exchange membrane fuel cell (PEMFC) can give various applications due to low temperatures of about 70–80 °C.

The performance of the cell is influenced by many factors. This performance can be greatly improved by the chemical structure of the membrane, which has a direct effect on proton transfer. Many researchers have studied alternative polymers for better conductivity. Nafion is the most commercially used membrane. Most reports of new materials have included information on ion content, protonic conductivity, and water uptake. Other polymer systems that would have even better performance than Nafion and/or have lower costs are being sought by researchers around the world.

One substitute for synthetic polymer is a natural polymer called chitosan. Chitosan is a derivative of chitin, a natural polysaccharide that occurs mainly in insects, marine invertebrates, fungi and yeasts. It is also the most abundant natural polymer next to cellulose. When N-deacetylation occurs, chitin is converted to chitosan, as shown in Fig. 1.

However, the N-deacetylation process is almost never complete. The degree of deacetylation (DDA), which determines the content of free amino groups in the polysaccharides, can be employed to differentiate between chitin and chitosan. Thus, the properties of chitosan rely on the amino and hydroxyl groups in its structure. Some researchers are studying the possibility of using chitosan as the membrane for a PEM fuel cell (Mukoma, Jooste, & Vosloo, 2004; Ramírez-Salgado, 2007; Wan, Creber, Peppley, & Bui, 2003; Yamada & Honma, 2005). Molecular modeling technique was used to improve ionic conductivity in chitosan membranes (López-Chávez et al., 2005), with a reported value of 2×10^{-2} S/cm using a COMPASS force field (Sun, 1998). From the experimental work of Wan et al. (2003), it was found that the intrinsic ionic conductivity was as high as 10^{-4} S/cm. On the other hand, many types of PEM fuel cell have been developed with the same technique (Ennari, 2008; Ennari, Neelov, & Sundholm, 2001; López-Chávez et al., 2005; Pozuelo, Riande, Saiz, & Compañ, 2006). Ennari (2008) studied the mechanism of ionic conductivity of the poly(ethylene oxide) sulfonic acid anion and PVF-based polyelectrolyte by using an atomistic molecular modeling technique.

The goal of this work is to calculate the ion conductivity of chitosan as the membrane of a PEM fuel cell with different amounts of water at a molecular level. The COMPASS force field (Sun, 1998) was used. Molecular modeling techniques can create an amorphous system composed of chitosan molecules, hydronium ions (also known as hydrated protons) and water molecules. Molecular dynamics results present dynamical data to calculate the ion conductivity, and coordination data to study the transport mechanism of the ion. Both water content and temperature effects are the main topics of this work.

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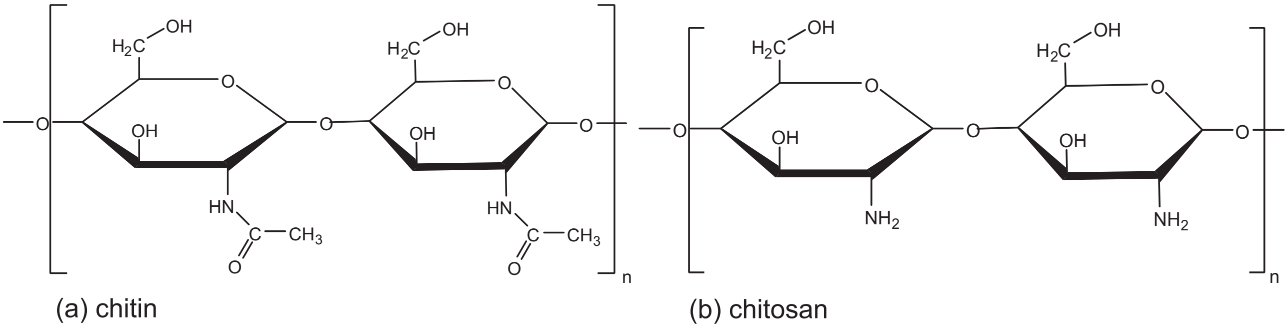

Fig. 1. Chemical structure of chitin and chitosan.

2. Computational details

Conducting polymer materials were constructed and simulated by means of the Accelrys commercial software (Materials Studio 4.3) using the COMPASS force field. The amorphous builder module was used to construct the system, and then the minimization and molecular dynamics were analyzed by the discover module. First, a water molecule and hydronium ion were constructed and minimized by the steepest-descent method. A chitosan monomer was constructed; then the polymer builder module was used to create a chitosan chain of 10 repeating units with minimization by the steepest-descent method. Then, 3D amorphous systems with periodic boundary conditions and containing a chitosan polymer chain with 10 repeating units, the hydronium ions, and various amounts of water were built using the amorphous cell module. The composition of each cell is summarized in Table 1. All systems contained two chains of polymeric chitosan with 10 amino groups; 20 hydronium ions; and 10, 20, 30 or 40% water (see Fig. 2). This figure illustrates the population of water surrounding polymeric chitosan referring to the practical usage of this membrane in fuel cell.

Minimization was performed until the maximum derivative 0.1 kcal/mol was reached. These optimum conformations were further confirmed by molecular dynamics running an NVT ensemble with an Andersen thermostat for temperature control. The temperatures during the dynamics simulations were 298, 320, 340 and 360 K. With sampling time steps of 1.0 fs, 200 ps long dynamics runs were used to study the dynamic properties of these cells. The van der Waals and Coulombic nonbonding interactions were calculated by the Ewald summation method.

Because of the complexity of natural chitosan, the conductivities of chitosan with various degrees of deacetylation (DDA) are calculated. The composition of each cell is summarized in Table 2.

Table 1
Description of the different simulated cells.

Cell	Number of particles			% of water	Volume of cell (Å^3)
	Chitosan	H_2O	H_3O^+		
Cell1	2	23	20	10	5176.640
Cell2	2	52	20	20	5843.672
Cell3	2	90	20	30	6717.889
Cell4	2	135	20	40	7752.987

Table 2
Description of the different simulated cells with various degrees of deacetylation.

System	Number of particles			% of water	Volume of cell (Å^3)
	H_3O^+	H_2O	Chitosan		
DDA90	20	138	2	40	7929.409
DDA80	20	141	2	40	8105.823
DDA70	20	144	2	40	8282.113

After molecular dynamics runs, the mean-square displacement (MSD) was calculated to obtain the diffusion coefficient and ion conductivity.

The diffusivity, D, is given by

$$D = \frac{1}{6N} \lim_{t\to\infty} \frac{d}{dt} \sum_{i=1}^{N} \langle [R_i(t) - R_i(0)]^2 \rangle \qquad (1)$$

The sum term of the right-hand side of Eq. (1) divided by N is the MSD. N is the number of diffusing particles, t is time and $R_i(t)$ is the position vector of particle α at time event t. This equation is valid only when the Einstein diffusion is valid. This means that the motion of a diffusing particle follows a random walk, i.e. the motion of a particle is not correlated with its motion at any previous time. To validate this equation, log MSD against log time was plotted in each case. The slope of the curve is 1.0 when the Einstein diffusion is reached.

Ion conductivity, σ, was been evaluated using the Einstein equation (Ennari, 2008; Pozuelo et al., 2006):

$$\sigma = \frac{Nz^2e^2D}{VkT} \qquad (2)$$

where σ, e, V, k, T and z are the ion conductivity, elemental charge, volume of the simulation cell, Boltzmann constant, temperature and total charge in units of e; respectively.

The distribution of the hydronium ions and water molecules in the system was investigated by computing the intermolecular pair correlation function, $g(r)$, which represents the probability of finding a pair of particles $A\cdots B$ at a distance r normalized with respect to the probability expected for a completely random distribution at the same density. The value of $g(r)$ can be converted into coordination numbers with the following expression:

$$n_{A\cdots B}(r) = 4\pi \frac{N_B}{\langle V \rangle} \int_0^r g_{A\cdots B}(r) r^2 \, dr \qquad (3)$$

where $n_{A\cdots B}(r)$ is the number of A particles coordinated with B particles within a radius r; $\langle V \rangle$ is the volume of the cell; N_B is the total number of B particles in the system; and $g_{A\cdots B}(r)$ is the pair correlation function between A and B (Ennari, 2008).

3. Results and discussion

In this section, the computational results will be discussed, including the ion conductivity and transport mechanism. Ion conductivity was studied using dynamical information. The transport mechanism of the ion was evaluated by the coordination data.

3.1. Dynamic properties of hydronium ions

The calculation of MSD can be used to analyze the dynamic properties of the hydronium ions. The mobility of hydronium ions for

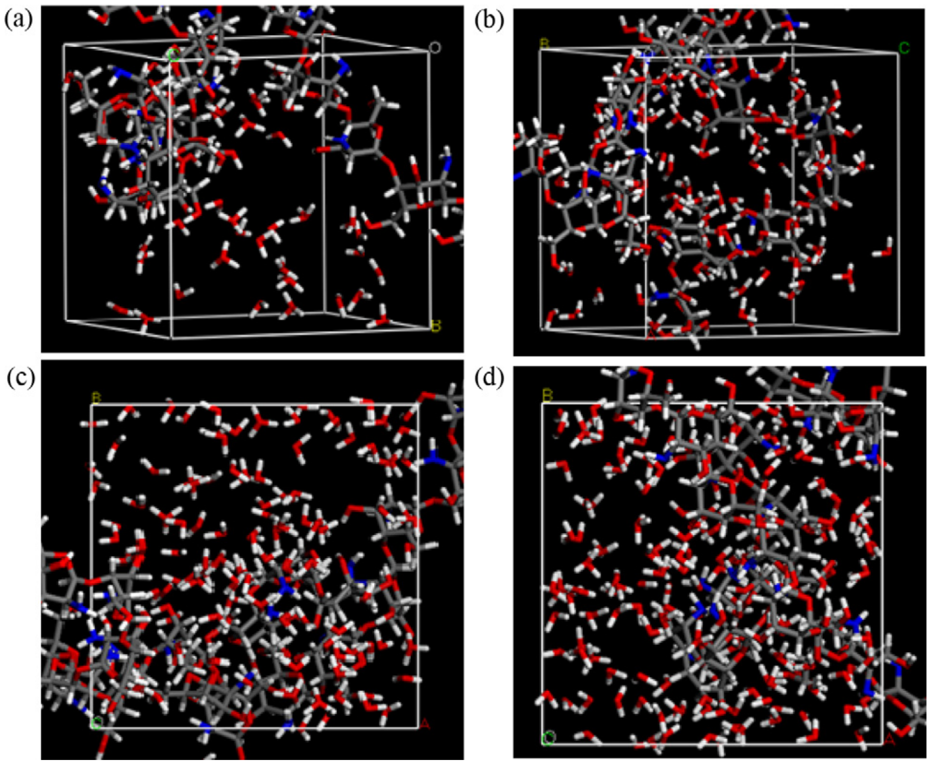

Fig. 2. Simulated cells containing chitosan, hydronium ions and (a) 10% water, (b) 20% water, (c) 30% water and (d) 40% water.

all systems was implemented by MSD over a time of 200 ps at 298, 320, 340 and 360 K (in Fig. 3). At certain time the MSD of Cell4 (40% water) was always larger than the others. This means that in Cell4 the hydronium ions had a longer trajectory than the others. The mobility of the hydronium ions slightly increases with the amount of water in the system (Ennari et al., 2001; Ennari, 2008; Pozuelo et al., 2006).

To check whether or not the Einstein diffusion is reached, the relationship between log MSD and log(t) is analyzed. Both Cell1 and Cell2 give the slope in the range of 0.65–0.75. While the slopes of Cell3 and Cell4 are 0.75–0.85 and 0.9–1.0, respectively. Thus the Einstein diffusion condition is reached in a 40% water system only. Therefore, the calculated value of 40% water is acceptable. Consequently, other systems will be calculated to compare the trend of hydronium ion mobility. The mobility of hydronium ions slightly increases when the amount of water in the systems increases.

The dynamical property was evaluated in a temperature range of 298–360 K. Because a PEM normally operates in this range, the effect of temperature on conductivity was considered. After considering each system, as temperature is increased, MSD is slightly changed. However, if the temperature is fixed at a certain value, the diffusivity still increases according to the increase in the amount of water in the system, as shown in Table 3.

MSD as a function of time was determined to obtain the self-diffusion coefficients of hydronium ions and water molecules in both systems. For all cases of Cell4, the Einstein diffusion of the hydronium ion was satisfied. The diffusion coefficients of the hydronium ion at 298 K for Cell1, Cell2, Cell3 and Cell4 are 5.5×10^{-11}, 0.072×10^{-9}, 0.182×10^{-9} and 0.32×10^{-9} m^2/s; respectively. This indicates that diffusivity of the ion increases as the amount of water increases. The diffusion coefficients of water at 298 K for Cell1, Cell2, Cell3 and Cell4 are 0.34×10^{-9}, 0.61×10^{-9}, 1.36×10^{-9} and 1.74×10^{-9} m^2/s; respectively. The value of ion conductivity calculated by using Eq. (2) for Cell4 is 7.14×10^{-2} S/cm. This value was compared with the experimental work of Wan et al. (2003). The values that they found were as high as 10^{-4} S/cm. Mukoma et al. (2004) found the conductivity of chitosan to be 5×10^{-3} S/cm. The corresponding method and result of López-Chávez et al. (2005) were compared with this result. They suggested that the percentage of water and sulfates may improve the ion conductivity in chitosan membranes, up to a value of 2×10^{-2} S/cm. Ennari (2008) obtained the conductivity of sulfonated PVF-based materials. The value of conductivity is $(91 \pm 9) \times 10^{-3}$ S/cm in a 40% water system. Such information was calculated for 298 K only; other values are shown in Table 3.

Table 3
Diffusivity (m^2/s) and ion conductivity (S/cm) for all systems at various temperatures.

System	298 K		320 K		340 K		360 K	
	10^9D	$10^2\sigma$	10^9D	$10^2\sigma$	10^9D	$10^2\sigma$	10^9D	$10^2\sigma$
Cell1	0.055	1.34	0.118	2.66	0.0967	2.04	0.078	1.56
Cell2	0.072	1.56	0.162	3.22	0.090	1.68	0.34	5.94
Cell3	0.182	3.38	0.192	3.32	0.475	7.74	0.31	4.80
Cell4	0.32	7.14	0.495	7.4	0.581	8.18	0.69	9.26

Considering to the ions' behavior in Cell4, the Einstein equation is valid because of Einstein diffusion and one can interprete that ions' motion has no correlation with their previous motion time. Thus the value of conductivity could be calculated for this system. The ion conductivities are 0.0714 S/cm at 298 K, 0.074 S/cm at 320 K, 0.0818 S/cm at 340 K and 0.0926 S/cm at 360 K. The temperature dependence of the conductivity in Fig. 4 shows that this parameter for hydronium ions also follows Arrhenius behavior.

Transport properties of the chitosan membrane with different DDA were calculated. All the DDA systems were considered only 40% water. Their MSD curves were also the same trend. The diffusion coefficient and conductivity of hydronium ions at 298 K was calculated as shown in Table 4. The diffusivity and conductivity of other DDA systems were a little higher than Cell4, due to the number of water molecules being a little higher in order to maintain a 40% water weight in all systems. From Table 4, the

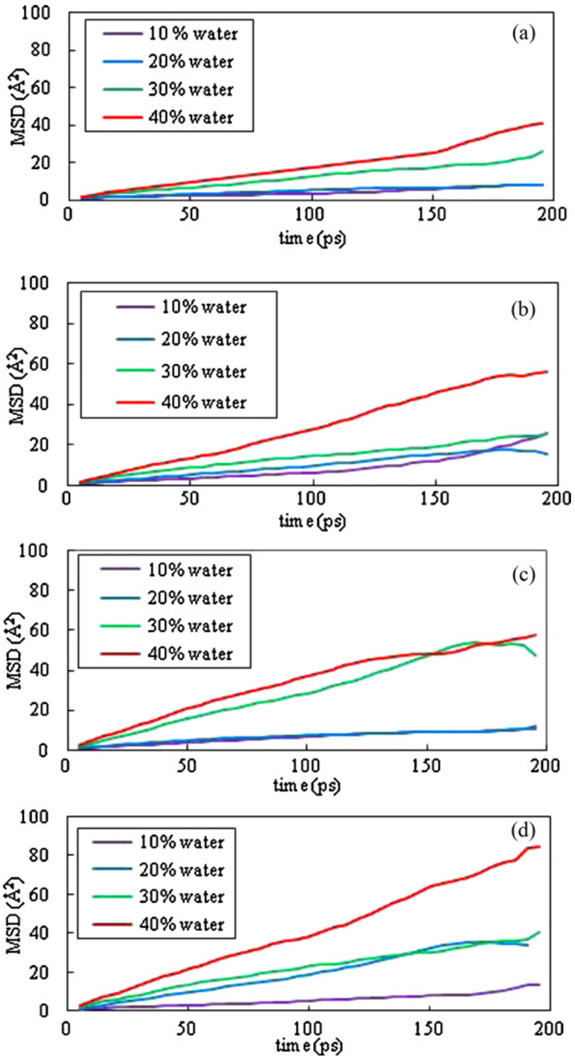

Fig. 3. Mean square displacement of hydronium ions as a function of time at (a) 298 K, (b) 320 K, (c) 340 K and (d) 360 K.

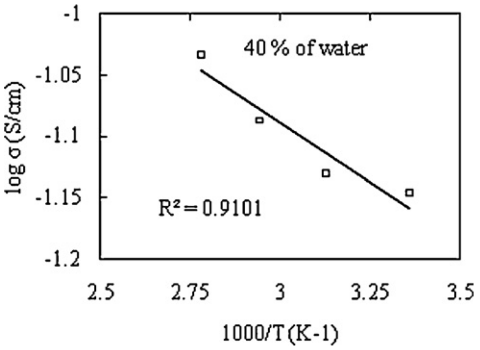

Fig. 4. Ion conductivity of the chitosan membrane in Cell4 at different temperatures.

Table 4
Diffusivity (m^2/s) and ion conductivity (S/cm) for all systems with various DDA at 298 K.

System	$10^9 D$	$10^2 \sigma$
Cell4 (DDA100)	0.32	7.14
DDA90	0.71	11.2
DDA80	0.49	7.56
DDA70	0.58	8.80

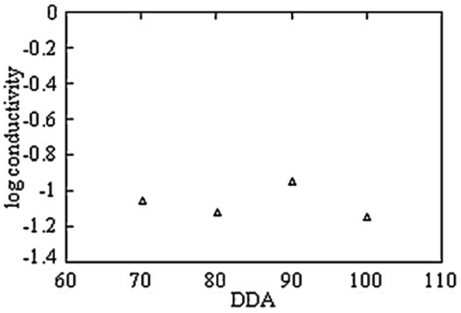

Fig. 5. Ionic conductivity of chitosan membranes with varied DDA (40% water).

ion conductivity of Cell4, DDA90, DDA80 and DDA70 are 0.0714, 0.112, 0.0756, and 0.088 S/cm respectively. From Fig. 5, the computational values do not follow the experimental data of Wan et al. (2003). In real materials, they found that the DDA of chitosan slightly affects the conductivity of a dry membrane. For a hydrated membrane, the conductivity did not follow this trend. The higher content of amino groups in chitosan membranes may contribute higher ionic conductivity. Because the amino groups in the chitosan backbone are partially protonated ($NH_2 + H_2O \leftrightarrow NH_3^+ + OH^-$ or $NH_2 + H_3O^+ \leftrightarrow NH_3^+ + H_2O$) and the proton transfer mechanism will also occur. However, this did not fit the results, due to this calculation technique being based on the diffusion of hydronium ions. In a hydrated system (40% water), the amount of water in the system is more significant than the functional group of chitosan. The reason will be discussed in the next section.

3.2. Coordination study

Coordination between particles in the systems was calculated by intermolecular pair correlation functions. The coordination of the hydronium ion can especially provide information about the mechanism of conductivity. Coordination was studied by the pair correlation function $g(r)$ as a function of the separation distance r.

Firstly, the amino group of chitosan was considered. The pair correlation function between the hydronium ion and the amino group is shown in Fig. 6a. The first and largest peak occurs at 2.75 Å. The coordination number calculated from these curves is described in Table 5. Thus, the number of hydronium ions which are located around the amino group in a chitosan chain decreases as the amount of water in the system increases. The pair correlation function between the oxygen atom in a water molecule and the nitrogen atom in the amino group of a chitosan chain is shown in Fig. 6b. The maximum peak is found in the broad range 2.8–3.5 Å. The coordination between the water molecule and the amino group of a chitosan chain increases as the amount of water in the system increases by about one or two molecules.

Secondly, the hydroxyl group of chitosan was considered. From Fig. 6c and Table 5, the position of the hydronium ion next to the hydroxyl group was found at 2.55 Å. The number of hydronium ions

Table 5
Coordination number (n) of hydronium ion, water and the functional group of chitosan.

$A \cdots B$	Cell1	Cell2	Cell3	Cell4	DDA90	DDA80	DDA70
$H_3O^+ \cdots NH_2$ (2.75 Å)	0.72	0.70	0.48	0.38	0.57	0.36	0.45
$H_2O \cdots NH_2$ (3.05 Å)	0.59	1.10	1.34	1.91	1.96	1.91	1.92
$H_3O^+ \cdots OH$ (2.55 Å)	0.72	0.49	0.39	0.28	0.32	0.27	0.28
$H_2O \cdots OH$ (2.75 Å)	0.70	1.14	1.10	1.48	1.38	1.49	1.32
$H_3O^+ \cdots C$ (3.55 Å)	1.17	0.93	0.64	0.48	0.505	0.502	0.55
$H_2O \cdots C$ (3.55 Å)	1.20	2.26	2.66	3.25	3.19	3.36	3.79
$H_3O^+ \cdots O=$ (2.85 Å)	–	–	–	–	0.02	0.06	0.39
$H_2O \cdots O=$ (2.85 Å)	–	–	–	–	1.84	1.71	1.89

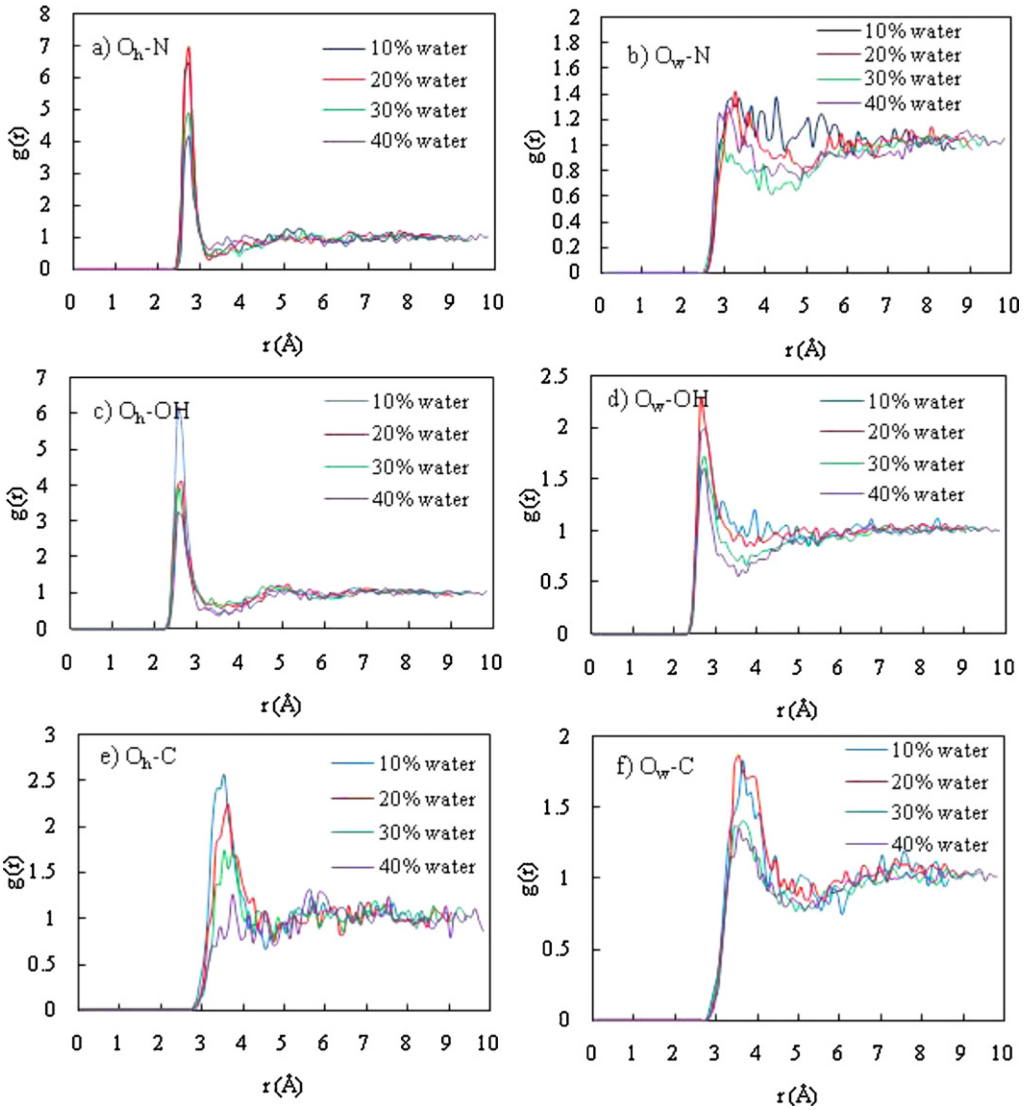

Fig. 6. The pair correlation function between the hydronium ion and the functional group of the chitosan chain: (a) hydronium ion – amino group, (c) hydronium ion – hydroxyl group, (e) hydronium ion – methoxyl group); and between the water molecule and the functional group of the chitosan chain: (b) water – amino group, (d) water – hydroxyl group, (f) water – methoxyl group.

located around the hydroxyl group in a chitosan chain decreases as the amount of water in the system increases. The pair correlation function between the oxygen atom in the water molecule and the oxygen atom in hydroxyl group of a chitosan chain is shown in Fig. 6d. The first coordination shell was found at 2.75 Å, and the coordination number of the water molecule around the hydroxyl group was about one molecule. The third functional group; the methoxyl group, was then considered. The pair correlation function between the oxygen atom in the hydronium ion and the carbon atom in the methoxyl group of a chitosan chain is shown in Fig. 6e. The first coordination shell was found at 3.55 Å. The coordination number was calculated as shown in Table 5. The coordination between the hydronium ion and the methoxyl group is decreased, driving an increase in the amount of water. The first coordination between the water molecule and the methoxyl group was found at 3.55 Å (Fig. 6f.). The coordination number of the water molecule around this functional group was found to be about one to three molecules.

For DDA systems the acetyl group was considered. The first coordination between the oxygen atom of a hydronium ion and the oxygen atom of an acetyl group was found at 2.85 Å (Fig. 7a). The coordination number of the hydronium ion around this functional group was very low (Table 5). The first coordination between the oxygen atom of a water molecule and the oxygen atom of an acetyl group was found at 2.85 Å (Fig. 7b). There were about two water molecules located around the acetyl group (Table 5). The conductivity should increase when the DDA increases as amino groups in the chitosan structure; this is the idea of the conductivity mechanism. Nevertheless, the 40% water or hydrated systems have no effect on the amino group, because the amount of water has more influence.

The location of hydronium and the water molecule is important in order to obtain the conductivity. The pair correlation function between the oxygen atom in the hydronium ion and the oxygen atom in the water molecule is shown in Fig. 8a. The first coordination shell was found at 2.55 Å. The coordination number in the first coordination shell was 1.06 in Cell1, while it was 1.34, 2.63 and 3.16 in Cell2, Cell3 and Cell4; respectively (Table 6). This means that coordination between the hydronium ion and water molecule increased corresponding to the amount of water in the system: especially the 40% water systems (Cell4, DDA90, DDA80 and DDA70), which had a coordination number about 3. This indicated that three molecules of water surrounded one hydronium ion, i.e. an Eigen ion ($H_9O_4^+$) was formed. The first peak of the pair

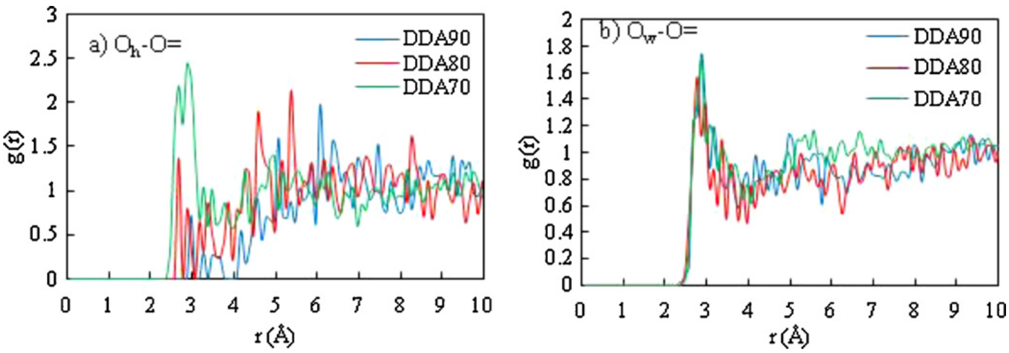

Fig. 7. The pair correlation function (a) between the hydronium ion and the oxygen atom in the acetyl group of a chitosan chain, and (b) between water and the acetyl group.

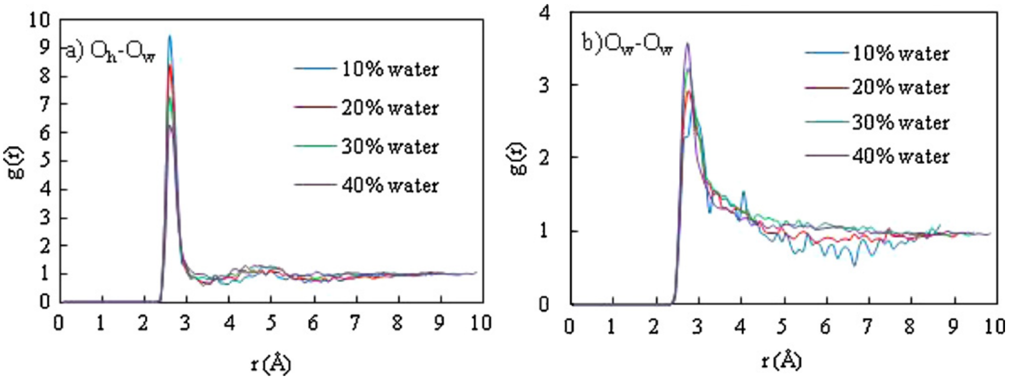

Fig. 8. The pair correlation functions (a) between the hydronium ion and water molecule and (b) between water and water.

correlation between oxygen atoms in water molecules appeared at 2.75 Å (Fig. 8b). The coordination numbers of water molecule of 40% water were about 3.5–3.72 (Table 6). This indicated that a water cluster was formed.

The water cluster and Eigen ion were important to obtain the Grotthuss mechanism, with interconversion between the Eigen and Zundel ions ($H_5O_2{}^+$) (Kim, Weck, Balakrishnan, & Bae, 2008; Kreuer, 2000; Kreuer, Paddison, Spohr, & Schuster, 2004; Paddison & Elliott, 2007). The proton defect follows the hydrogen bond, which diffuses by hydrogen bond breaking and forming processes. In this technique, the transport properties were calculated from the mobility of particles without forming and breaking bonds. Thus, the computed conductivity value was higher than the reference experimental data. The Eigen ion and water cluster supported the diffusivity of hydronium ions in the 40% water system. When the amount of water in the system increased, the hydronium ions were not mainly located near the functional group of chitosan, but were diffused throughout the water sites.

Much research must be carried out on polyelectrolytes with different chemical structures to assess the reliability of full molecular dynamics to predict the ion conductivities of membranes. In the amino group ($—NH_2$), the nitrogen atom has a lone pair of electrons; thus it is a high electron density group. Commercial PEM such as Nafion, PVF-SA and PEO (Ennari, 2008) have a particular group such as a sulfonic group ($—SO_3{}^-$) which has high electron density. A high electron density group can promote the transportation of cations by collecting the cations around them and transferring these cations to the neighboring group. When the hydrogen of the amino group was substituted by the acetyl group ($—COCH_3$), the electron of nitrogen was shared with the acetyl group. The charge of the nitrogen connection to the acetyl group is weaker than that of the nitrogen connection to the amino group. Therefore, the DDA or amino group per cation decreases, the conductivity decreases. This suggestion was suitable for a dry membrane (Wan et al., 2003), but a hydrated membrane is different. The amount of water in the system is important to obtain conductivity. The functional groups of chitosan are more water-absorbent.

Table 6
Coordination number of hydronium ion–water and water–water.

A···B	Cell1	Cell2	Cell3	Cell4	DDA90	DDA80	DDA70
$H_3O^+\cdots OH_2$(2.55 Å)	1.06	1.34	2.63	3.16	3.35	3.22	3.12
$H_2O\cdots OH_2$ (2.75 Å)	0.87	2.02	2.92	3.58	3.72	3.62	3.50

The coordination data indicate that functional groups of chitosan have very high hydrations: a $2H_2O$/amino group, a $1H_2O$/hydroxyl group and a $3H_2O$/methoxyl group. The amount of water in the system has an influence on conductivity: especially in the 40% water system where an Eigen ion and a water-cluster are formed. Water molecules located around the hydronium ions can support the ion diffusion throughout the system.

4. Conclusions

This work presented the ion conductivity mechanism of a chitosan membrane based on a molecular level. Firstly, the structures of each particle were formulated and minimized to obtain a stable conformation. Several amorphous systems containing chitosan, hydronium ions and various amounts of water were considered under periodic boundary conditions. These amorphous systems were simulated by classical molecular dynamics simulation. Secondly, the diffusion coefficient and ion conductivity were calculated from the MSD. The study of the pair correlation function can locate the hydronium ion and water molecule.

The self-diffusion coefficient can be used to represent ion conductivity. When the amount of water in the system increased, the diffusivity increased. The 40 wt% of water system was suitable for transferring the ions, following Arrhenius behavior. The value of conductivity simulated for a hydronium ion is on the order of magnitude 10^{-2} S/cm in a 40 wt% of water system, which is higher than what was experimentally found. Hence, the hydronium ions can diffuse through the system without creating and breaking bonds, and with no effect of impurity. However, the simulation results did not agree with experimental work when the DDA varied. This is because the amount of water made the diffusivity more efficient than the interaction between the functional group of chitosan and the ions.

The location of the hydronium ion and the fixed group of chitosan were considered. In a 40% water system, hydronium ions are not mainly located around the functional groups of chitosan, but are elsewhere in the water sites. The strong coordination between hydronium ions and water molecules increases the ion conductivity, because the Eigen ion and water cluster are important in obtaining conductivity. Molecular dynamics simulation was used to estimate the diffusion coefficient and ion conductivity. The coordination between particles is predictable, allowing a better understanding of the dynamical behavior of the system.

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References

Ennari, J. (2008). Modeling of transport properties and state of water of polyelectrolytes containing various amounts of water. *Polymer*, *49*, 2373–2380.

Ennari, J., Neelov, I., & Sundholm, F. (2001). Estimation of the ion conductivity of a PEO-based polyelectrolyte system by molecular modeling. *Polymer*, *42*, 8043–8050.

Kim, E., Weck, P. F., Balakrishnan, N., & Bae, C. (2008). Nanoscale building blocks for the development of novel proton exchange membrane fuel cells. *Journal of Physical Chemistry B*, *112*, 3283–3286.

Kreuer, K. D. (2000). On the complexity of proton conduction phenomena. *Solid State Ionics*, *136*, 149–160.

Kreuer, K. D., Paddison, S. J., Spohr, E., & Schuster, M. (2004). Transport in proton conductors for fuel-cell applications: Simulations, elementary reactions, and phenomenology. *Chemical Reviews*, *104*, 4637–4678.

López-Chávez, E., Martínez-Magadán, J. M., Oviedo-Roa, R., Guzmán, J., Ramírez-Salgado, J., & Marín-Cruz, J. (2005). Molecular modeling and simulation of ion conductivity in chitosan membranes. *Polymer*, *46*, 7519–7527.

Mukoma, P., Jooste, B. R., & Vosloo, H. C. M. (2004). Synthesis and characterization of cross-linked chitosan membranes for application as alternative proton exchange membrane materials in fuel cells. *Journal of Power Sources*, *136*, 16–23.

Paddison, S. J., & Elliott, J. A. (2007). Selective hydration of the 'short-sidechain' perfluorosulfonic acid membrane. An ONIOM study. *Solid State Ionics*, *178*, 561–567.

Pozuelo, J., Riande, E., Saiz, E., & Compañ, V. (2006). Molecular dynamics simulations of proton conduction in Sulfonated poly(phenyl sulfone)s. *Macromolecules*, *39*, 8862–8866.

Ramírez-Salgado, J. (2007). Study of basic biopolymer as proton membrane for fuel cell systems. *Electrochimica Acta*, *52*, 3766–3778.

Sun, H. (1998). COMPASS: An ab initio force-field optimized condensed-phase applications overview with details on alkane and benzene compounds. *Journal of Physical Chemistry B*, *102*, 7338–7364.

Wan, Y., Creber, K. A. M., Peppley, B., & Bui, V. T. (2003). Ionic conductivity of chitosan membranes. *Polymer*, *44*, 1057–1065.

Yamada, M., & Honma, I. (2005). Anhydrous proton conductive membrane consisting of chitosan. *Electrochimica Acta*, *50*, 28372841.