Theoretical simulations of proton conductivity: Basic principles for improving the proton conductor

D.W.M. Hofmann, L.N. Kuleshova*, B. D'Aguanno

CRS4, Parco Scientifico e Technologico, Sardegna Ricerca, Edificio 1, Loc. Piscina Mana, Pula 09010, Italy

ARTICLE INFO

ABSTRACT

Classical molecular dynamics (MD) simulations of proton conduction have been performed, to get insight into basic principles of potential improvements of proton conductivity in polyelectrolyte membranes. For the simulations the reactive force field for water (RWFF) was used, which allows bond dissociation of water, acids and hydronium ions. The effects are shown to be fundamental relevance for the diffusion of protons in membranes. One and two-dimensional conductors, and a Nafion™ membrane have been modeled in our simulations. The two-dimensional model imitates a metal phosphate; the one-dimensional model imitates an idealized pore of hydrated Nafion membranes. The MD simulations of proton conductivity of the metal phosphate show the dissociation of the acid —POH groups and their participation in the proton transport. Several simulations are performed with acids of different strength and the effect of the acid's strength on the diffusion and on the conductivity is analyzed. The importance of the ion coupling on the conductivity is firstly proved in tubes, which imitate an ideal pore inside a membrane. Afterwards, the coupling is investigated in a real hydrated Nafion membrane by a non-equilibrium MD simulation. The results suggest a soliton-like behavior for proton conductivity in membranes.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

The modeling of polyelectrolyte membranes, for example, Nafion™ (Du Pont de Nemours, Wilmington, DE), on different theoretical levels, has provided many insights into membrane's structure and function, including morphology, structure and properties of absorbed water, proton transport, role of the side chain, etc. [1]. Problems still rise in theoretical simulations of the proton conductivity and in a detailed understanding of the mechanism of the proton conduction. It is of special interest, since proton transport in acid solutions is much more rapid process than the transport of other small sized ions: $349.8 \, cm^2 \, \Omega^{-1}$ for H^+ vs. $73.5 \, cm^2 \, \Omega^{-1}$ for K^+ and $38.68 \, cm^2 \, \Omega^{-1}$ for Li^+. The unusual high conductivity is based on the handover of protons along hydrogen-bonded chains, formed by water molecules. The handover is caused by dissociation/formation of H—O covalent bonds and accompanied by reorientation of surrounding water molecules (Grotthuss mechanism [2]). For a successful modeling of the conductivity this mechanism has to be taken into consideration.

The first approach to a more appropriate description of the proton "hopping" mechanism appeared to be that of Huckel [3], followed by Bernal and Fowler [4], which required proton transfer from hydronium to a rotating water molecule, in which rotation was the rate-determining step. This mechanism was further improved, with the introduction of quantum-mechanical tunneling of a proton to water, by Conway et al. [5]. A good review of earlier work was given by Conway [6]. In the following the mechanism of the proton's diffusion was studied by quantum chemistry, where the diffusion and the proton transfer were simulated by an excess proton. In first publications the diffusion mechanism of the excess proton was studied for small water systems [7–9], later simulations were extended to carbon nanotubes [10] and to the Nafion surface decorated with sulfonate groups [11]. Obviously, simulations with an excess proton neglect possible cooperative effects between several protons. In the same time, the coupling of several protons can significantly influence the conductivity. The coupling of the ions becomes recognizable only for long simulation times (some nanoseconds). Hence, a reasonable simulation has to be performed for many protons, a large number of atoms, and a long simulation times, which makes MD the most adequate approach. Recently, along with various semi-classical methods [12–16], reactive force fields have been developed [17,18]. This new kind of force fields can simulate the breaking and formation of bonds on a classical level and close the gap between quantum mechanics and traditional force field simulations. They open new possibilities to treat computer simulations of large and reactive systems over a long (several nanoseconds) simulation time.

* Corresponding author. Tel.: +39 03463092725; fax: +39 0709250216.
E-mail addresses: hofmann@crs4.it (D.W.M. Hofmann), lukulki@crs4.it (L.N. Kuleshova), bruno@crs4.it (B. D'Aguanno).

The special reactive force field for water (RWFF) has been developed in our preceding work [19]. This force field allows, in combination with classical molecular dynamics, the calculation of macroscopic physical properties and, in particular, of the conductivity. The classical approach is favorable in simulations, because the conductivity is a cooperative effect of all charged particles in a given system. Therefore the simulations have to include a large number of atoms and have to be repeated sufficiently to obtain a significant statistics. The ability the RWFF describes properly the proton transfer between hydronium and water molecule, as well as other properties of water has been shown by simulations on a Nafion membrane [20]. The kinetics of the proton transfer was investigated and found to be of the second order, and the elevated conductivity in membranes was well reproduced.

Here we present the results of further investigations, focusing on the aspect of engineering an ideal proton conductor. The RWFF is extended to simulate the dissociation of acid groups. This enables us to investigate the influence of the acid's strength on the conductivity. In mechanistic models the contribution of the acid groups to the conductivity is named as a surface conductivity [21].

Two kinds of proton conductors have been investigated: one with hydrogen phosphate groups and the other with sulfonate groups. The MD simulations have been performed on a model for proton conducting metal phosphates, on tubes, imitating idealized channels in Nafion membrane, and on a realistic model of a hydrated Nafion membrane. The metal phosphates are of interest as proton conductors by themselves [22], as well as fillers for composite membranes [23]. Along with the dissociation of water molecules, the dissociation of acid groups of an ionic polymer and/or filler plays an important role, too. The reactive force field allows the inclusion of both of these processes into MD simulation. The tubes, imitating idealized channels in Nafion membrane, were modeled in order to investigate the role on proton coupling in conductivity, while the real hydrated Nafion membrane was used here to investigate the role on a hydrogen-bonded network in the excitation energy dissipation in Nafion matrix.

2. Models and parameterization

2.1. Modeling of metal phosphate

The purpose of this model was to investigate the effects of confinement's properties (i.e. dissociation constants) on transport of protons and water. Since the hydrogen bonded network plays an important role in proton transfer, to engineer an ideal two-dimensional proton conductor, firstly we constructed an "ideal" hydrogen bonded chain of water molecules with the hydrogen bridge distance $O\cdots H$ of 1.73 Å (Fig. 1a). The chain was stabilized by adding phosphate groups. The tetragonal coordination of oxygen atoms of this chain was completed by coordination with hydrogen atom of POH groups. Hydrogen atoms of water, not engaged in hydrogen bridges were coordinated with oxygen atom of POH groups (Fig. 1b). Afterwards, the remaining three oxygen atoms of the phosphate residues were connected, by atoms of tetravalent metal into the two-dimensional layer (Fig. 1c). The model of the bilayer confinement was not intended to be realistic. Nevertheless, as it follows from Fig. 1d, the resulting hypothetical structure of the bilayer mimics very well the known experimental structure of $Zr(PO_4H)_2$ (Fig. 1d) [24].

The elementary unit cell of the model consists of two water molecules, which are stabilized by two phosphates groups, the last are connected via two metal atoms. A supercell for MD simulations was formed with 25 elementary unit cells along the water chain and 4 unit cells in the transverse. In total the supercell contained 200 interlayer water molecules and 4000 atoms in the two layers above and below the water. The simulation was performed with DL_POLY_2 [25] at standard conditions ($P = 1$ atm, $T = 298$ K) in NPT ensemble with a time step of 0.2 fs. The overall time for the calculations has been 0.4 ns, which corresponds to 2,000,000 iteration steps. The first 200,000 steps have been used for the equilibration of the system.

2.2. Modeling of an idealized Nafion pore

The purpose of this model was to investigate the influence of the proton coupling on conductivity. A hypothetical model of one-dimensional conductor, imitating an idealized pore in Nafion membrane, has been constructed by rolling up the chain of Nafion polymer around an "ideal" hydrogen-bonded chain of water molecules with the hydrogen bridge distance $O\cdots H$ of 1.73 Å. To complete the tetrahedral coordination of the oxygen atoms of this chain, C—SO₃ and C—CF₂C groups in proportion of 1:8, accordingly to real Nafion polymer are used. By the further supplementation with carbon atoms, fluorine atoms and the corresponding side chain, this model results in an ideal straight tube (see Fig. 2). The diameter of the helix was set to 10 Å. This diameter corresponds to the channels connecting clusters of water in Nafion [26]. On the helix 64 moieties have been placed (56C— CF₂—C and 8 C—SO₃). By avoiding the overlap of the van der Waals spheres of the moieties the length of the tube results in 87 Å. The helix was filled with water molecules. The volume inside of the tube gives place to 59 water molecules. The resulting ratio between sulfonate groups and water molecules λ is about 8, which corresponds to a moderate humidification of a Nafion membrane.

The simulation was performed with DL_POLY_2 at standard conditions ($P = 1$ atm, $T = 298$ K) in NPT ensemble with a time step of 0.2 fs. The overall time for the calculations has been 1 ns, which corresponds to 5,000,000 iteration steps. The first 500,000 steps have been used for the equilibration of the system.

2.3. Modeling of the real Nafion membrane

To mimic the hydrated Nafion membrane we used 36 Nafion monomers $CF_3(CF_2)_{11}CF(CF_3)OCF_2CF(CF_3)OCF_2CF_2SO_3^-$ with an equivalent weight of 1081 g mol⁻¹ Nafion per sulfonate group, how it was described in [20]. This weight coincides with the average equivalent weight per sulfonate in the most studied Nafion membranes Nafion® 117. The simulations of hydrated Nafion were performed with DL_POLY_2 at standard conditions ($P = 1$ atm, $T = 298$ K) for water content $\lambda = 6$. In the first step the systems were equilibrated in NPT ensemble for 1,000,000 iterations with a time step of 0.2 fs. The equilibration runs were followed by 4,000,000 production iterations in NVT ensemble.

2.4. Parameters of the simulations

The parameters for the interatomic interactions in bilayered hydrogen phosphate were taken from the "data mining" force field [27]. For the metal atoms we set the parameters of zirconium atom. For O and H atoms of POH hydrogen phosphate residue and for atoms of intersectional water we used the parameters of our RWFF [19] in order to allow dissociation of OH group of hydrogen phosphate and proton exchange between water molecules and acid hydroxyl group of phosphate. The intramolecular interactions of Nafion and the intermolecular interactions Nafion–water were described by the Dreiding force field [28]. The electrostatic interactions were calculated by Ewald summation. The atomic charges in the RWFF were 0.834e⁻ for oxygen and +0.417e⁻ for hydrogen atoms. These values are common to a large number of force fields for water [4] and guarantee a correct dipole moment for water.
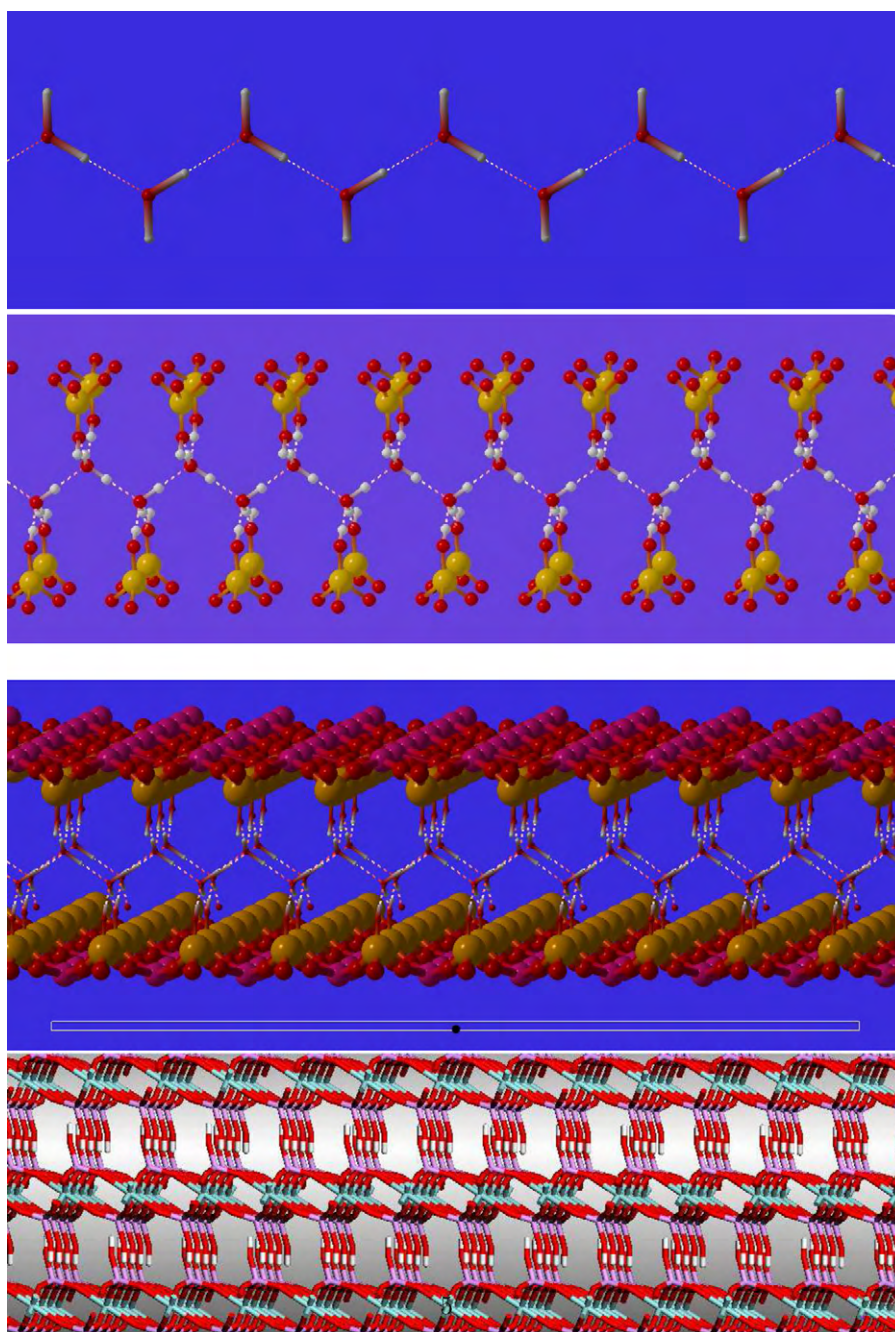
Fig. 1. Construction of the ideal metal phosphate.

3. Results and discussion

3.1. Metal phosphate

3.1.1. Proton transfer

The MD simulations performed with RWFF on the system of water in the bilayer confinement of Zr-phosphate demonstrated the principal possibility of spontaneous association and dissociation of hydroxyl groups of water and a metal phosphate. Freely associating PO^- and dissociating POH groups, as well as water molecules, participate in proton transfer and proton transport processes. The diffusion of the protons is commonly divided in two different mechanisms [21,1]: the vehicle mechanism, which describes the diffusion of the hydrogens together with water as hydronium, and the hopping mechanism, which describes the dif-

fusion connected to the proton transfer. Important result of the MD simulations is that for the total diffusion of the protons both contributions are nearly of the same importance. To visualize these processes and to make the point of discussion more apparent, we have prepared a movie, using the available by MD simulations trajectories. The full video can be found in the Supplement materials to the publication. In Fig. 3 we show three snapshots of this movie. In the initial configuration, Fig. 3, one can see that the marked water molecule (its atoms are colored in dark blue) is fully integrated in the hydrogen-bond network, formed by water molecules and phosphate groups of the bottom layer. The oxygen atom has two hydrogen bonds and each of the hydrogen atoms forms a hydrogen bond. Some of the phosphate groups are protonated and ready to dissociate, others are free and can serve as proton acceptors. In several ps the water molecule forms two hydrogen bridges with
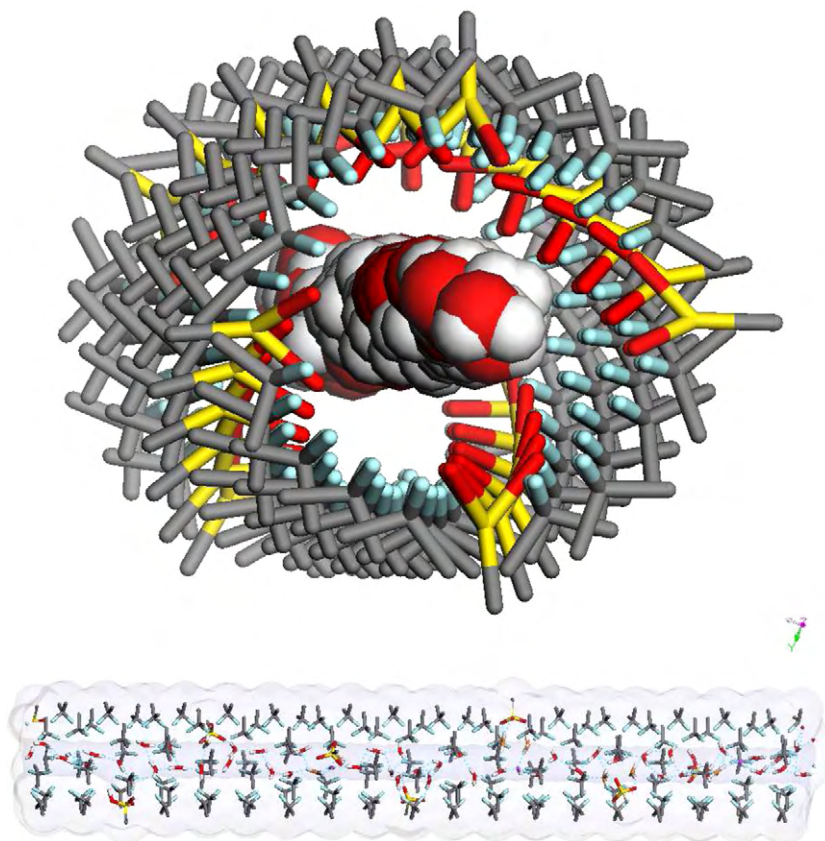
Fig. 2. An idealized Nafion pore.

dissociated PO⁻ group from opposite layer, Fig. 3b, and after several vibrations in this position it transfers one of its protons to the opposite PO⁻ group. From the video and Fig. 3c it is clear that the second proton can be transferred just after following translation of the water molecule along the phosphate surface.

In other words, the proton diffusion is realized by repeated hopping and translation movement steps of all particles of the system involved in the proton transport. (It is necessary to also mention that the differentiation between proton and hydrogen atom makes little sense, since they continuously alter their states during proton transport). Particles involved in proton conduction are H_3O^+, H_2O, =PO⁻, and =POH. All of these can perform rotations. In contrast to the phosphate groups, water and hydronium can additionally translate. The sum of these movements results in the so-called vehicle mechanism. In addition to these movements, proton transfer (hopping) can occur from H_3O^+ to H_2O or PO⁻ and from POH to H_2O. (The direct transfer from POH to PO⁻ is not possible in our model for geometrical reasons.) Conduction, connected to this proton hopping refers to the hopping mechanism.

Our video supports the interpretation of the transport mechanism given by Agmon [29]. He states that the proton transfer succeeds quickly and it is not the restricting step. In fact, in our video water and hydronium form a Zundel ion $H_5O_2^+$. Inside this ion the proton vibrates forward and backward. An effective proton transfer requires the decay of this ion. The decay requires that oxygens of the Zundel ion are separated by diffusion. This decay is slow, since the ion is stabilized by further water molecules as the Eigen ion $H_9O_4^+$ and $H_{13}O_6^+$. Therefore the decay requires the rearrangement of the local network formed by the water molecules. As a result the hopping and the diffusion mechanism have to be alternating.

A careful inspection of the proton transfers gives a hint for a reason of the increased conductivity in comparison with diffusion mechanisms according Eq. (1). Some time it happens that two proton transfers occur quickly, one after the other. The incoming proton on one side of the water molecules squeezes out another hydrogen atom. In chemistry such kind of reactions are well known as electrophilic substitution, and in solid physics as a hole hopping mechanism. These cooperative effects will be discussed in more details in the coming sections.

3.1.2. Dissociation and diffusion

In first approximation the conductivity of a solution is proportional to the diffusion coefficient of the ions. In our systems the protons n_{H^+} are the only mobile charge carriers and the conductivity can be expressed by the proton diffusion D_{H^+} and by the concentration of protons n_{H^+}/V (1) [30]:

$$\sigma_D = \frac{n_{H^+} + q_{H^+}}{Vk_BT}D_{H^+},\tag{1}$$

The number of protons (or hydroniums, $n(H^+) = n(H_3O^+)$) and the degree of dissociation α depend on the strength of the acid group, which is defined as pK_a:

$$pK_a = -\log\frac{n(R-O^-)*n(H_3O^+)}{n(R-OH)*n(H_2O)}\tag{2}$$

Different degrees of dissociation can be easily simulated with the RWFF [19]. By changing slightly the charges on the oxygen atoms of the phosphate, we increase (or decrease) the strength of the PO—H bonds. For very diluted solutions the relation between the dissociation constant and the conductivity can be expressed by the Ostwald dilution law [31]. For higher concentrations, the diffusion
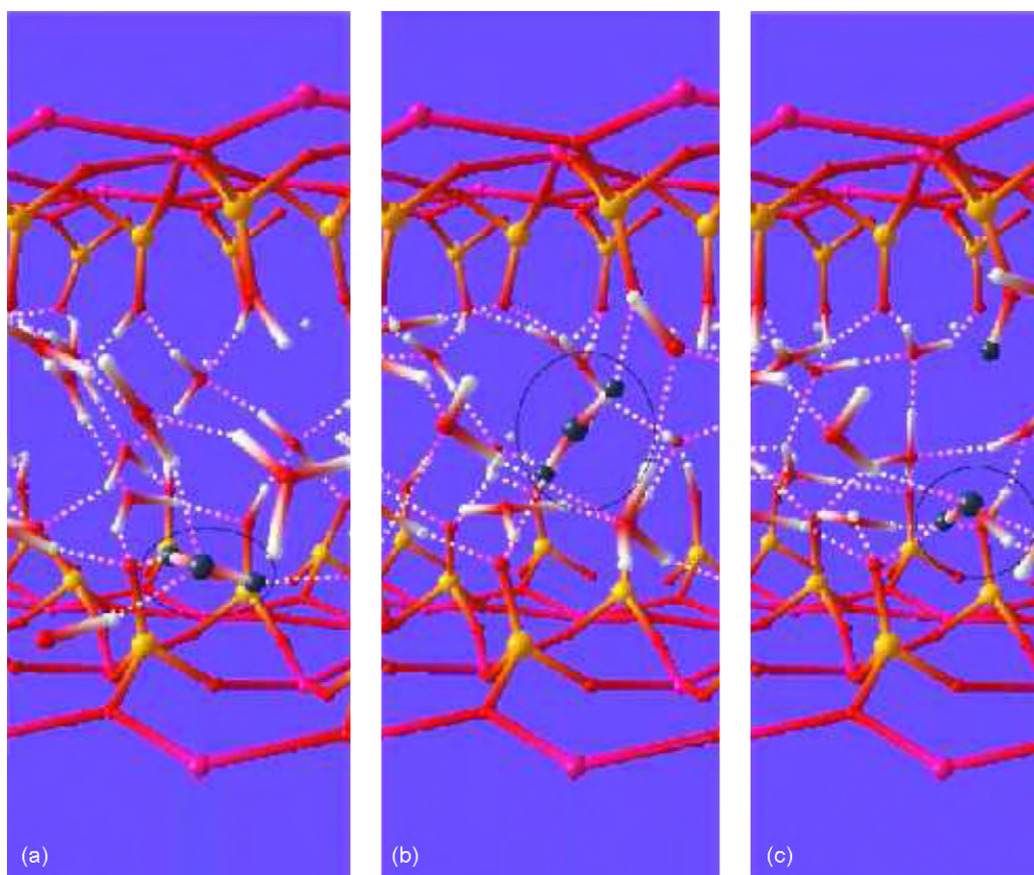
Fig. 3. Water and proton dynamic in the metal phosphate. (a) Initial configuration, reference water molecule is marked in dark blue. (b) Reference water molecule forms H-bonds with two dissociated PO^- groups of opposite layers. (c). The water molecule continues to move with interchanged proton and PO^- group of opposites layer associates the marked hydrogen to form POH group. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

constant depends on the ion concentration ($D \mapsto D(c_{ion})$). Until the concentration values c_{ion} do not exceed 0.1 M, the Debye–Huckel equation can be applied [32]. This equation takes into account the polarization of the solvent around the ion. For higher concentrations the coupling between the different ions becomes important, but this we will discuss in the next section.

In this section we demonstrate the deviation of the proton diffusion from the cited laws due to the proton transfer via the Grotthuss mechanism. We performed three MD simulations by using different charges q on the O atoms of POH and estimated the diffusion constants by means of the Einstein relation [30]:

$$D = \lim_{t \to \infty} \frac{1}{6t} \left\langle \left[\vec{R_i}(t) - \vec{R_i}(0) \right]^2 \right\rangle = \lim_{t \to \infty} \frac{1}{6t} msd \qquad (3)$$

In Table 1 we show the results obtained with different charges q. The Table contains the numbers of different species, found after an equilibration of the system: the number of dissociated groups n (PO^-), the number of nondissociated groups n (POH), the number of hydroniums n (H_3O^+), and the number of water molecules n (H_2O). The calculated dissociation constant pK_a and the estimated diffusion coefficients of proton D(H) are tabulated too.

One can see that the number of hydronium ions $n(H_3O^+)$ in the system almost coincides with the number of dissociated POH groups n (PO^-). The O—H bond weakens accordingly with decrease of the charge on the oxygen atom. Correspondingly, the number of dissociated POH groups increases and the pK_a decreases. While the pK_a depends monotonically on q (O_{POH}), the diffusion coefficient D (H) runs through a maximum. For the charge q (O_{POH})=−0.7e− with $pK_a = 0.5$ we obtain D(H) = 0.081* 10^{-9} m^2 s^{-1}. The lower as well as the higher dissociation pK_a results in lower values for the

diffusion coefficients. This nonlinear dependence can be explained by the Grotthuss mechanism of the proton transfer, contributing to the diffusion. With a charge of −0.6e− 86% of POH groups are fully dissociated, and we have mainly hydroniums in interlayer space. Here the Grotthuss proton transfer is restricted by lack of proton acceptors and the diffusion of protons is reduced. With a charge of −0.8e−, POH groups almost do not dissociate (1.2%) and the Grotthuss proton transfer is restricted by the lack of proton donors. In this system the diffusivity is reduced too.

In our former work we have pointed out that the kinetics for the proton transfer in the membrane is of the second order [20]. According to this finding, the proton transfer $r_{ProtonTransfer}$ can be expressed as function of concentrations of water and hydronium:

$$r_{ProtonTransfer} = kc(H_2O)c(H_3O^+) = kxc_0(H_2O)(1-x)c_0(H_2O) \qquad (4)$$

From this expression it follows that the diffusion of hydrogen atoms by the Grotthuss mechanism should have a maximum if the concentrations of water molecules and hydroniums occur in equal amounts ($x = 0.5$). In this case the optimal 2-dimensional proton conducting metal phosphate should have $pK_a = 0$.

3.2. Idealized Nafion pore: conductivity and ion coupling

In the above paragraph we mentioned the relation between diffusion and conductivity. However, for high concentrations of salts the conductivity is influenced by the interaction between the ions, and the conductivity is not furthermore proportional to the diffusion coefficient. In general, the conductivity lowers for ion pairing of anions and cations. However, in special cases the conductivity can rise. Since long time this behavior has theoretically been pre-

Table 1
The dissociation constant and proton diffusivity in the Zr-phosphate.

q (O_{POH}) [e^-]	n (P—O)	n (H_3O)	n (P—OH)	n (H_2O)	pK_a	D (H) [10^{-9} m^2 s^{-1}]
−0.6	172	171	28	28	−1.6	0.045
−0.7	71	73	129	125	0.5	0.081
−0.8	2.3	7.2	197.7	188	3.4	0.048

dicted for ionomers, where just one type of ions, anions or cations, is mobile [33]. Our simulations [20] confirms this findings for the case of Nafion, where the protons are the only moveable charge carriers. The increased conductivity in ion channels plays a decisive role in biochemistry [34] and solid conductors [35]. In this section we discuss the coupling of the ions and its effect on the conductivity. In particular, we are interested in the coupling of the protons and hydroniums with the acid group of the Nafion. For this purpose we constructed an ideal pore of Nafion (see model 2.2). In this model the charge of the oxygen atoms in the acid group SO_3 was varied and the effect on diffusion and conductivity was investigated.

To take into account ion coupling Eq. (1) must be modified by an additional factor $H_R(c)$ [35]:

$$\sigma = \frac{1}{H_R(c)} \frac{n_{H^+} q_{H^+} D_{H^+}(c)}{V k_B T} \quad (5)$$

Commonly, the correction factor $H_R(c)$ is called the Haven ratio. The discrepancy between the diffusion and conductivity can be understood by analyzing the following expression for conductivity:

$$
\begin{aligned}
\sigma &= \lim_{t \to \infty} \frac{1}{V k_B T 6t} \left\langle \left\{ \sum_i q_i [R_i(t) - R_i(0)] \right\}^2 \right\rangle \\
&= \frac{n_{H^+} D_{H^+}}{V k_B T} + \lim_{t \to \infty} \frac{1}{V k_B T 3t} \left\langle \sum_{i<j} [R_i(t) - R_i(0)][R_j(t) - R_j(0)] \right\rangle \\
&= \sigma_D + \sigma_{collective}
\end{aligned}
\quad (6)
$$

Since the protons are the only diffusing ions in the system, the conductivity can then be expressed in terms of the diffusion coefficient for H$^+$ (Eq. (3)) and a cross-term between different hydrogen atoms. These two parts correspond to the conductivity, based on the diffusion σ_D, the vehicle mechanism, and to the collective behavior of proton motions $\sigma_{collective}$, which includes the proton transfer.

Rather than the diffusion, which depends on the mean square displacements (*msd*) of the charged particles, the conductivity is a property of the overall system. It means that the conductivity is proportional to the square displacements of the centers of the charges. To obtain the conductivity by MD simulations and statistical significance for it, we repeated the simulations 20 times with different starting configurations. The conductivity was obtained by averaging the square displacements.

To optimize the collective behavior of ions, we have taken a model of an idealized pore of Nafion described in Section 2.2. The selected water content $\lambda = 8$ allows us to avoid interference of effects, caused by very high concentration of protons, as described in Section 3.1.2. At the selected water content the proton transfer and, consequently, the proton diffusion becomes independent on the concentration of water, since the proton has enough water around it to find an adapted proton acceptor. That is to say, the kinetics of the proton transfer changes, for low proton concentrations from a second order to a pseudo-first order reaction.

In Fig. 4 we plot the *msd* of the hydrogen atoms, to estimate the proton diffusion and the *msd* of the centers of charges, to estimate the conductivity. As expected, the diffusion assumes nearly constant values within the selected water content for different acidities of the sulfonate groups, reached by the variation of charges q on the O atoms. The conductivity, in opposite, demonstrates a strong dependence on concentration of protons.

In Table 2 we list the charges on oxygen atoms of the sulfonate groups, the hydrogen diffusion coefficient, the degree of dissociation and the conductivity. The degree of dissociation α is calculated as the ratio between dissociated and nondissociated sulfonate groups.

$$\alpha = \frac{n(SO_3^-)}{n(SO_3 H)} \quad (7)$$

For the charge of $q = -0.55e^-$ only a few (7%) sulfonate groups are dissociated and the conductivity is low ($\sigma = 0.009$). The degree of dissociation rises up to 92% with increasing charge. However, the conductivity runs through a maximum for an intermediate rate of dissociation, at a charge of $-0.54e^-$. For a higher degree of dissociation, the conductivity lowers, even if more charged carriers (protons) are available.

The results obtained can be explained by collective movement of protons and sulfonate groups in the tube. For a low degree of dissociation the conductivity is low, due to the lack of available protons. For an intermediate degree, the sulfonate groups and protons contribute in a collective way to the conductivity by the Grotthuss mechanism. When all $SO_3 H$ groups in the tube are dissociated, they do not interact furthermore with the protons and do not participate in the proton transport, and conductivity is reduced.

3.3. Ion coupling in a pore of the real Nafion membrane

As was remarked in the last paragraph, the total conductivity can increase compared to a simple diffusion mechanism due to the positive coupling of the movement of ions. If the Haven ratio goes to zero, the conductivity, theoretically, can rise untill it is infinite. In the literature this type of superconductivity has been mentioned for organic conductors like polyacetylene (PA). The surprisingly high conductivity of polyacetylene was discussed in 1976 [36], for which Shirakawa was honored with 2000 the Nobel Prize in Chemistry. A short time after 1978, the underlying mechanism was identified as a topological soliton [37] and reproduced by means of EVB simulations [38]. A comprehensive overview of solitons, including proton conductors, is given in [39]. Of course, real systems and, especially Nafion membranes, do not have infinite conductivity, but soliton-like waves inside the pores might significantly increase the conductivity. Solitons can occur, if the system features a very special coupling, which suppresses the normal dispersion of energy in the system. Therefore an exact knowledge of the couplings inside the system is very important. The coupling of particles in a system can be most easily detected by studying of non-equilibrium states [40]. For this purpose an unit of the system (here an atom) should get an additional kinetic or potential energy. Then during the simulation

Table 2
Proton diffusion, degree of dissociation and conductivity in the ideal pore.

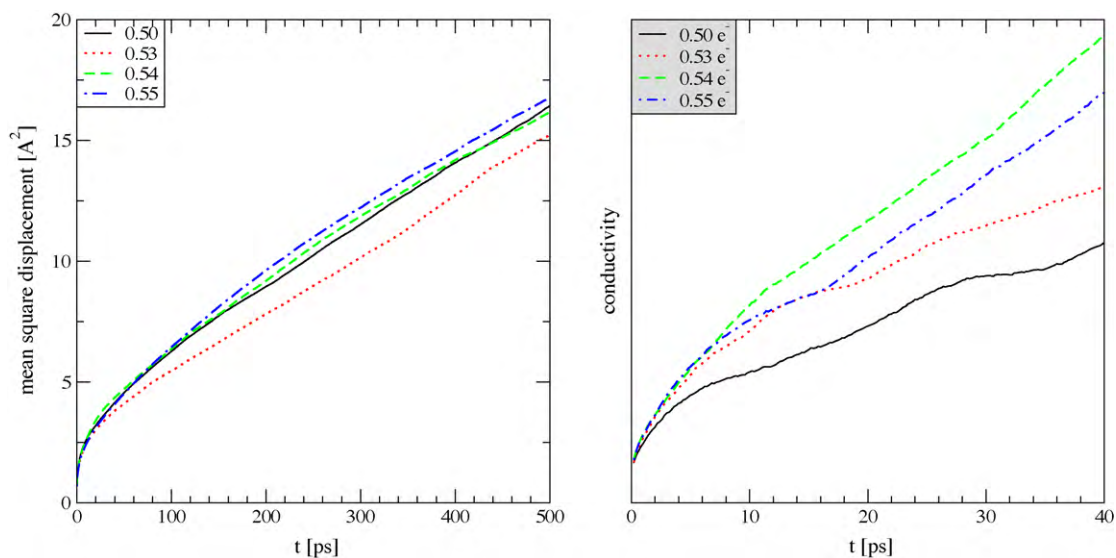| $q(O_{SO_3 H})$[e^-]	D (H) [10^{-9} m^2 s^{-1}]	α [%]	σ
−0.50	0.025	92	0.009
−0.53	0.025	40	0.010
−0.54	0.023	27	0.019
−0.55	0.024	7	0.016

Fig. 4. Diffusion and conductivity for different charges q on the O atoms.
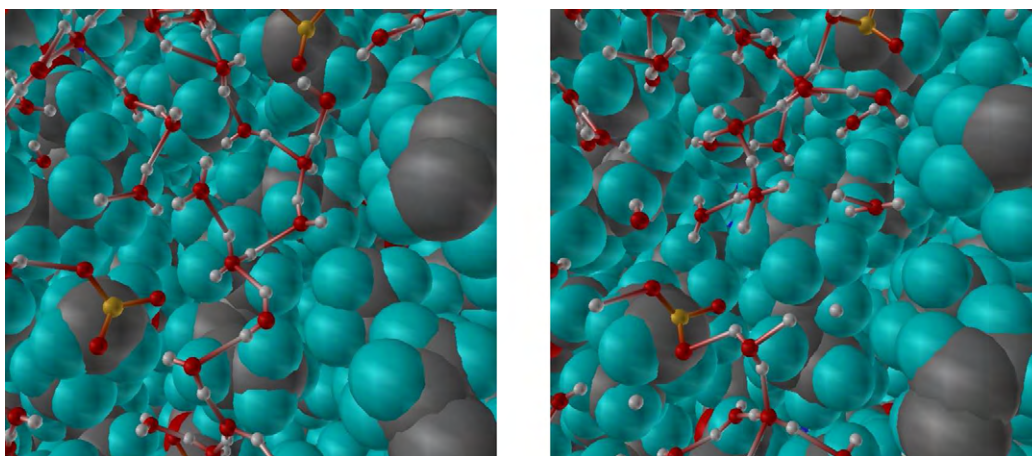

Fig. 5. Initial and final configuration of the Nafion membrane: the initial network of water is completely destroyed at the end of the simulation and nearly all hydrogen bonds are broken.

one follows the dispersion of this extra-energy within the system.

To implement this procedure inside the Nafion model (see Section 2.3), firstly, the system was equilibrated. Secondly, we have chosen a narrow pore with the hydrogen-bonded network of hydronium ion and water molecules. Afterward, one hydrogen atom of this network was shifted and the simulation was continued keeping the energy and the pressure constant. In Fig. 5 the initial and the final configuration of this simulation are shown. One can see that the impulse of energy applied to hydrogen bonded network destroys this network, but Nafion matrix shows no visible changes. This result means that the kinetic energy supported by an impulse is only marginally transferred to the nonpolar phase and is conserved mainly within the polar phase. Hence, the excited proton moves and transfers its energy and its impulse to the next hydrogen atom of the network generating in this way a soliton-like wave. We have prepared a video, illustrating this process; one can find it in the Supplementary material of this publication. In Fig. 6 to make recognizable the dispersion of the kinetic energy several snapshots from this film have been superimposed by only plotting atoms with high kinetic energy.

To further investigate the impact of the proton's coupling on conductivity we plan to perform the calculations for differ-
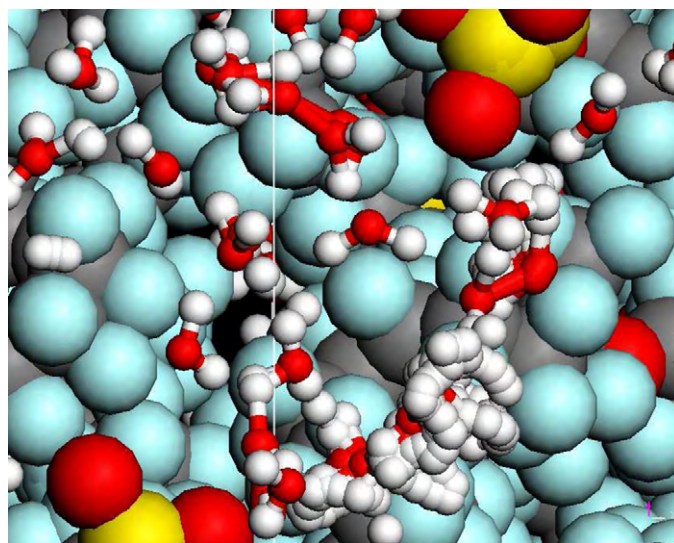

Fig. 6. Energy dispersion in Nafion: in the picture we show the initial configuration. This picture is superimposed with 20 snapshots, where we plot only atoms with high kinetic energy. The full film is in the supplement.

ent temperatures. This is linked to the fact that solitons, as it is known, show phase transition at high temperatures (e.g. super-conductors). If the mechanism of proton conduction in membrane is soliton-like, we expect a decrease in the coupling at high temperature and a corresponding decrease in the conductivity values.

4. Conclusions

The results obtained by MD simulations with RWFF on three modeled systems have given new insights into mechanism of proton conductivity and allowed to get some basic principles of improvement of proton conductivity in polyelectrolytes. The incorporation of the reactive force field in the classical MD simulation, along with the possibility to include the Grotthuss proton transport, has allowed modeling of a dissociation constant and investigation of the role of acid group dissociation of polyelectrolyte on proton and water transport processes. In particular, it was shown that maximum of a diffusion in Zr-phosphate appears at $pK_a = 0.5$. Similarly, in an idealized Nafion tube it was found that conductivity also gets a maximum value with the rate of dissociation of sulphonate groups of 27%. This result demonstrates that proton conduction in tube has some common features with topological solitons. In analogy to a double/single bond flip in the polyacetylene (PA), one can consider a covalent/hydrogen bond flip in the water hydrogen-bonded chain (see Fig. 1a). The coupling of hydrogen's movements with the vibrations of acid groups of confinement can be considered as an analogy to the coupling of the movements of the electrons with the vibrations of the atoms in PA. Since the topological solitons are very sensitive to impurities and irregularities inside a pore [41], in a real membrane we can expect just soliton-like conductivity. Anyway, the well developed mathematical instruments of soliton theory can be applied to optimize proton conducting membranes. This concerns optimization of the pore topology, the distribution of acid groups inside the pores, the rate of dissociation of the acid groups and the temperature of the system.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jpowsour.2009.10.019.

References

[1] K. Kreuer, S. Paddison, E. Spohr, M. Schuster, Chem. Rev. 104 (2004) 4637.
[2] C.J.T. de Grotthuss, Ann. Chim. 58 (1806) 54.
[3] E. Huckel, Z. Elektrochem. Angew. Phys. Chem. 34 (1928) 546.
[4] J. Bernal, R. Fowler, J. Chem. Phys. 1 (1933) 515.
[5] B.E. Conway, J. Bockris, H. Linton, J. Chem. Phys. 24 (1956) 834.
[6] B.E. Conway, Modern Aspects of Electrochemistry, Butterworths, London, 1964.
[7] J. Lobaugh, G. Voth, J. Chem. Phys. 104 (1996) 2056.
[8] R. Vuilleumier, D. Borgis, J. Phys. Chem. B 102 (1998) 4261.
[9] D. Marx, M. Tuckerman, J. Hutter, M. Parrinello, Nature 397 (1999) 601.
[10] C. Dellago, M.M. Naor, G. Hummer, Phys. Rev. Lett. 90 (2003) 105902.
[11] S. Dokmaisrijan, E. Spohr, J. Mol. Liquids 129 (2006) 92.
[12] M. Tuckerman, K. Laasonen, M. Sprik, M. Parrinello, J. Phys. Chem. 99 (1995) 5749.
[13] W. Heitler, F. London, Zeitschrift für Physik A Hadrons and Nuclei 44 (6) (1927) 455.
[14] T. Day, A. Soudackov, M. Čuma, U. Schmitt, G. Voth, J. Chem. Phys. 117 (2002) 5839.
[15] E. Spohr, P. Commer, A. Kornyshev, J. Phys. Chem. B 106 (41) (2002) 10560.
[16] M. Petersen, F. Wang, N. Blake, H. Metiu, G. Voth, J. Phys. Chem. B 109 (9) (2005) 3727.
[17] A. van Duin, S. Dasgupta, F. Lorant, W. Goddard III, J. Phys. Chem. A 105 (2001) 9396.
[18] K. Yin, Q. Xia, D. Xu, Y. Ye, C. Chen, Comput. Chem. Eng. 30 (2006) 1346.
[19] D.W.M. Hofmann, L.N. Kuleshova, B. D'Aguanno, Chem. Phys. Lett. 448 (2007) 138.
[20] D.W.M. Hofmann, L. Kuleshova, B. DAguanno, J. Mol. Model. 14 (2008) 225.
[21] P. Choi, N. Jalani, R. Datta, J. Electrochem. Soc. 152 (2005) 123.
[22] G. Alberti, M. Casciola, Solid State Ionics 97 (1997) 177.
[23] R. Vivani, G. Alberti, F. Costantino, M. Nocchetti, Microporous Mesoporous Mater. 107 (2008) 58.
[24] G. Alberti, U. Costantino, R. Millini, G. Perego, R. Vivani, J. Solid State Chem. 113 (1994) 289–295.
[25] W. Smith, T. Forester, J. Mol. Graph. 14 (1996) 136.
[26] K. Mauritz, R. Moore, Chem. Rev. 104 (2004) 4535.
[27] D.W.M. Hofmann, L. Kuleshova, Crystallogr. Rep. 50 (2005) 335.
[28] S.L. Mayo, B.D. Olafson, W.A. Goddard III, J. Phys. Chem. 94 (1990) 9997.
[29] N. Agmon, Chem. Phys. Lett. 244 (1995) 456.
[30] A. Einstein, Annalen der Physik 17 (1905) 549.
[31] W. Ostwald, Journal fur Praktische Chemie 31 (1885) 433–462.
[32] P. Debye, E. Hückel, Physikalische Zeitschrift 24 (1923) 185.
[33] M. Lonergan, D. Shriver, M. Ratner, Electrochim. Acta 40 (1995) 2041.
[34] J. Gwan, A. Baumgaertner, J. Chem. Phys. 127 (2007) 045103.
[35] A. Lidiard, Il Nuovo Cimento 7 (1958) 620–631.
[36] C. Chiang, H. Shirakawa, C. Frincher, Am. Phys. Soc. 39 (1977) 1098.
[37] A. Heeger, S. Kivelson, J. Schrieffer, W. Su, JETP Lett. Rev. Mod. Phys. 60 (1978) 781.
[38] W. Förner, J. Ladik, D.W.M. Hofmann, M. Seel, A. Godzik, F. Martino, J. Mol. Struct. (Theochem.) 188 (1989) 231.
[39] A. Davydov, Solitons in Molecular Systems, Kluwer Academic Publisher, 1990.
[40] D.W.M. Hofmann, W. Förner, J. Ladik, Phys. Rev. A 37 (1988) 4429.
[41] D.W.M. Hofmann, W. Förner, P. Otto, J. Ladik, J. Phys.: Conds. Matter. 2 (1990) 4081.