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Modelling of transport properties and state of water of polyelectrolytes containing various amounts of water

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ABSTRACT

Atomistic molecular modelling is used to construct sulfonated PVF-based polyelectrolyte materials containing 0, 10 or 40 wt% of water. The systems contain hydronium ions, with which the classical diffusion of the hydronium ions can be simulated, and particles called protons, with which the proton hopping mechanism can be simulated. System containing 40 wt% of water is conducting. Both the proton hopping and the classical diffusion mechanisms occur in the system and neither of them is dominating. The interactions between ions are calculated and they are found to be relatively small. Diffusion coefficients of the protons, hydronium ions and the water molecules are reported and the movement of ions is studied. The location of the protons, the hydronium ions and the water molecules is studied at the atomistic level. In system containing 40 wt% of water, water clusters are seen. There are no remarkable differences between the results that are measured for similar materials or calculated in this study.

1. Introduction

Ion-conducting polymer membranes are at the focus in materials science today due to their potential applications in environment-friendly energy sources, *i.e.* fuel cells suitable for several electronic equipment, medical devices and electrical vehicles [1–6]. A special group of these materials are the proton-conducting polyelectrolytes, which have promising applications in low-temperature fuel cells in zero emission vehicles and electrochemical devices [7,8].

The polymer membranes, which are commercially available, are based on perfluorinated sulfonic acid polymers, *e.g.* Nafion® [9]. In search for better but less expensive membranes, sulfonated poly(vinyl fluoride), PVF-based materials have been prepared and studied experimentally [10,11]. This work collects results of modelling of three similar sulfonated PVF-based materials containing various amounts of water (0, 10 or 40 wt%).

Molecular modelling offers molecular lever information of the material and it is used in several investigations, *e.g.* to get information of the mechanisms of the conduction or the structure of the material [12–15]. Modelling studies have shown that the proton conduction mechanisms can be divided to several steps, which involve dissociation of the proton from the acidic site, transfer of the proton to the aqueous medium, screening by water molecules of the hydrated proton from the sulfonic acid anion group and diffusion of the proton in the water cluster or channel within the polymer matrix [16]. We have earlier reported results of the modelling studies of PEO-based polymer electrolytes [17–19]. We use model, which involve hydronium ions and particles called protons, whose parametrization has been reported earlier [17]. The hydronium ions or protons are not bonded to the anion, and thus the dissociation step cannot be studied. However, by studying the coordination between the anion and the hydronium ion or between the anion and the proton, it can be seen whether the transfer of the proton or the hydronium ion from the anionic site to the water phase takes place in the material. The diffusion of the proton or the hydronium ion involves coordinations between protons and water molecules or between hydronium ions and water molecules, which are also studied.

One goal of this work is to study the location of the water in the simulated water containing cells. The nature of the polymer electrolyte system gives a possibility to at least three different types of the water: water clusters associated with the ionic sites, free water clusters and water associated with the hydrophobic polymer backbone [10]. There has been several studies aiming at understanding the structural and dynamical properties of the free water molecules, which are confined to a small regions forming small pores or clusters inside a solid material and at their influence on the properties of the material, *e.g.* on the ion mobility [20–25]. It has been shown that the pores have influence on the transport of ions and on the permittivity of the absorbed water and thus also on the conductivity [26]. It also seems that ionically bond water

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clusters are important to obtain conductivity. Several studies have focused on discovering the microstructure of Nafion membrane [23,26–29]. Small-angle-X-ray scattering (SAXS) experiments have indicated the existence of small roughly spherical water clusters in Nafion membrane [30]. These clusters are believed to have a high concentration of sulfonic acid groups [31]. However, also other types of water can be found in the polymer electrolyte system, *e.g.* spectroscopic and calorimetric measurements show that sulfonated PVF-based membranes and similar kind of materials (*e.g.* styrene-grafted and sulfonated poly(vinylidene fluoride) membranes, PVDF-*g*-PSSA) contain water, that is weakly bonded to hydrophobic polymer backbone [32,33].

The proton conduction mechanisms in polyelectrolytes have been intensively studied [1,7]. The simulation method used in this work includes both protons and hydronium ions and thus both the proton hopping and the classical diffusion mechanism of the hydronium ion can be seen. The presence of the hydronium ion in the real membrane has been detected from the IR spectra [34]. To report the dynamical behavior of the protons and of the hydronium ions is one of the main goals of this paper. The movement of the protons and the hydronium ions is followed for 2000 ps and different types of proceeding are reported. Diffusion coefficients, values for the conductivity and interactions between ions are estimated to get better understanding of the dynamical behavior of the system.

2. Theory

Intermolecular pair correlation functions ($g(s)$) give the probabilities of finding a pair of particles at distance r apart relative to the probabilities expected for a completely random distribution at the same density [35]. In the present study Eq. (1) was used to calculate the coordination numbers:

$$n_{x\ldots z}(r) = 4\pi\frac{N_z}{\langle V\rangle}\int_0^r g_{x\ldots z}(s)s^2\,\mathrm{d}s \tag{1}$$

where $n_{x\ldots z}(r)$ is the number of x particles coordinated to particle z within a radius r, $\langle V\rangle$ is the volume of the cell, N_z is the total number of z particles in the system and $g_{x\ldots z}(s)$ is the radial distribution function between x and z.

The diffusion coefficients were calculated by using the following equation:

$$D_\alpha = \frac{1}{6N_\alpha}\lim_{t\to\infty}\frac{\mathrm{d}}{\mathrm{d}t}\sum_{i=1}^{N_\alpha}\left\langle[\mathbf{R}_i(t)-\mathbf{R}_i(0)]^2\right\rangle \tag{2}$$

where D_α is the tracer diffusion coefficient for the particle α, N_α is the number of diffusing particles, t is the time and $\mathbf{R}_i(t)$ is the position vector of particle α at time event t. In Eq. (2) the sum term on the right side divided by N_α is called the mean square displacement (MSD). Eq. (2) is valid only when the motion of the diffusing particle follows a random walk, *e.g.* the motion of the particle is uncorrelated with its motion at any previous time, *i.e.* Einstein diffusion is reached. The Einstein diffusion is reached when the MSD is linear in time, *i.e.* in Eq. (3)

$$6t^nD_\alpha \propto \left\langle|\mathbf{R}_i(t)-\mathbf{R}_i(0)|^2\right\rangle \tag{3}$$

$n=1$. This was tested by calculating the slope of the plot log(MSD) against log(t). In the case of Einstein diffusion, the slope of this curve is one and Eq. (2) can be used to calculate the diffusion coefficient. In case of anomalous diffusion $n<1$ in Eq. (3) and Eq. 2 is not valid. This means that some feature in the environment prevents the particle from performing a random walk.

The ionic conductivity σ was determined by using the Einstein equation [36]:

$$\sigma = \frac{e^2}{6tVkT}\Big(\sum_i z_i^2\left\langle[\mathbf{R}_i(t)-\mathbf{R}_i(0)]^2\right\rangle + 2\sum_{j>i} z_iz_j\left\langle[\mathbf{R}_i(t)-\mathbf{R}_i(0)]\times[\mathbf{R}_j(t)-\mathbf{R}_j(0)]\right\rangle\Big) \tag{4}$$

where t is the time, V is the volume of the cell, k is Boltzmann's constant, T is the temperature and R is the position vector of the diffusing particle. The first term of the right hand side in Eq. (4) is the sum over individual mean square displacements weighted with the charges and the second term is the sum of correlation of displacements of ions describing the interactions between different ions.

3. Computational details

HP ProLiant DL145 Cluster of CSC (Centre for Scientific Computation Ltd, Espoo, Finland) and own personal computers were used to perform the computational results. The calculations were carried out with the software programs InsightII and Discover version 4.0.0P and Materials Studio 4.0 from Accelrys Inc. In addition own codes were used for the calculations.

Four different 3D amorphous systems called cell1, cell2, cell3 and cell3b corresponding to systems having 0, 10, 40 wt% of water were constructed with periodic boundary conditions. The composition of the systems is summarized in Table 1. All systems contained various amounts of grafted poly(vinyl fluoride) sulfonic acid anions (PVF-SA anions) having five sulfonic acid anion groups in each molecule and 50 vinyl fluoride units, see Fig. 1. All systems contained also protons, hydronium ions and CO_2, CH_4, O_2 and H_2 gas molecules. Cell1 was water-free, while cell2 contained 10 wt% and cell3 contained 40 wt% of water. Cell3b corresponds to cell3, but it is larger. The larger cell size gives to the water molecules a possibility to form larger water clusters, like Nafion contains [30]. The parameters used for protons, hydronium ions and anions are previously reported [37]. They were added to the PCFF forcefield. The new forcefield was called NEWPCFF forcefield and it was used for all calculations. The hydronium ion is used to model the classical diffusion of the hydronium in the system. Since the hopping mechanisms cannot be modelled explicitly in systems containing polymers, the hopping mechanisms were imitated by a particle called proton. The proton has proton's mass and charge, but it's van der Waals radius is derived based on condensed phase properties of molecules containing highly polarized hydrogen, such as water [37]. Thus the proton can react with surrounding molecules via a strong electrostatic interaction and model the proton hopping mechanisms.

Ten cells with different starting structures were constructed for all systems studied. All cells were first minimized by Steepest descents for 200 iterations and two cells of each systems having the lowest energies were selected for further calculations. These six cells were minimized by Steepest descents and Conjugate gradients until the maximum derivative was less than 0.1 kcal/(mol Å). To obtain the final densities, a 500–1000 ps long molecular dynamics

Table 1
Number of X particles N(X) and the amount of water (c) in the cells studied

Cell	N(PVF-SA)[a]	$N(H^+)$	$N(H_3O^+)$	$N(H_2)$	$N(CO_2)$	$N(CH_4)$	$N(O_2)$	$N(H_2O)$ (c)
Cell1	2	5	5	4	4	4	4	0 (0 wt %)
Cell2	2	5	5	4	4	4	4	38 (10 wt%)
Cell3[b]	2	5	5	4	4	4	4	230 (40 wt%)
Cell3b[b]	8	20	20	3	3	3	3	759 (37 wt%)

[a] A grafted poly(vinyl fluoride) sulfonic acid anion, whose backbone has 50 vinyl fluoride units, see Fig. 1.

[b] A larger cell corresponding to cell3 was made to see whether the water will form larger clusters in larger cell.

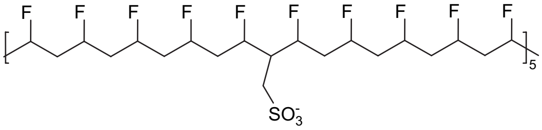

Fig. 1. The structure of the PVF-SA anion.

calculation using the Ewald summation method and NPT ensemble at 298 K was performed. The initial density of all cells was 1.5 g/cm^3. The final densities for the cell1, cell2, cell3 and cell3b were 1.310 g/cm^3 and 1.309 g/cm^3, 1.200 g/cm^3 and 1.1200 g/cm^3, 1.115 g/cm^3 and 1.120 g/cm^3, and 1.120 g/cm^3 and 1.120 g/cm^3, respectively. The final density values of cell1 are in agreement with the experimental value of the density of PVF 1.38–1.72 g/cm^3 [2,34] and to the value obtained by our own measurements 1.45 g/cm^3. The simulated densities correspond to volumes 7624.3 Å^3 and 7629.3 Å^3 in cell1, 9396.2 Å and 9405.9 Å in cell2 and 15135.1 Å and 15055.9 Å in cell3 and 55292.0 Å in cell3b.

When the final density was reached, the cells were minimized by Steepest descents and Conjugate gradients until the maximum derivative was less than 0.1 kcal/(mol Å) and 2100 ps long molecular dynamics runs were performed using the NVT ensemble in 298 K. The CMM method was used to calculate the non-bonding interactions. The update width parameter was 1.0 Å and the accuracy parameter was set to “Fine” to use 4th order in the Taylor series expansion and explicit interaction for more neighbouring cells. The time step was 1 fs.

4. Experimental materials

The simulated cells are compared to membranes prepared in our laboratory. The preparation of the membranes is reported in detail earlier [10]. The membranes are based on poly(vinyl fluoride), PVF, film manufactured by DuPont. The type of this film, *i.e.* of the Tedlar® film (registered trade mark by DuPont), is TTR10SG3. Proton irradiation was used to induce grafting to the polymer. The sample was sulfonated with 2.5 vol% chlorosulfonic acid in dichloroethane. The irradiation lowers the crystallinity of the films significantly. Wide amorphous areas are formed to the material and the sulfonation takes place in these areas [10]. The simulated cells are amorphous.

5. Results

5.1. Coordination between the PVF-SA anion and protons or between PVF-SA anion and hydronium ions

The coordination was studied by calculating the intermolecular pair correlation functions and coordination numbers, see Table 2.

Table 2
Coordination number *N* in the first coordination shell between particles X and Y

Particles (X···Y)	*N*(cell1)	*N*(cell2)	*N*(cell3)
S···H$^+$	0.5	0.6	0.1
S···OH$_3^+$	1.0	0.9	0.5
F···H$^+$	0.2	0.2	0.07
F···OH$_3^+$	0.2	0.2	0.05
F···OH$_2$		0.4	0.7
S···OH$_2$		5.2	7.0
C(polymer)···OH$_2$		2.6	–
C(graft)···OH$_2$		6.4	8.7
C(middle)···OH$_2$		2.5	–
H$^+$···OH$_2$		2.6	3.5
OH$_3^+$···OH$_2$		2.0	4.0
OH$_2$···OH$_2$		2.3	4.0

C(polymer) includes all carbon atoms in the polymers.
C(graft) includes only carbon atoms in the grafts.
C(middle) includes only those backbone carbon atoms that are five or more bond away from the nearest graft.

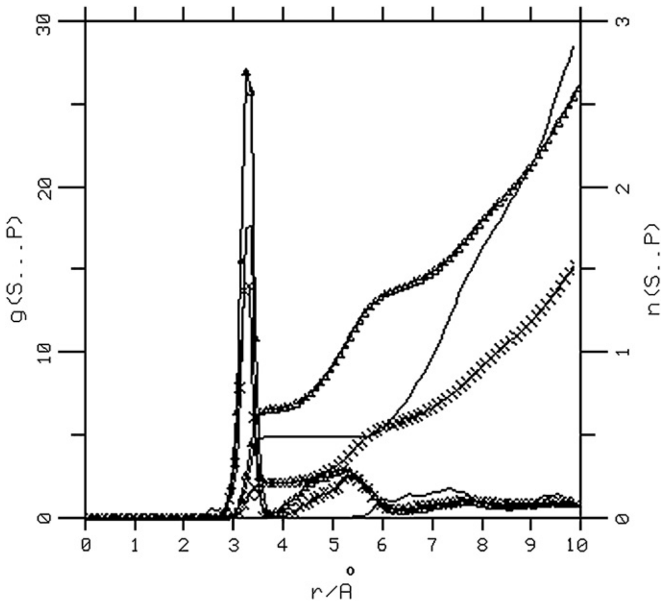

Fig. 2. The average pair coordination function and the coordination numbers between the sulphur atoms in PVF-SA anions and the protons in cell1 marked with a solid line, in cell2 marked with triangles and for cell3 marked with crosses.

The coordination numbers in cell3 and in cell3b were very similar and thus only results from cell3 are reported. First the coordination between the sulfonic acid anion groups in PVF-SA and the protons, and the coordination between the anion and the hydronium ions are discussed to see the location of the protons and hydronium ions in the system. The pair coordination function and the coordination numbers between the sulphur atoms in PVF-SA anion and protons is shown in Fig. 2. The first coordination shell is at 3.25 Å in all cells. The coordination numbers are 0.5, 0.6 and 0.1 in cell1, cell2 and cell3, respectively, see Table 2. Thus the coordination number in first coordination shell in cell1 is similar to the coordination number in first coordination shell in cell2. In cell3 the coordination number is smaller than in other cells. In water-free system the second coordination shell is first at 6.9 Å, while in cell2 and in cell3 the second coordination shell is at 5.3 Å. This is due to the water molecules, which are located around the sulfonic acid anion group in cell2 and cell3. The coordination numbers in the second coordination cell are 1.4 in cell2 and 0.6 in cell3. Thus the protons are more strongly coordinated to the sulfonic acid group in cell2 than in cell3, while in cell3 they can better transfer to the anionic site to the water phase.

The pair correlation function and coordination numbers between the sulphur atoms in the sulfonic acid group and the oxygen atoms in the hydronium ion is shown in Fig. 3. The main peak is at 3.9 Å in all cells and in cell1 also a shoulder at 3.5 Å can be seen. The coordination numbers are 1.0 in cell1, 0.9 in cell2 and 0.5 in cell3, see Table 2. In cell2 and cell3 a second coordination shell can be seen at 6.1 Å with coordination number 1.3 in cell2 and 0.8 in cell3. This coordination shell has its origin in the water molecules, which are located around the sulfonic acid anion. Therefore this coordination shell is not seen in the water-free system. As a conclusion it can be seen that the coordination between the sulfonic acid group in the anion and the protons and also the coordination between the anion and the hydronium ions decreases with increasing amount of water.

The coordination between the fluorine atoms in the backbone of the polymer and between the protons or the hydronium ions is weak in cell1 and cell2 and very weak in cell3, see Table 2. The protons and the hydronium ions give very similar results. Thus it seems that the protons and the hydronium ions are not mainly located around the backbone of the polymer and especially in cell3 they are elsewhere.

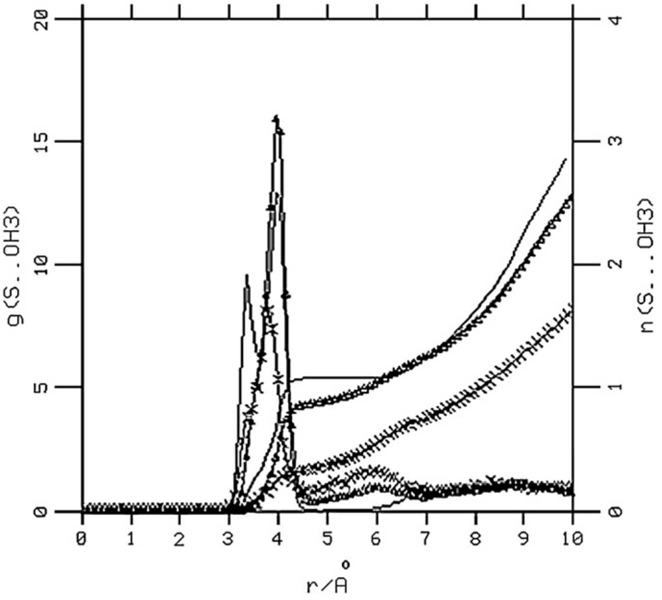

Fig. 3. The average pair coordination function and the coordination numbers between the sulphur atoms in PVF-SA anions and the oxygen atoms in the hydronium ions in cell1 marked with a solid line, in cell2 marked with triangles and for cell3 marked with crosses.

5.2. *Coordination between the protons and the water molecules and coordination between the hydronium ions and the water molecules*

The coordination between the protons and water molecules and between the hydronium ions and the water molecules is essential for the conductivity. While weak coordination between the anions and the protons or the hydronium ions increases conductivity, a remarkable coordination between mobile water molecules and protons or between water and hydronium ions increases conductivity. From Table 2 it can be seen that coordination number between the protons and the oxygen atom in the water molecules is 2.6 in cell2 and 3.5 in cell3 in the first coordination shell at 2.0 Å. The second coordination shell is at 4.3 Å with coordination numbers 4.7 in cell2 and 13 in cell3.

The coordination between oxygen atom in hydronium ions and oxygen atom in water molecules is also studied. The main peak is at 2.6 Å and the second peak is at 5.1 Å corresponding to coordination numbers 2.0 and 5.9 in cell2 and 4.0 and 18 in cell3, respectively. The coordination numbers show that the coordination between the protons and the water molecules and between the hydronium ions and the water molecules increases as the amount of the water in the system increases and especially strong effect is seen in the second coordination shell. From the FTIR spectra it has been seen that in the experimental sulfonated PVF-based membrane the positive particles are coordinated to water molecules and complexes like H_3O^+ and $H_5O_2^+$ are found [9].

5.3. *The location of water*

To get information of the location of the water in cell2, cell3 and cell3b, several pair correlation functions were studied. The results were very similar in cell3 and cell3b, *e.g.* the coordination numbers were the same. This indicates that the size of the water clusters was not determined by the size of the simulated cell. Experimental work has shown that in sulfonated PVF and in similar materials water of three different types is associated to the material: non-freezing ionically bounded water close to the sulfonic acid anion groups, freezing bound water weakly bound to the polymer backbone and freezing free water in water clusters [10,38,39]. All these different water types are studied in the simulated cells.

First the ionically bounded water is discussed. The average pair correlation function between the sulphur atom in the sulfonic acid anion groups and the oxygen atom in water molecules has two coordination shells in cell2 and cell3. The first coordination shell is at 3.9 Å corresponding to the coordination number 5.2 in cell2 and 7.0 in cell3. The second coordination shell is at 6.25 Å corresponding to the coordination number 10 in cell2 and 24 in cell3. In all cells, also in cell3b, there are only two coordination shells. Thus there is much more water around the sulphur atom in cell3 than in cell2. Experimental studies has shown that the sulfonated PVF membranes have typically 5–12 water molecules per sulfonic acid group in primary solvation shell depending on the preparation method of the material [10]. The water uptake of the membrane is found to be dependent on the number of the sulfonic acid anion groups in the membrane and of the distribution of the sulfonic acid groups, which varies in membranes prepared in different ways [10]. It has been reported that the membranes containing only ionically bounded water are not ionically conducting [10]. Thus other water types are also important and will be discussed next.

The average pair correlation function between the oxygen atoms in water shows three coordination shells: first at 2.8 Å with coordination number 2.3 in cell2 and 4.0 in cell3 and second coordination shell at 4.8 Å with coordination number 8 (cell2) and 15 (cell3) and third at 6.8 Å with coordination number 12 (cell2) and 41 (cell3). Thus in cell3 some microphase separation is seen, while in cell2 the water clusters are quite small. We have previously seen that the formation of microphase separation had a strong increasing effect to the conductivity in the PEO-based polyelectrolyte materials [19]. Water molecules connected only to other water molecules have been found in wet experimental sulfonated PVF-based materials [9]. The simulated results are also in agreement with the experimental data concerning pure water, *e.g.* in pure water the distance between oxygen atoms in the first coordination shell is reported to be 2.9 Å with an error of about 6% [40–42].

To see if there is any water weakly bound to the polymer in the cells, the average pair correlation function between the carbon atoms in the backbone and the oxygen atom in the water molecules was calculated (see Table 2 and Fig. 4 for results in cell2). Because there are many water molecules coordinated to the sulfonic acid anion group, the pair correlation function between the carbon atoms in the grafts and oxygen atoms in the water molecules was studied. Strong coordination was found in the first coordination shell corresponding to the coordination number of 6.4 in cell2 and 8.7 in cell3. Strong coordination was also found between the carbons' one or two bonds away from the graft and oxygen atoms in the water molecules. Pair correlation function is also calculated between carbon atoms that are five or more bonds away from the nearest graft (middle carbon atoms) and between the oxygen atoms in the water molecules. In cell2 a small coordination is found and the coordination number is 2.5, while in cell3 no remarkable coordination is seen. The pair correlation function between all carbon atoms in the backbone and water molecules is very similar to the pair correlation function between the middle carbon atoms and water molecules due to the high number of the later carbon atoms in the systems studied. A small coordination with coordination number 2.6 can be seen in cell2, and in cell3 no coordination is found. The experimental studies of similar materials have shown that a great number of water molecules are connected with the hydrophobic polymer backbone [9]. In simulations it was seen that the sulfonic acid group collects many water molecules around it and these water molecules are coordinated also to the carbon atoms, which are in the vicinity of the graft. If the amount of water is high, the water starts to build water clusters and there is very little or no water in the parts of the backbone, which are not in the vicinity of the sulfonated graft. Thus the coordination numbers are smaller between the carbon atoms, which are in the vicinity of

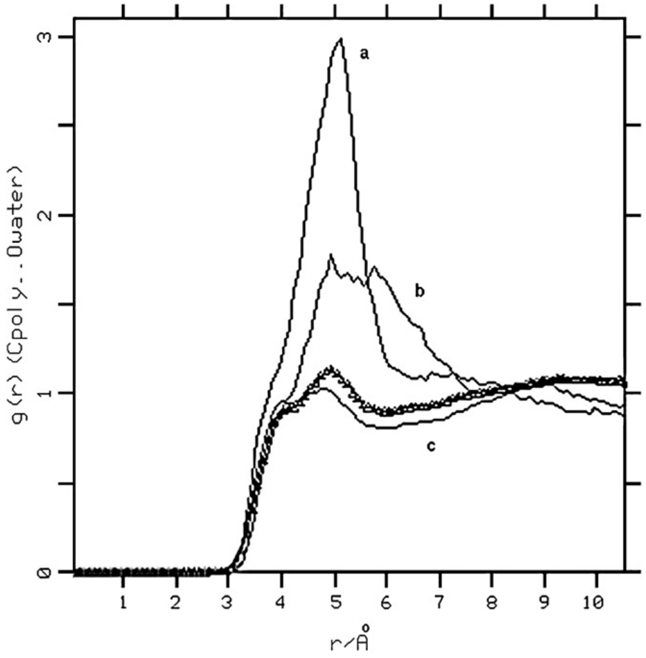

Fig. 4. The average pair correlation function between all carbon atoms in the backbone and the oxygen atoms in the water molecules is marked with triangle, the pair correlation function between the carbon atoms in the graft and the oxygen atoms in the water molecules is marked with a, the pair correlation function between the carbon atoms next to the graft and the oxygen atom in the water molecules is marked with b, and the pair correlation function between the carbon atoms, that are five or more bonds away from the nearest graft, and the oxygen atoms in the water molecules is marked with c.

the graft, and water molecules in cell2 than in cell3, and in cell3 the coordination numbers are smaller between the middle carbon atoms and the water molecules than in cell2. There was no coordination between the middle carbons and the protons or between the middle carbons and the hydronium ions in cell3.

6. The dynamical study

6.1. Diffusion coefficients

The MSD as a function of time was determined to get the self-diffusion coefficients of ions and water molecules in the studied systems. In cell1 and cell2, no Einstein diffusion was found. The anomalous diffusion of the ions is due to the polymers, strong interaction between the protons or hydronium ions and anions and small amount of water in the system. In cell3 the Einstein diffusion is reached and the average diffusion coefficient is $(0.36 \pm 0.07) \times 10^{-9}$ m^2/s for the protons, $(0.38 \pm 0.09) \times 10^{-9}$ m^2/s for the hydronium ions, $(0.068 \pm 0.018) \times 10^{-9}$ m/s^2 for the oxygen atoms in the sulfonic acid anion group and $(1.29 \pm 0.02) \times 10^{-9}$ m^2/s for the water molecules. Thus the velocities of the hydronium ions and the protons are similar in cell3. This shows that both the proton hopping and the classical diffusion mechanisms occur in cell3. However, neither the proton hopping nor the classical diffusion mechanism is dominating. The literature value for the diffusion coefficient of water in water is 2.26×10^{-9} m^2/s [43], which is of course larger than the value in the polymer containing system. The diffusion coefficient of the studied material has not been measured. However, diffusion coefficients of water molecules in PVDF-*g*-PSSA, Nafion 117 or sulfonated polyarylene membranes have similar magnitudes (about $0.1–1 \times 10^{-9}$ m^2/s) [32]. The value of the diffusion coefficient depends on many factors, *e.g.* on the type of the polymeric matrix and water uptake of the material [32]. The simulated diffusion coefficients of the protons are smaller in cell3 than in pure water. The literature value for protons diffusion in water is 9.31 [45]. The movement of protons or hydronium ions in cell3 is much higher than in other cell. Figs. 5 and 6 illustrate the dramatic difference between the movement of the protons or the hydronium ions in cell3 and in other cells. Fig. 5 shows the 2000 ps long trajectory of one proton and Fig. 6 shows a 2000 ps long path of one hydronium ion in different cells.

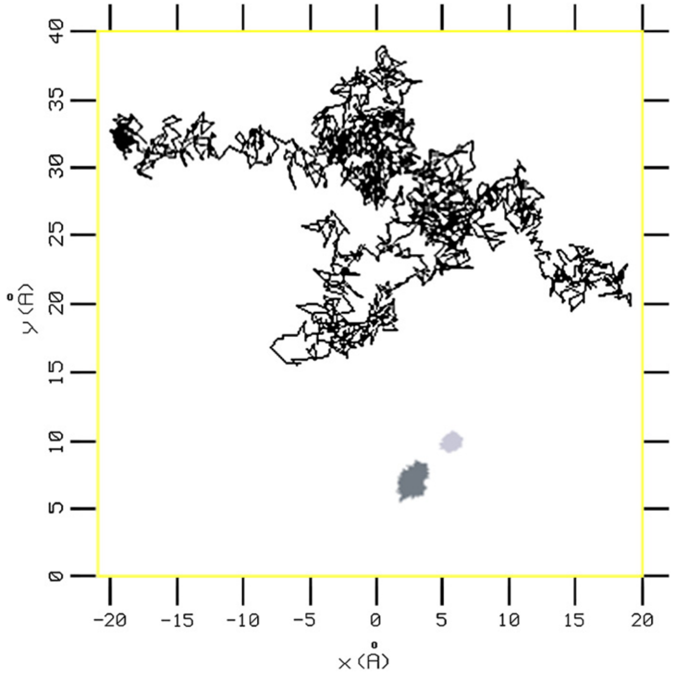

Fig. 5. The 2000 ps long trajectories of one proton ion in cell1 (marked with a grey line), cell2 (marked with a dark grey line) and cell3 (marked with a black line).

Displacements of the protons or hydronium ions as a function of time (2000 ps) were explored in all cells (one example of the figures in cell2 and cell3 is shown in Fig. 7). This study shows that in cell1 and cell2, the protons and the hydronium ions are trapped

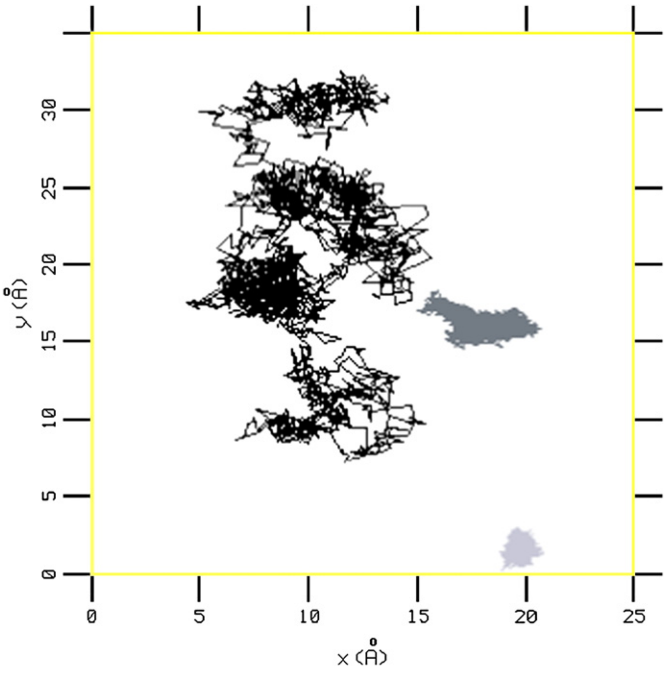

Fig. 6. The 2000 ps long trajectories of one hydronium ion in cell1 (marked with a grey line), cell2 (marked with a dark grey line) and cell3 (marked with a black line).

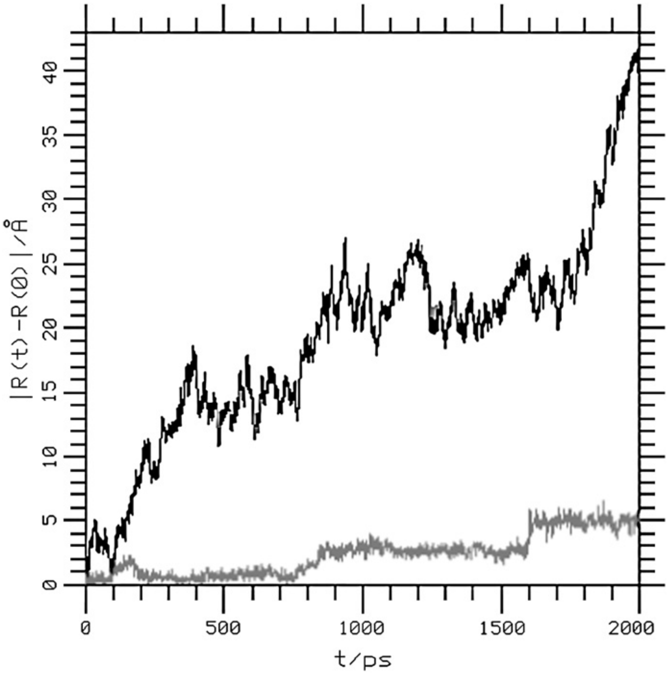

Fig. 7. Displacement of one proton during 2000 ps in cell3 (marked with a black line) and in cell2 (marked with a dark grey line).

into small areas in the system and proceed by small jumps or by very slow drifting. The movement by jumps from one cavity to another is typical for small molecules in polymers. The jumps can take place, when a channel opens by means of fluctuation, from one cavity to another. In our system the protons and the hydronium ions are also trapped in the vicinity of the anions by strong electrostatic interactions. During 2000 ps, there are typically 0–1 jumps in cell1, 1–3 jumps in cell2 and 6–9 in cell3. The jumps are very quick (just few picoseconds long). The cavities are largest in cell3 and smallest in cell1. In cell3 the protons and the hydronium ions are occasionally also proceeding by quick zigzag motion for a rather long time, even for several tens of picoseconds (the end of Fig. 7 offers an example of this motion). The movement by jumps from one cavity to another is a typical motion for small particles in the polymer and the zigzag motion in water. In cell3 the water molecules have built clusters, where the zigzag motion of the protons or hydronium ions can occur, while in other cells the movement of the protons or the hydronium ions is more similar to their movement in pure polymer matrix. Since the proceeding in the zigzag motion is very effective, the formation of water clusters is essential for the conductivity of this kind of polyelectrolytes. Instantaneous individual coordinations were studied and it was seen that in cell3, protons and hydronium ions moved from the vicinity of one anion to the vicinity of another anions in another water pores.

6.2. Conductivity and interactions between ions

In cell3 the Einstein diffusion was reached for ions, which means that their motion is uncorrelated with their motion at any previous time and that Eq. (4) is valid. Thus the value of conductivity could be calculated for this system. Fig. 8 shows the total correlation function of ions' displacement including MSD of ions and correlations between ions for one cell3. The value of the conductivity calculated by using Eq. (4) for cell3 is 91 ± 9 mS/cm. Measurements have given rather similar values for similar type of materials. Nafion 117 has conductivities 50–140 mS/cm (52 mS/cm at the room temperature) and for PVDF-based sulfonated materials (PVDF-*g*-PSSA) measured conductivities are in the level of 30–150 mS/cm [44–47,10]. For sulfonated PVF-based material the measured conductivities are 10–20 mS/cm ± 20% [33,10]. Since in our model the proton can move from one water molecule to another without creating and breaking bonds, the model gives higher conductivities than the measurements. However, the magnitude of the simulated value of conductivity is right, and thus the simulations can be used to estimate the conductivity of the material under study.

The interactions between ions in one cell3 are shown in Fig. 9. The interactions are relatively small, less than 30% of the total

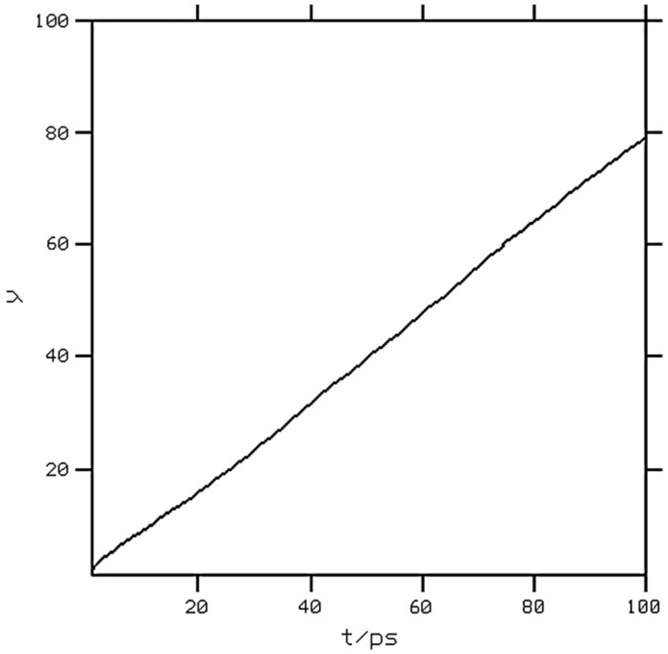

Fig. 8. The total correlation function of ions displacement (y) in Å^2 including the MSD of the ions and the correlations between different ions for one cell3.

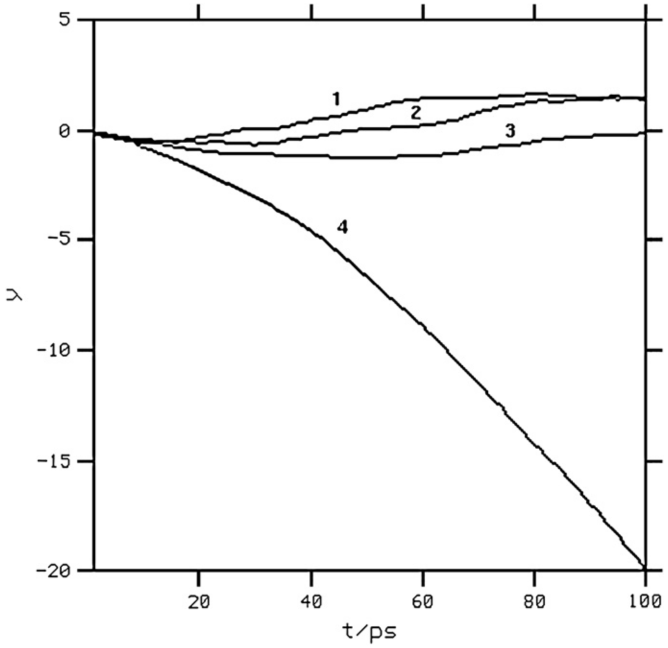

Fig. 9. The cross-correlation functions of ion displacements (y) in Å^2 as a function of time in one cell3. The interaction between the protons and the oxygen atoms in the sulfonic acid anion groups is marked with 1, between the oxygen atoms in the hydronium ions and the oxygen atoms in the sulfonic acid anion groups is marked with 2, between the oxygen atoms in the sulfonic acid anion groups is marked with 3, and between the protons and the oxygen atoms in the hydronium ions is marked with 4.

correlation function of ions' displacement in the calculation range of the conductivity. The interactions between protons and hydronium ions were the most remarkable interactions from all interactions between different ions, while the interactions between sulfonic acid anions were the smallest interactions between ions. This is because the sulfonic acids are bonded to the backbone and cannot move close to each other, while the protons and the hydronium ions can move and be close to each other.

7. Conclusions

Three 3D amorphous systems containing grafted poly(vinyl fluoride) sulfonic acid anions, hydronium ions, protons and 0, 10 or 40 wt% of water were constructed with periodic boundary conditions to study the location of the ions and water and the transport properties of the materials. Similar materials containing large amorphous regions have been prepared in our laboratory and the measured and simulated results were compared. The conductivity occurs mainly at the amorphous part of the film and thus it is meaningful to simulate amorphous systems. There are no remarkable differences between the results that were measured from the real material or calculated from the simulated systems in this study. The simulations are able to explain the experimental results.

The location of the protons and the hydronium ions is studied by calculating several pair correlation functions and coordination numbers. Usually the coordination between the sulfonic acid group in the anion and the proton as well as the coordination between the anion and the hydronium ion decreases as the amount of water increases. However, the coordination numbers between the protons and the sulfonic acid anion group as well as between the hydronium ions and the anions are very similar in water-free and 10 wt% of water containing system. The coordination numbers are bigger both in the first coordination shell and in the second coordination shell for water-free system or system containing only small amount of water than that for cell3. The coordination between the protons and the water molecules and between the hydronium ions and the water molecules increases as the amount of the water in the system increases and especially strong effect is seen in the second coordination shell. This indicates that the protons and the hydronium ions are mostly located in the vicinity of the anionic sites in cell1 and cell2, while in cell3 the protons and the hydronium ions are transported from the vicinity of the anions to the water pores. The coordination between the protons and the fluorine in the backbone of the polymer or between the hydronium ion and the fluorine in the backbone of the polymer is weak. Thus the protons and the hydronium ions are mainly not located around the backbone of the polymer. This coordination is especially weak in cell3, which is conducting.

The location of the water is studied. Experimentally three different types of water are observed in similar materials: ionically bounded water close to the sulfonic acid anion groups, water weakly bound to the polymer backbone and free water in water clusters [48,10,32]. Also in the simulations these water types are studied. In cell2 the water is mostly located in the vicinity of the anions. However, some water molecules are also close to each other and small amount of water is coordinated to the middle carbons in the polymer backbone. In cell3 a microphase separation is found. Most of the water molecules in this system are in water clusters. In Nafion very large water clusters are seen [30,48]. To ensure that the size of the water clusters in the simulations is not determined by the size of the simulation cell, similar systems containing larger cell sizes (like cell3b) were constructed and studied. However, the results were always the same: as the size of the cell gets larger, the size of the water clusters remains the same. Thus both the simulations and the experimental work suggest that the material studied has much smaller water clusters than Nafion has [10]. There are also water molecules in the anionic sites in cell3. It has been reported that after the fist coordination shell around the anion is complete, the movement of the proton is promoted by the more effective shielding of the proton from the anion by the water molecules [48]. The average amount of water molecules in cell3 in the first coordination shell is 7, which is enough to produce conductivity in this material. It seems that the ionically bounded water and the formation of water clusters are important to produce conductivity. The experimental results show that in materials, which are similar to the simulated systems, many water molecules are weakly bond to the hydrophobic polymer backbone. However, the simulation show that in cell3 there is a remarkable coordination only between the water molecules and the carbon atoms, which are in the graft or close to the graft and not between the water molecules and the middle carbon atoms, which are five or more bonds away from the nearest graft. Thus it seems that the water weakly bound to the polymer backbone in the parts of the backbone, where the anions are not in the vicinity, is not important in producing the conductivity.

The dynamical behavior of protons and hydronium ions is studied in all cells. The motions of protons and hydronium ions were different in different cells. In cell1 and cell2 the protons and the hydronium ions moved mostly by quick rare jumps (typically only 0–3 jumps are seen during 2000 ps). This kind of motion is typical for small molecules in polymers. In cell3 the protons and the hydronium ions made many jump (about 6–9 during 2000 ps) and also proceed by zigzag motion even for several tens of picoseconds. The zigzag motions are typical to small molecules in water. In cell3 the zigzag movement can take place in the water pores, while in other cells the protons and the hydronium ions move like in pure polymer matrix. Because the proceeding by the zigzag motion is very effective, the formation of water pores increases the conductivity.

The diffusion of the protons, the hydronium ions, anions and water molecules are studied. In experimental work it has been found that proton conductivity of the membrane is related to the critical water content, which varies in different materials [49]. In cell1 and cell2 the critical water content was not exceeded and the Einstein diffusion was not reached. In cell3 the Einstein diffusion is found and the average self-diffusion coefficient is very similar to the protons and to the hydronium ions (about $0.4 \times 10^{-9}\ \mathrm{m^2/s}$). Thus both the proton hopping and the classical diffusion mechanism occur in cell3 and neither of them is dominating. The diffusion coefficient of water is about three times higher than the diffusion coefficients of the protons or of the hydronium ions.

The value of the conductivity is 91 ± 9 mS/cm in cell3. The interactions between ions are relatively small. The used model gives a little higher value for the conductivity than the measurements. This can be due to the fact that the proton can move from one water molecule to another without creating and breaking bonds in our model. However, the simulated diffusion coefficient of the hydronium ion is similar to the diffusion coefficient of the proton. Thus also other factors, *e.g.* error limits of the calculation and the experimental method, can have influence on the deviation. Also the exact amount of water in the experimental material is not known. However, the magnitude of the simulated value of the conductivity is correct.

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