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Dissipative Particle Dynamics simulation hydrated Nafion EW 1200 as fuel cell membrane in nanoscopic scale

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ABSTRACT: The microphase separation of hydrated perfluorinated sulfonic acid membrane Nafion was investigated using Dissipative Particle Dynamics (DPD). The nafion as a polymer was modelled by connecting coarse grained beads which corresponds to the hydrophobic backbone of polytetrafluoroethylene and perfluorinated side chains terminated by hydrophilic end particles of sulfonic acid groups [1, 2]. Each four water molecule coarse grained in a bead to obtain the same bead size as built in Nafion model. The morphology of hydrated Nafion is studied for branching density of 1144, an example of Nafion EW1200, water content of 10%, 20% and 30% and polymer molecular weight of 5720, 11440 and 17160. The results show water particles and hydrophilic particles of Nafion side chains spontaneously form aggregates and are embedded in the hydrophobic phase of Nafion backbone. The averaged water pore diameter and the averaged water clusters distance were found to rises with water volume fraction.

Introduction

During the last two decades, world-wide efforts have been mounted into the research, design and development of polymer electrolyte membrane (PEM) fuel cells, for stationary and portable applications. The significant demand for efficient and green energy systems for transportation made PEMFC attractive for researcher and designer. Synthesis and characterization of novel specific materials which are appropriate for the operation of the device with little or no humidification and over a broad temperature range has been one of the most field related to this technology. The critically important electrolyte serves not only as a separator of the electrodes and reactant gases but also as the medium through which protons are transported (anode to cathode) and with the external flow of electrons (also anode to cathode) complete the electrical circuit [1]. Perfluorinated sulfonic acid membrane Nafion is the most common membrane materials used in polymeric electrolyte fuel cell. It is due to their exceptional chemical, mechanical and thermal stability as well as their advantage to conducting proton [2]. Although Nafion has received the extensive studies among the various membranes types, there is still some serious limitations such as of high manufacturing technology and cost, restrictive range stability and a significant degree of hydration is required in order to obtain sufficient proton conductivity [3]. Therefore, the development of new materials with advanced

characterization is taking a central role in fuel cell research. Nafion is a comb polymer composed of a hydrophobic Teflon ([–CF2–CF2–]) backbone to which relative short side chains are attached (Figure 1).

$$-[(CF_2\text{-}CF_2)_n\text{-}CF\text{-}CF_2]_m$$
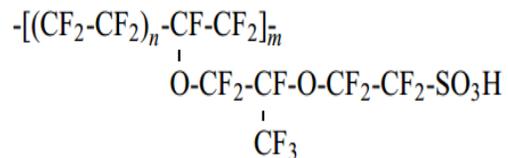$$O\text{-}CF_2\text{-}CF\text{-}O\text{-}CF_2\text{-}CF_2\text{-}SO_3H$$
$$CF_3$$

Fig. 1. Chemical formula of Nafion

The Nafion equivalent weight (EW) is determined by the average distance between the side chains along the backbone. The intense hydrophilic nature of the SO_3 group causes a Nafion membrane to swell when exposed to humid environments.

Expressing the water content by the average number of water molecules per SO_3 group, then for a membrane with an EW of 1100 (g/eq.) at room temperature the water uptake ranges from $\lambda \sim 1$ (at 0% relative humidity) to $\lambda = 14$ (at 100% relative humidity) [4-5]. Experimental methods such as X-ray and neutron scattering technologies have been widely utilized to probe the hydrated morphology of Nafion membranes [6]. In addition to wide-angle X-ray scattering (WAXS), small-angle X-ray scattering (SAXS) to has been employed to demonstrate the

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Nomenclature

			Greek Symbols	
A_{ij}	repulsive parameter		$\omega^C(r_{ij})$	conservative weight function
A	$CF_2CF_2CF_2CF_2$		χ	Flory-Huggins parameter
B	$OCF_2CF(CF_3)O$		$\omega^R(r_{ij})$	The random force weight function
C	$CF_2 - CF_2 - SO_3H$		σ	is the noise amplitude
C_s	The spring constant		ξ_{ij}	randomly numbers
dt	Time step size		K_B	the Boltzmann constant
F_{ij}	DPD forces		γ	damping factor
$K_B T$	Temperature unit in DPD		**Subscripts**	
MW	Molecular Weight		ij	pairwise
m_i	DPD beads mass		i	DPD beads index
R_C	beads cut off radius		B	Boltzmann
r_i	DPD beads position		**Superscript**	
r_0	equilibrium bond length		C	Conseravtive
$R_c\left(m/K_BT\right)^{0.5}$	Unit of time in DPD		D	Dissipative
v_i	DPD beads velocity		R	Random
W	$(H_2O)_4$		S	Spring

size of ionic clusters based on a hard-sphere interference model [7].

Infrared (IR) and Raman spectroscopy and transmission electron microscopy (TEM) [8-12] has been performed to investigate the structure and swelling behavior of hydrated Nafion.

Further structural studies has been carried out on dry and water-swollen SSC PFSA membranes with SAXS and SANS experiments [13]. Besides swelling, it has been well established that a microphase separation occurs in the hydrated Nafion membrane due to the amphifilic character of the polymer, which yields to form a hydrophilic and a hydrophobic phase composition in bicontinuous formed environment. The water molecules are associated with the SO3 groups and together they constitute a hydrophilic phase that is surrounded by the majority hydrophobic (Teflon) phase. A X-ray experiments conclude that the phase separated structures involve water clusters of ~5 nm diameter connected by pores with averaged sizes of~1nm to 2nm [9]. Although agreement exists about the phase separation, there is still concerning and discussion about the size and shape of water clusters and pores as hydrophilic phase [1].

A detailed review given by Mauritz and Moore [6] summarizes the state of understanding of Nafion. However, as protons flow through Nafion, a water profile be created across the membrane [14] due to electro-osmotic drag [15-16]. So the membrane may be dry out at anode side or flooding at the cathode side especially at higher electric current densities. The proton conductivity decrement by water content increment may limit the fuel cell to reach to high current density. It is so needed to have detailed information about the pore morphologies of hydrated membrane such as pore size and connectivity. Several model have been proposed and develop to analyses Nafion structure based on scattering data. The cluster-network model proposed by Gierke et al. [9] has been the most widely used model in the history of PFSA ionomers[3]. Additional models were developed following this work such as the modified (depleted-zone) core-shell model developed by Fujimura et al. [17], a fibrillar model proposed by Rubatat et al. [18], a channel model by Kreuer [19] and a parallel cylindrical channel model by Schmidt-Rohr [20].

A framework has been provided by these models in order to understand the morphologies of hydrated PFSA membranes based on experimental efforts. There is still lacking of molecular level details of Nafions due to the complexity of their morphology. It would be desirable to use full-scale molecular dynamics (MD) or simulations to reach molecular structure of PFSA membranes, but such an approach is out of reach since the system size that can be simulated via MD is too small for generating the large-scale pore networks. In addition, the time scale at which equilibration of morphologies are formed is too large to MD approach.

At finest level, ab initio molecular dynamics (AIMD) calculations have been performed to investigate proton transfer and dynamics under conditions of high density of perfluorinated sulfonic acid groups [21-22]. On larger scale the classical molecular dynamics (MD) simulations have been carried out on structural correlations and transport properties of PEMs [23-25].

Vishnyakov and Neimark [23] indicated that their results might have been affected by the limited size of the simulated system size (box length~5 nm with

corresponding 1000 water molecules) and simulation time. So they remarked that their study was not sufficient to make a clear conclusion about the real processes in hydrated Nafion membranes. MD simulations by Elliot *et al.* [26] considered a polymer with very low equivalent weight (side chain was connected to only 2 CF3 fragments) as the problem of very small system size with just hundred water molecules. To analyses length and time scales that are several orders of magnitude greater and longer than atomistic simulations, it is necessary to perform coarse-grained modeling. Bond fluctuation model [27], reference interaction side model [28], self-consistent mean field theory [29] were the first employed coarse grained model. Dissipative particle dynamics (DPD) simulations has been employed to study the modeling morphology evolution of a wide range of copolymer systems in order to investigate rheological properties of polymer [30-31], polymers viscoelasticity [32] and micro phase separation in copolymers and block copolymers [33- 34]. Dissipative particle dynamics was used for first time by Yamamoto and Hyodo [24] to investigate the micro phase separation in Nafion morphology at varying degrees of hydration. Their results indicated that a bicontinuous phase, in which sulfuric acid and water regions form a connected network. Comparative study of DPD and other meso scale methods has been performed by Wu et al. [35- 36].

Dorenbas *et al.* [37] investigated the Nafion membrane micro phase separation by DPD and water diffusion trends via a Direct Monte Carlo Simulation. Alghough considerable research have been carried out by DPD on membrane morphology [38-40] in recent five years, there are still some lack of detailed information on proton exchange membrane such as polymer size which has not been focused in the literature works.

The aim of present study is to investigate the hydrated PSFA membrane morphology at different hydrated level via Dissipative Particle Dynamics method. The morphology is obtained via the membrane network contours, water cluster sizes and structure characteristics. A Nafion polymer is modeled via connecting soft core potential bead which corresponds to a group of several atoms by a bond potential.

Water is modeled by the same size beads as adopted in nafion polymer model corresponding a specific number of water molecules.

Theory and mathematical formulation
Disipative particle dynamic

The DPD method was first introduced by Hoogerbrugge and Koelman [41-42] to rectify shortcomings of the Lattice Boltzmann Method (LBM) stemmed from lattice artefacts, and opened new ways to capture spatiotemporal hydrodynamic phenomena in scales much larger than those addressed by MD method and its counterparts.

The method was first proposed for simulating hydrodynamic behavior of isothermal fluids and further

developed by Espanol and Warren [43] and Spanol [44] who included stochastic differential equations and conservation of energy . The formulation used here is due to Groot *et al.* [45-46].

Dynamics of soft DPD particles are governed by Newton's second law of motion in Lagrangian reference coordinates System as follow:

$$dr_i = v_i dt, \; dv_i = \frac{F_i}{m_i} dt = \frac{1}{m_i}\sum_{j\neq i} F_{ij}$$
$$F_{ij} = F_{ij}^C + F_{ij}^D + F_{ij}^R + F_{ij}^S \tag{1}$$

where r_i and v_i are the position and velocity vectors of the indexed bead i in Cartesian coordinate respectively, dt is the simulation time step, m_i is the bead mass and F_i is the overall force vector applied on the bead i. F_{ij} is the vector sum of the three pairwise-additive conservative (F_{ij}^C), dissipative (F_{ij}^D) and random (F_{ij}^R) and a harmonic spring force (F_{ij}^S) as follows:

$$F_{ij}^C = A_{ij}\omega^C(r_{ij})\frac{r_{ij}}{r_{ij}} = A_{ij}\left(1 - \frac{r_{ij}}{R_C}\right)\frac{r_{ij}}{r_{ij}} \tag{2}$$

Where A_{ij} is maximum repulsion force adjusting the repulsive strength between beads i, j, R_C is the cut-off radius (or particle effective diameter) and DPD length scale beyond which the interparticle repulsive interactions are ignored, and $\omega^C(r_{ij})$ is the conservative weight function. The repulsive parameter A_{ij} is set at $25K_BT$ for density $\rho = 3$ to match the compressibility of water at room temperature if each bead represents a water molecule [46]. In the present study as will be discussed later each bead stands for four water molecule, so the repulsive parameter is set at $100K_BT$ for water beads.

The repulsion parameter between other same type beads are chosen to have the same value of water beads. The repulsion parameters of different type beads corresponds to the mutual solubility, expressed as Flory-Huggins χ-parameter. The relation is as follow when the reduced density has the value of $\rho = 3$ [45].

$$A_{ij} = A_{ii} + 3.27\chi_{ij} \tag{3}$$

The values of the repulsion parameters A_{ij} and Flory-Huggins χ- parameter and, were determined previously in ref [47] and are listed in Table 1 and Table 2 respectively.

Table 1
DPD beads definitions and repulsion parameters [47].

		A	B	C	W
$CF_2CF_2CF_2CF_2$	A	104	-	-	-
$OCF_2CF(CF_3)O$	B	104.1	104	-	-
$CF_2 - CF_2 - SO_3H$	C	114.2	108.5	104	-
$(H_2O)_4$	W	122.9	120	94.9	104

Table 2
Flory Huggins parameters for each bead pair [47].

Pair	χ
A-B	0.022
A-C	3.11
A-W	5.79
B-C	1.37
B-W	4.90
C-W	-2.79

The pairwise random force is present as follows to induce movement by stochastic agitation and to compensate for the lost degrees of freedom due to coarse-graining:

$$F_{ij}^R = \sigma \omega^R(r_{ij}) \xi_{ij} dt^{-\left(\frac{1}{2}\right)} \frac{r_{ij}}{r_{ij}}$$

$$\langle \xi_{ij}(t) \rangle = 0 \tag{4}$$

$$\xi_{ij}(t)\xi_{kl}(t') = (\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})\delta(t - t')$$

Where $\omega^R(r_{ij})$ is the random force weight function, σ is the noise amplitude for randomly generated numbers (ξ_{ij}) with Gaussian white-noise statistics, zero mean and unit variance.

They are uncorrelated for different pairs of particles while meeting the condition $(\xi_{ij} = \xi_{ji})$ to maintain centrality of the pairwise force.

The Mersenne Twister pseudo random numbers generator [48] is utilized to yield double precision equidistributed uniform numbers (θ_{ij}) between 0 and 1:

$$\xi_{ij} \approx 12^{-\left(\frac{1}{2}\right)} \times (\theta_{ij} - 0.5) \tag{5}$$

This distribution not only resembles Gaussian random numbers but also excels in computational efficiency [49]. The drag force in macro-scale hydrodynamics is modelled in meso scale by dissipative forces varying as a function of inter-particle relative velocity.

This force emulates the impediment generated by surrounding particles against the movement of a given bead.

The combination of dissipative and random forces creates a DPD thermostat, enabling the system to reach a guaranteed equilibrium [41].

Random force (F_{ij}^R) and dissipative force (F_{ij}^D) work in sync so that any extra excitement induced to the system is dampened. The dissipative force is given by:

$$F_{ij}^D = -\gamma \omega^D(r_{ij})(r_{ij}.v_{ij}) \frac{r_{ij}}{r_{ij}^2} \tag{6}$$

Where ω^R stands for the dissipative weight function and γ is the damping factor or drag coefficient. Stationary solution to the Fokker –Planck equation in the form of Gibbs function is achieved only when dissipation –

fluctuation theorem is satisfied in equilibrium temperature T by the following relation [43]:

$$\omega^R(r_{ij}) = \left[\omega^D(r_{ij})\right]^{\frac{1}{2}}, \sigma = (2K_BT\gamma)^{\frac{1}{2}} \tag{7}$$

K_B is the Boltzmann constant. This suggests that one of the weight functions in dissipative or random force can be chosen arbitrarily.

We utilize the generalized form of the weight function introduced by Fan *et al.* [50] as:

$$\omega^D(r_{ij}) = \left[\omega^R(r_{ij})\right]^2 =
\begin{cases}
\left(1 - \frac{r_{ij}}{R_C}\right)^S, & r_{ij} < R_C \\
0, & r_{ij} \geq R_C
\end{cases} \tag{8}$$

Note that R_C sets the interaction range in dissipative and random forces. By substituting $S = 2$ the conventional DPD weight function is recovered. The (F_{ij}^R, F_{ij}^D) forces act along the line of centers and conserve both linear and angular momenta [51]. The spring force is given by the derivative of a harmonic potential defined between pairs of connected beads and is given by:

$$F_{ij}^S = -C(r_0 - r_{ij}) \frac{r_{ij}}{r_{ij}} \tag{9}$$

Where C represents the spring constant and r_0 is the equilibrium bond length. The positions and velocities of the DPD particles may be solved in accordance to the above equations by implementing a modified version of the velocity-Verlet algorithm [51].

$$r_i(t + dt) = r_i(t) + dtv_i(t) + \frac{1}{2}dt^2F_i(t)$$
$$\tilde{v}_i(t + dt) = v_i(t) + \lambda dtF_i(t)$$
$$F_i(t + dt) = F_i(r(t + dt), \tilde{v}_i(t + dt)) \tag{10}$$
$$v_i(t + dt) = v_i(t) + \frac{1}{2}dt(F_i(t) + F_i(t + dt))$$

In the present study, the interaction cut off radius R_c, the bead mass m and temperature K_BT are selected respectively as the unit of length, mass and energy. The noise parameter σ is set at 3 so the friction parameter has the value of 4.5. The equilibrium bond distance is set at $r_0 = 0.86$ for the average distance of nearest bead at bead density of $\rho = 3$ and the spring constant of $C = 100$ to obtain a stiff chain against stretching. The unit of time is calculated by $R_c \left(m/K_BT\right)^{0.5}$, which corresponds to a time about tens of picoseconds. The time independent equation is solve via a modified version of velocity-Verlet at empirical variable of $\lambda = 0.65$ and time step size of $dt = 0.05$. The sulfuric acid due to its hydrophilic character corresponds to a low value of the repulsion parameter

between W and C beads ($A_{wc} = 94.9$). The hydrophobic character of these beads yields to the high values of the repulsion parameters of 122.9 for A Beads and 120 for B beads, respectively.

The choice of the value of 104 for the diagonal terms, was motivated by the fact that each water bead contains 4 water molecules. The value of 104 for the diagonal terms reproduces the compressibility of liquid water at room temperature using equation 14 and 16 in ref. [51], since the density in the simulations is set at 3. The value of $\rho = 3$ was chosen. The selection was due to the computational effort increases linearly with and therefore the lowest value for which these equations are still valid was selected. A second reason is that for densities higher than 3 for polymer systems a scaling relation like equation 3 has not been derived which relates the repulsion parameters directly with x_{ij} values.

The x_{ij} were deduced in ref [47] by estimation of the mixing energies of the bead components using the Monte Carlo approach. The authors ensured a high quality estimate of the mixing energies by calculating partial atomic charges, using ab initio molecular orbital calculation at the B3LYP/6-31G(d) level. For further details read the work of Yamamoto and Hyodo [47].
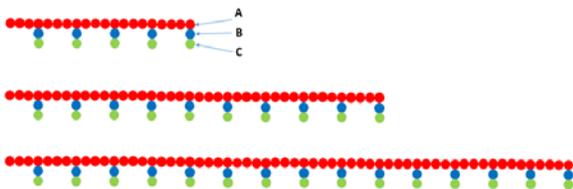

Fig. 2. Bead representation of the membrane polymers structure

Simultaion details

The present study concerns with the Nafion polymer with equivalent weight of 1144 and three molecular weight. The Nafion morphology is then investigated in three water volume fraction of 0.1, 0.2 and 0.3 which correspond to hydration level of $\lambda = 2.7, 6 \ and \ 10.3$. A cubic with a unit cell length of 40 (DPD length units) is considered in the present study which is scaled by the unit of length R_c and corresponds to a dimension of 28.4 nm in each direction. Periodic boundaries were assumed in all boundaries. Each simulation run involved the dynamics of 192,000 beads ($= \rho 40^3$, $\rho = 3$) and contained several thousand of polymer chains.

The number of A, B, C and W beads in various water content and corresponding hydration level are presented in Table 3.

The modeled membrane polymers are shown in figure 2. The present Nafion modelling corresponds to the Nafion with equivalent weight of 1200 which can stands for Nafion EW1200 a commercial one. The Nafion with different repeating unit stands for polymer with different molecular weight.

Table 3
Number of polymer molecule in the system for various molecular weight at different percentage of water content.

Water content%	MW=5720	MW=11440	MW=17160	Hydration level
0.1	5760	2880	1920	2.67
0.2	5120	2560	1706	6
0.3	4480	2240	1493	10.28

The molecular weight variation is related to the repeating monomer unit which yields to molecular weight has no effect in calculated hydration level and this parameter just relates to the equivalent weight. The Nafion polymer and water bead are initially dispersed in the simulation box. According to the synthesis process of the Nafion membrane in the case of the casting procedure this initial condition is reasonable with respect to a solution in an alcohol and water mixture at the initial stage of the experimental process. The time evolution of DPD beads is calculated up to the equilibrium structure of hydrated Nafion polymer. The maximum equilibration is observed about $t = 50000$, which corresponds to 1000000 time step according to the time step size of 0.05 in DPD reduced unit. In addition the size of time step was examined to test if the energy levels changes near its correct value $K_B T = 1$. The numerical simulation is accomplished by DL_Meso_DPD open source package [52]. The RDF of water beads as the most important parameter in results are compared in two time step size of 0.025 and 0.05. As shown in figure 3, the obtained RDF at molecular weight of m=5 and hydration level of $\lambda = $ water 10 has no significant changes in two different the time steps. Also the ref. [35-36] selected the 0.05 as time step size for polymeric membrane simulation and the comparison was done in present work for further confidence.
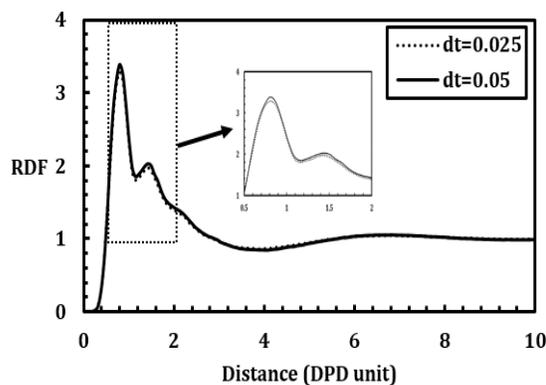

Fig. 3. Radial distribution function (RDF) of water beads for MW= at hydration level of $\lambda = water 20$ obtained at $t(DPD) = 20000$ using time step of dt $= 0.05$ and dt $= 0.025$

Results

The size of the water aggregates or clusters and the average distance between them are demonstrated via the

Radial Distribution Function (RDF) or pair correlation function g(r) of the water beads. Interpretation of RDF plots is straightforward. Points which are located at distances from a water bead where the values of RDF are higher than 1 are more likely to be part of the water network than not. Distances for which RDF drops below the value of 1 are an indication of the water aggregation boundary, i.e. pore radius R_{pore} is then estimated. The average separation between clusters D_{cl} can be derived from the position of the 2nd maximum in the RDF plots. The time progressing morphology of Nafion1200 with three molecular weight of

at different hydration level are shown in figure 4. At initial times a small domain of water aggregation forms very small water clusters. As time progressing, the formed aggregated water which are surrounded by hydrophilic beads of polymer (sulfonic group in Nafion molecule) which were the end bead of nafion chains (beads C in figure 2). The water and hydrophilic beads of nafion are embedded in the hydrophobic nafion beads. The structure equilibrium are abtained at different time for various hydration level as indicated in caption of figure 5.
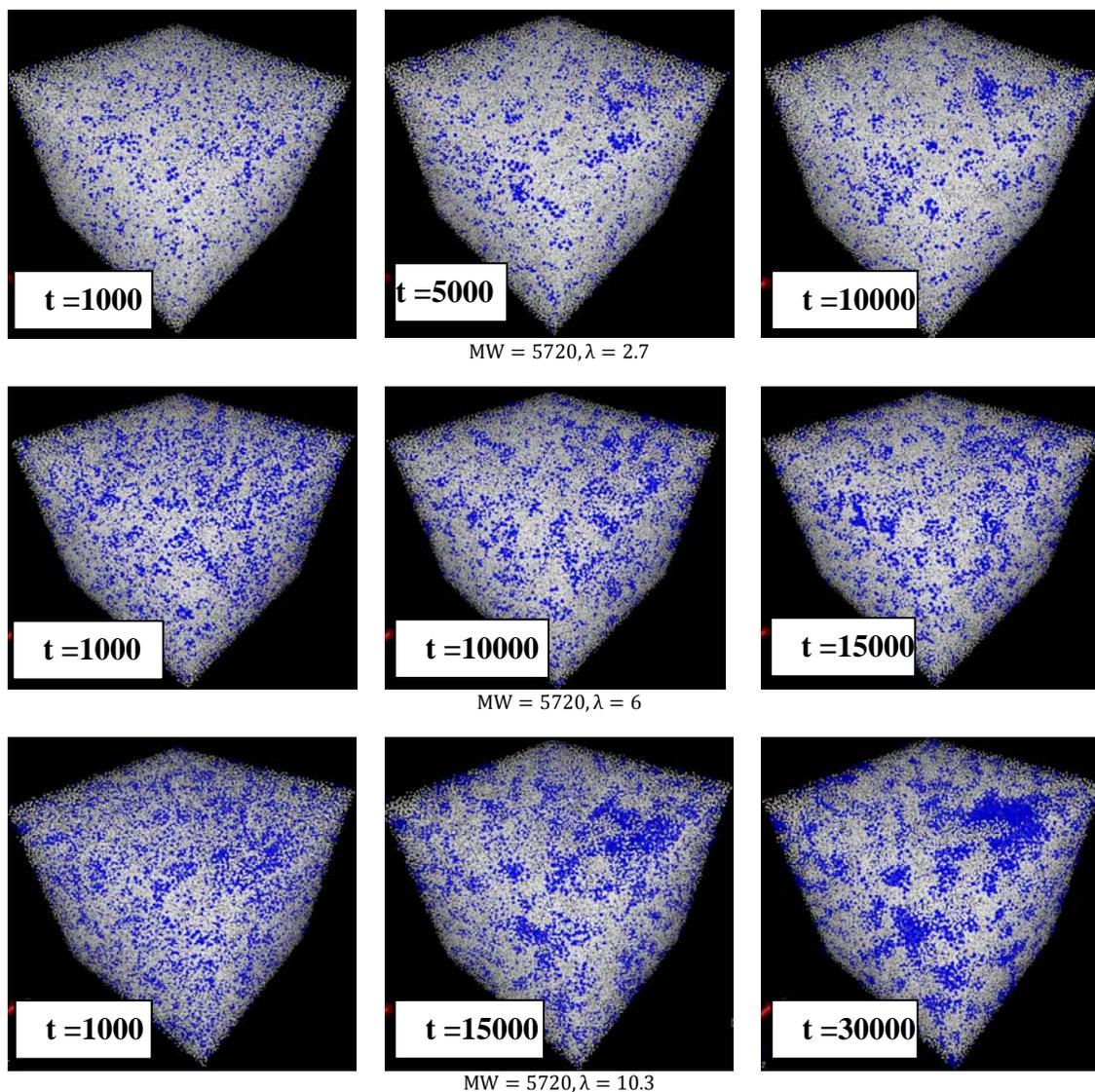

Fig. 4. Morphologies of the Nafion with as time progressing for different hydration level. (Nafion polymer are shown with silver and water beads are shown with blue beads.)

The figure 5 also shows that the water cluster becomes larger by increasing the hydration level.

This phenomenon is observed for Nafion morphology with other molecular weight. Water cluster size augmentation are shown in figure 5 in which the water beads with

sulfonic group are shown in by iso-surfaces at density $\rho = 1.5$ for nafion with MW = 11440 and three hydration level.
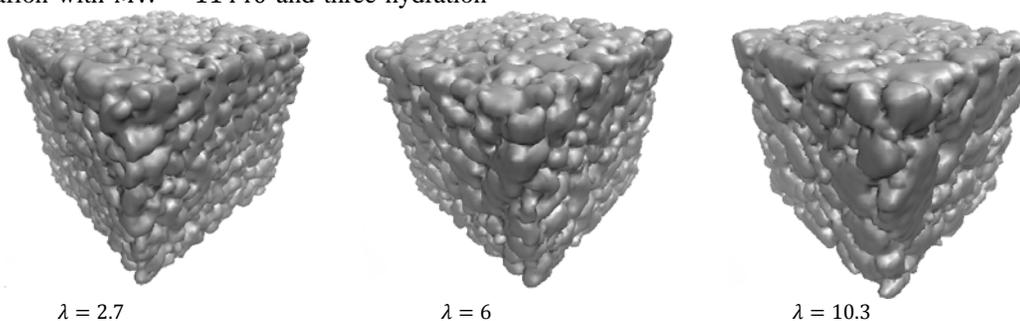

$\lambda = 2.7$ $\lambda = 6$ $\lambda = 10.3$

Fig. 5. Iso-surface Representation of water beads region including sulfonic acid group.at density $\rho = 1.5$ for hydrated Nafion with $MW = 11440$ and three different hydration level

The porous or sponge-like structure are expected as the knowledge of small angle x-ray scattering[13]. Unlike the cluster network model results in which the spherical shapes were observed for water network model [53], here the results show the water clusters obviously are never spherical from a visual inspection of the simulated structure. It is due to the stochastic nature of the molecule interaction which yields the aggregation forms in random structure. The water network then, has formed via undistinguished water cluster connecting channel. There are unstructured pathes in the nafion structures as well as water network structure. This open pathes can link any point to another point elsewhere in the water network. The same type pathes are exist in the Nafion structure. Therefore, there is a percolating structure for both water and nafion network like a bicontinuous phase separation in a block copolymer system. The Nafion morphology quantitative parameter should be extracted via the RDF graph as indicated in previous section. The radial distribution function (RDF) of water beads are shown in figure 6 for molecular weight of mw=10 at different hydration level. The distance are converted to physical value based on nanometer. The RDF curves experience two peaks in their raising which corresponds to first and second nearest water accumulation in the water clusters. The curve in its decreasing manner cut the RDF=1 value in first peak at the position which shows the averaged water cluster size in the system. Then the RDF reach to second peak at a position which stands for the second water cluster and its position in distance axis shows the distances of water clusters.

The values at which RDF drops below the value 1 increases with water content. Also the 2nd maximum shifts towards larger distance with increase of water content. This indicates that for these membranes the (average) water cluster size R_{pore} and the (average) distance between clusters D_{cl} increase with hydration level. This trends are observed for Nafion with MW = 5720, 17160 (figure 7 and figure 9).
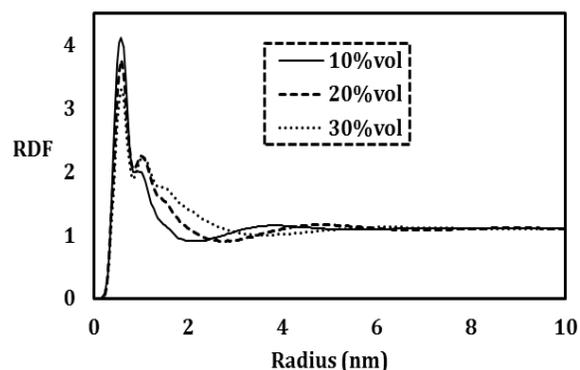

Fig. 6. Radial distribution function (RDF) for water beads at three water content of 10%, 20% and 30% for Nafion 1144 with molecular weight of MW = 11440

There are several experimental results in which the size of pore radius and water cluster systems to be proposed about 4 nm and 5 nm respectively [9, 54]. So it can be said that the mesoscopic results can reliably explain the structure of the Nafion polymer. It can be observed from the figure 7 and figure 9 that pore radius size is linearly relates with the water content. The increment rate of the pore radius by water content augments by molecular weight increment in the studied range of Nafion polymer molecular weight. Unlike pore radius, average cluster distances becomes larger at higher value of molecular weight.
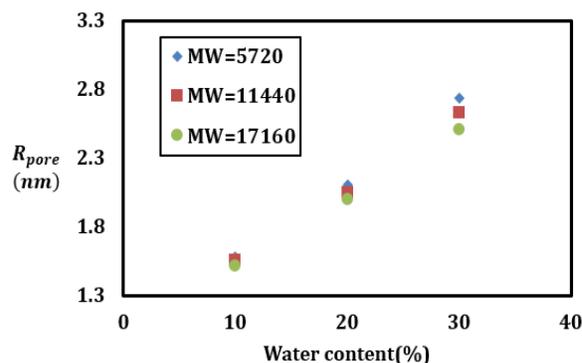

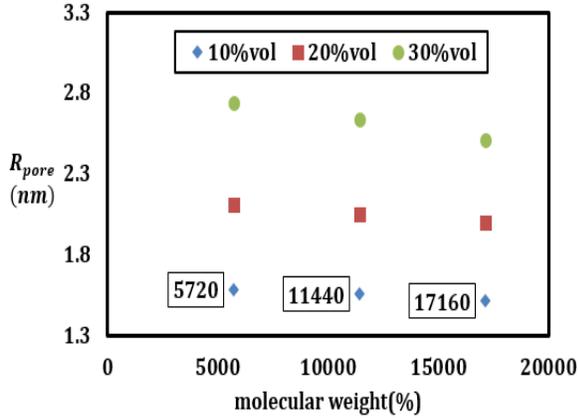**Fig.7.** Average pore radius R_{pore} versus water content at different molecular weight

Fig. 8. Average pore radius R_{pore} versus molecular weight at different water content
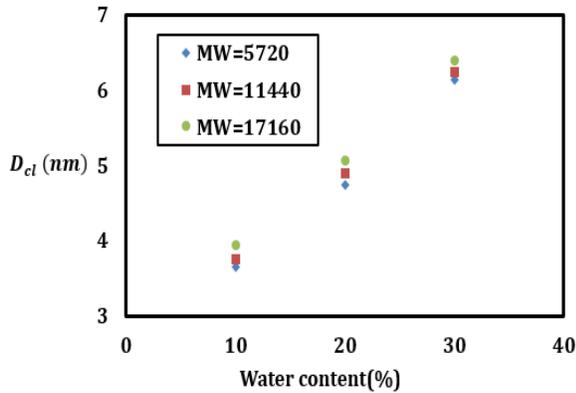

Fig. 9. Averaged distance between water clusters D_{cl} versus water content at different molecular weight
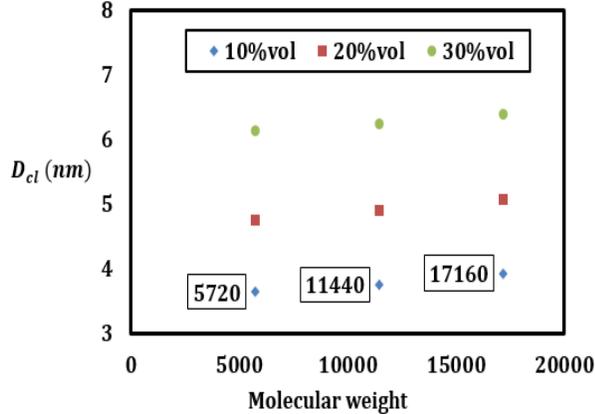

Fig. 10. Averaged distance between water clusters D_{cl} versus molecular weight at different water content

It should be noted that pore radius has more sensitive to molecular weight with respect to water cluster distances. It is extracted from the rate of these parameters changes versus molecular weight (figure 8 and figure 10). Finally it is observed that the Nafion polymer structure experiences more changes by water content with respect to molecular weight. The meso scale simulation of hydrated Nafion by DPD is confirmed to be one of the reputable structures for

actual materials. The results of mesoscopic study can be used to extract the atomistic level properties such as proton conductivity [53].

Conclusion

Dissipative particle dynamics as a mesoscopic method is implemented to study the structure of hydrated Nafion membrane. Soft beads represents some molecules and interact each other through three forces named dissipative, conservative and stochastic. Nafion molecules is made via connecting three different beads with spring force. Each four water molecules is coarse grained in a bead to reach the same size with respect to other beads. The system starts from a random distribution of beads and equilibrated. The morphology then shows a porous medium with bicontinuous structure which included a connected water network. The calculated pore radius in structure shows agreement with the results of experiments in range of 4 to 5 nm. The pore radius and water cluster distances shows increment with water content. Pore radius becomes smaller by increasing the molecular weight in the studied range. Finally the water cluster distances become larger at higher molecular weight.

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