Atomistic simulation study of the hydrated structure and transport dynamics of a novel multi acid side chain polyelectrolyte membrane

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Corresponding Author: Mr. Soumyadipta Sengupta,

Corresponding Author's Institution:

First Author: Soumyadipta Sengupta

Order of Authors: Soumyadipta Sengupta; Rakesh Pant; Pavel Komarov; Arun Venkatnathan; Alexey Lyulin

Abstract: Perfluoroimide acid (PFIA) belongs to a new class of Multi Acid Side Chain (MASC) polyelectrolyte membranes. Classical molecular dynamics simulations were carried out to study the hydrated nanostructure of PFIA and transport of water molecules and hydronium ions at T=300 K and T=353 K for a range of hydration levels. The radial distribution functions showed negligible change with temperature. The PFIA chain radius of gyration was minimally influenced by hydration and temperature which makes it suitable for fuel cells. Our simulations showed the formation of a large continuous water phase cluster in PFIA at high hydration levels which has also been observed in conductive probe atomic force microscopy experiments. These large continuous clusters lead to significantly higher vehicular diffusion rates for water molecules and hydronium ions at higher hydration levels. The vehicular diffusivity constants for water molecules and hydronium ions for PFIA were comparable to those for Nafion at both T=300 K and T=353 K. The vehicular proton conductivity values for PFIA were observed to be higher than those for Nafion at both T=300 K and T=353 K which agrees qualitatively with the experimental trends.

MSc Soumyadipta Sengupta
Department of Applied Physics
Theory of Polymers and Soft Matter
Eindhoven University of Technology
P.O. Box 513, 5600 MB
Eindhoven, The Netherlands
Telephone +31684274539
Email s.sengupta@tue.nl

6th September, 2017

Dear Professor Suleyman Allakhverdiev,

We thank you for giving us an opportunity to submit a revised version of our article. We have submitted a different document which details our response to each of the reviewers.

We had responded to the Reviewer-2 comments in the R2 decision mail. We have again responded to the identical Reviewer-2 comments in R3 decision. We have pointed out the corrections, suggested by Reviewer-2, in our manuscript in our response to reviewers' document. We have also added 3 new citations to improve our literature survey as suggested.

We sincerely hope that our article is accepted for publication in the prestigious International Journal of Hydrogen Energy (IJHE) at this review stage. We shall be grateful to you.

Please also see the figure widths below.

Thanks and Regards
Soumyadipta Sengupta

NOTE-

- 1) All the units in the graphs and paper are the ones which are normally used in this field and has also been used in other similar papers in IJHE journal.
- 2) There is only one MS Word (2013) source file containing all the images and tables embedded next to the relevant text. This has been uploaded under the heading 'LaTeX Source Files'
- 3) A separate PDF manuscript file has also been uploaded. This file contains all the figures and tables at appropriate places. I found contradictory information regarding keeping figures and tables in the manuscript file in the submission system. I had also contacted Elsevier support but they could not clarify. Please let me know if there is some problem.
- 4) All **images** are in **colour**.
- 5) All the figures except Figure 2 are vector images. A high resolution (>300 dpi) version for Figure 2 has been embedded in the MS Word file.

FIGURE WIDTHS

Figure-1: 1-column
Figure-2: 1-column
Figure-3: 2-column
Figure-4: 2-column
Figure-5: 2-column
Figure-6: 1.5-column
Figure-7: 2-column
Figure-8: 1.5-column
Figure-9: 2-column
Figure-10: 1-column

Response to reviewers

Editor

Additionally your literature survey needs improvement; please expand it. Additional related papers can be found in the International Journal of Hydrogen Energy (IJHE), as well as in other energy and fuel cells related publications.

We have added three new citations [43][44][51]. All these papers use classical MD to study polyelectrolyte membranes. [44] and [51] are from IJHE.

We had responded to the same Reviewer-2 comments in R3 revision. We are doing it again below.

Reviewer #2

We thank Reviewer 2 for the positive remarks and for pointing out three important corrections.

(1) Ref 55 and discussion of it should be omitted or at least clarified that it is NOT a simulation of a PEM, but instead one of an anion exchange membrane (hydroxide diffusion, not protons, which is a different computational challenge).

- 1) Ref [55] has been omitted and all related discussions of this reference have also been removed.

"Zhang W, van Duin ACT. ReaxFF Reactive Molecular Dynamics Simulation of Functionalized Poly(phenylene oxide) Anion Exchange Membrane. J Phys Chem C 2015;119:27727–36. doi:10.1021/acs.jpcc.5b07271." was reference [55] originally.

There is no mention of this study now throughout the paper.

(2) At the end of the sentence "In addition, the lower computational cost of classical MD simulations as compared to ReaxFF, SCI-MS-EVB and ab initio MD simulations permits the use of classical MD methods to simulate relatively large system sizes ($>10^4$ atoms) and relatively long physical time scales (up to a few tens of nanoseconds) which makes a detailed study of hydrated morphology of PEMs feasible" the current Ref 76 (Knox) should be cited. As far as I know, that was the first large scale classical MD simulation of PEM morphology (2 million atoms for ~ 100 ns).

- 2) Knox paper has been cited at the end of the mentioned sentence. This paper is now Ref [68]. It has been highlighted in yellow in the manuscript (page-8, para-1)

(3) This sentence: "The diffusion of protons in a model Nafion pore lined with sulfonate groups has also been studied using the MS-EVB model [64] to understand the effect of spacing of sulfonate groups on proton transport" should be modified to replace "the MS-EVB model [64]" with "an approximate 2-state MS-EVB model [64]" so it is not confused with the more physically accurate SCI-MS-EVB simulations.

- 3) “an approximate 2-state MS-EVB model [66]” has been used now at the place requested. This is also highlighted in yellow in the manuscript (page-7, para-2).

$\lambda = 5$

$\lambda = 20$

Highlights

- Classical molecular dynamics simulations were performed for Perfluoroimide acid
- Perfluoroimide acid chains did not show any considerable temperature sensitivity
- Large continuous water clusters were observed at high hydration levels
- Proton conductivity trends were qualitatively consistent with experiments

Atomistic Simulation Study of the Hydrated Structure and Transport Dynamics of a Novel Multi Acid Side Chain Polyelectrolyte Membrane

Soumyadipta Sengupta^a, Rakesh Pant^b, Pavel Komarov^c, Arun Venkatnathan^b and Alexey V. Lyulin^a

a. Theory of Polymers and Soft Matter, Department of Applied Physics, Technische Universiteit Eindhoven, P.O. Box 513, 5600 MB, Eindhoven, The Netherlands

b. Department of Chemistry and Centre for Energy Science, Indian Institute of Science Education and Research, Dr. Homi Bhabha Road, Pashan, Pune 411008, Maharashtra, India

c. Institute of Organoelement Compounds RAS, Moscow 119991 and Tver State University, Tver 170100, Russian Federation

Corresponding Author- Soumyadipta Sengupta, Email- s.sengupta@tue.nl, Phone- +31 684274539

Keywords

Multi Acid Side Chain PEM

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Accessible Volume

Proton Conductivity

Abstract

Perfluoroimide acid (PFIA) belongs to a new class of Multi Acid Side Chain (MASC) polyelectrolyte membranes. Classical molecular dynamics simulations were carried out to study the hydrated nanostructure of PFIA and transport of water molecules and hydronium ions at $T=300$ K and $T=353$ K for a range of hydration levels. The radial distribution functions showed negligible change with temperature. The PFIA chain radius of gyration was minimally influenced by hydration and temperature which makes it suitable for fuel cells. Our simulations showed the formation of a large continuous water phase cluster in PFIA at high hydration levels which has also been observed in conductive probe atomic force microscopy experiments. These large continuous clusters lead to significantly higher vehicular diffusion rates for water molecules and hydronium ions at higher hydration levels. The vehicular diffusivity constants for water molecules and hydronium ions for PFIA were comparable to those for Nafion at both $T=300$ K and $T=353$ K. The

vehicular proton conductivity values for PFIA were observed to be higher than those for Nafion at both $T=300$ K and $T=353$ K which agrees qualitatively with the experimental trends.

1. Introduction

Fuel cells are seen as a promising source of energy especially in the transportation sector. Hydrogen is an energy-dense fuel [1] which helps in increasing the range of fuel cell powered vehicles. Large-scale energy storage is necessary for energy produced from sustainable but intermittent sources of energy like wind and solar. These sources will, in turn, promote a hydrogen based economy because of the low cost of producing energy needed to generate hydrogen by techniques like water splitting [2][3][4]. For a hydrogen based economy, energy storage solutions play a key role. Flow batteries [5] are one of the solutions proposed for energy storage.

Polyelectrolyte membrane (PEM) is a key component in polyelectrolyte membrane fuel cells (PEMFC) and flow batteries. In a PEMFC, the polyelectrolyte membrane separates the hydrogen and oxygen streams and also allows the passage of protons. In organic and inorganic flow batteries, the polyelectrolyte membrane separates the catholyte and anolyte and allows the passage of protons [6][7][8]. Crossover of electrolytes in a battery results in higher charging and shorter discharging times [9] and this crossover is also prevented by the presence of polyelectrolyte membrane. Efficiency of PEMFCs and flow batteries are affected by the proton conductivity of PEMs [10]. In addition, the PEMs need to retain proton conductivity at temperatures near or above the operating temperature (353 K) of PEMFCs.

Nafion is a widely used membrane material for flow batteries [7] and PEMFCs [11]. A standard variety of Nafion (Nafion-117)¹ has good proton conductivity (0.01 S/cm for 50% Relative Humidity (RH)) [12] and good mechanical stability at room temperature, but loses water upon increase of temperature. Due to this loss of water, the proton conductivity of Nafion degrades [11][13]. There are other perfluorosulfonic acid (PFSA) membranes with lower EW (Equivalent Weight- weight of ionomer per mole of acid) than Nafion which display higher proton conductivity than that of Nafion [14]. Unfortunately, these membranes also lose their proton conductivity at low hydration levels. In addition, the low EW also causes a loss of mechanical integrity due to lesser number of tetrafluoroethylene (TFE) units in the polymer backbone [14]. Alternative aromatic backbone membrane materials like SPEEK (Sulfonated Poly Ether Ketone) [15], PEEK (Poly Ether Ketone) [16] have also been used primarily because of their low cost. However, these materials have lower proton conductivities than that of PFSA membranes [17]. Alternative membranes which

Fig. 1. (a) PFIA chain (n=6, m=10) for EW-625 (b) Nafion chain (n=7, m=10) for EW-1100; n represents the length of a monomer and m represents the degree of polymerization; the red ovals highlight the side chain protogenic groups

¹ Nafion 117 is a 183 micrometre thick Nafion membrane

have high proton conductivity at both low and high hydration levels, which corresponds to high and low temperatures respectively, and high mechanical integrity are needed to work effectively in both PEMFCs and flow batteries.

Multiple acid side chain (MASC) PEMs, which have multiple protogenic groups, like *ortho bis* acid [18], *meta bis* acid [19] and perfluoroimide acid (PFIA) (Fig. 1(a)) [18] have been developed to serve this purpose. There have been experiments[20] which have shown that the average current through a PFIA membrane is significantly higher than that in a Nafion™ 212 membrane², which has an EW of 1100 [21], at 300 K. It has also been observed in experiments[22] that PFIA has significantly higher proton conductivity than NAFION™ NR211³, which has an EW of 990-1050 [23], across a wide range of hydration levels at 353 K. For instance, PFIA and Nafion have a proton conductivity of 0.1 S/cm [22] and 0.05 S/cm [22] for 50% RH at 353 K respectively.

According to DFT (Density Functional Theory) simulations [19], the number of water molecules required for dissociating both the side chain protogenic groups among these three MASC membranes was the least for PFIA. This was due to larger separation of the protogenic groups in PFIA which allowed for more hydrogen bonding in between the protogenic groups and greater charge distribution along the chain [19]. An experimental [18] study showed that aromatic side chain MASC membranes like *ortho bis acid* displayed higher proton conductivity than PFSA membranes at high hydration levels but their proton conductivities dropped below those for PFSA membranes at low hydration levels. PFIA, on the other hand, displayed higher proton conductivity than PFSA membranes at both low and

² Nafion™ 212 is a 50.8 micrometre thick Nafion membrane

³ NAFION NR™ 211 is a 25.4 micrometre thick Nafion membrane

high hydration levels [18]. An added advantage of the PFIA MASC membrane is the high level of crystallinity it displays due to which its mechanical integrity is preserved at high temperatures. For example, a common variety of PFIA has an EW of 625 but has the crystallinity comparable to ionomers of EW~1000 [24]. This is due to the comparable number of TFE units in the PFIA monomer to that in EW~1000 PFSA membrane monomer.

The PFIA side chain has two protogenic groups whereas side chains of conventional PFSA membranes like Nafion (Fig. 1(b)), Aciplex and Hyflon have only one protogenic group. The protogenic groups makes the side chain hydrophilic which leads to phase separation and formation of water phase clusters [25]. Therefore, it is important to study an MASC PEM like PFIA and better understand the effects of the extra side chain protogenic group. This is the main goal of the present study.

There have been some recent FTIR (Fourier Transform Infrared Spectroscopy) experiments[22] which have shown that both the protogenic groups in PFIA dissociate at different hydration levels. The surface morphology of the PFIA membrane has been compared with other PFSA membranes in another recent conductive probe atomic force microscopy experiment [20]. A molecular simulation study of PFIA will help in further understanding of the hydrated membrane morphology and transport dynamics. Classical Molecular Dynamics (MD) simulations, which use a non-reactive and non-polarizable force field, have been performed for a commonly used PEM like Nafion to understand the effect of ordering of side chain groups on proton transport [26] as well as the details of the hydrated nanostructure of Nafion at different hydration levels and different temperatures and their effect on the proton transport [27][28][29]. The water and proton transport were found to agree with experimental trends for Nafion classical MD simulations [26][29][30]. Water phase clustering and percolation phenomenon has also been studied for Nafion using

classical MD [31][32]. In addition to Nafion, other PFSA membranes like Aciplex [33], Hyflon [34], PFSI (Perfluorosulfonyl Imide) [35] have also been analysed using classical MD, and their corresponding diffusive transport parameters for water molecules and hydronium ions were also found to be consistent with experimental data. There are also many recent studies to analyse the hydrated structure, morphology and percolation transition of aromatic [36][37][38][39][40][41][42][43][44] and PFSA [45][46] PEMs using classical MD simulations. Classical MD simulations of aromatic backbone PEMs like SPEEK and PEEK have demonstrated transport properties in agreement with experiments [38][40]. A classical MD study showed the amount of phase separation to be a key factor affecting the transport behaviour inside hydrated sulfonated block co-polyimide PEMs [47]. Predictions of water uptake of sulfonated poly ether imide PEM were consistent with experiments in a classical MD simulation study [48]. Classical MD simulations have even been used to study the effect of crosslinking on chitosan membrane conductivity [49]. Recent classical MD studies of anion exchange membranes (AEM) have correctly captured the effects of different functional groups and the effects due to positions of these functional groups on conductivity [50][51]. Nafion doped with protic-ionic liquid has also been simulated using classical MD in which the transport characteristics were found to be consistent with experiments [52]. A point to be noted in all the aforementioned examples is that classical MD is well suited to study different types of PEMs. Therefore, classical MD simulations of PFIA, which are absent at the current moment, will provide a good starting point for investigating PFIA hydrated nanostructure and dynamics.

Protons are transported inside the hydrated nanostructure of PEM's primarily by a combination of vehicular mechanism [53][54][55], which is due to mobility of protonated water molecules, and the Grotthuss mechanism in which the proton hops across hydrogen

bonds [56]. Classical MD simulations have been routinely employed to study the relationship between the membrane morphology and vehicular diffusion of hydronium ions (protonated water molecules) and water molecules [26][27][28][30][31]. However, the study of Grotthuss mechanism is necessary for a complete understanding of proton transport in PEMs. To achieve this, methods such as Self Consistent Iterative Multistate Empirical Valence Bond (SCI-MS-EVB) [54][57], ReaxFF simulations [58] and *ab initio* MD simulations [59][60][61] have been employed.

A SCI-MS-EVB study of Nafion decomposed the amount of proton diffusion into the Grotthuss and vehicular components. These two components were found to be of similar relative magnitude but anti-correlated which resulted in a smaller overall proton diffusion [62]. Another SCI-MS-EVB simulation study showed that the Zundel ions (H_5O_2^+) are stabilized within the first solvation shell of sulfonate group [63]. Yet another SCI-MS-EVB simulation study showed a sub diffusive proton transport behaviour over several hundreds of picoseconds at various hydration levels in PFSA membranes [64]. It was also concluded in a SCI-MS-EVB study that proton swapping between sulfonate groups is the primary charge transport mechanism in PFSA PEMs and that interaction between sulfonate groups and hydrated protons had a small influence on proton transport [65]. It was found that a more flexible side chain in 3M PEM as compared to Hyflon, which has a shorter side chain, enhanced the proton swapping mechanism in the former [65]. The diffusion of protons in a model Nafion pore lined with sulfonate groups has also been studied using an approximate 2-state MS-EVB model [66] to understand the effect of spacing of sulfonate groups on proton transport.

As observed from the above studies, the inclusion of Grotthuss mechanism provides a complete picture of proton transport. However, the computational cost of these methods and

the limitations of simulated physical time and system sizes are also noteworthy. For example, a recent SCI-MS-EVB study required tens of millions of compute hours to simulate 12 chains of Nafion for few nanoseconds of physical time [67]. *Ab initio* MD simulation studies usually simulate small system sizes (~1000 atoms) for relatively small physical times of less than 200 ps [59][60][61]. While classical MD simulations provides only the description of vehicular diffusion of protons, these methods still continue to be a very popular tool where a qualitative agreement of diffusion coefficients can be obtained with experiments. In addition, the lower computational cost of classical MD simulations as compared to ReaxFF, SCI-MS-EVB and *ab initio* MD simulations permits the use of classical MD methods to simulate relatively large system sizes ($>10^4$ atoms) and relatively long physical time scales (up to a few tens of nanoseconds) which makes a detailed study of hydrated morphology of PEMs feasible [68].

In the present study, PFIA was simulated across a range of hydration levels for two different temperatures using classical MD simulations. Structural properties like radial distribution functions (RDFs), radius of gyration, side chain lengths are analysed to understand the hydrated nanostructure. The size of the separate water phase inside hydrated PFIA was studied using cluster distributions and accessible water volumes at different hydration levels. The classical transport dynamics was also analysed using mean square displacements (MSD) of hydronium ions and water molecules. Finally, Nafion and PFIA vehicular proton conductivities were compared with the experimental proton conductivity trends.

2. Computational methods

The structure of PFIA monomer is shown in Fig. 1(a). The value of n represents the length of a monomer and the value of m represents the degree of polymerization for the PFIA chain. A common variety of PFIA has an EW (i.e., the weight of the PFIA macromolecule divided by the number of protogenic groups) of 625 [22][69] which means that value of n should be 6 in this case. The number of monomers in a single PFIA molecule is taken as 10 for this study (Please refer to Supplementary Material Section I).

The *pcff* (Polymer Consistent Force Field) [70] was used for simulating the polymer matrix, water molecules and hydronium ions. Polyelectrolytes like Nafion, SPEEK, sulfonated co-polyimides and other polymers have been accurately modelled using *pcff* previously [59][71][72][73]. Water molecules [59][71][74][75] and hydronium ions [59][71][72][73] have also been modelled previously using *pcff*.

PFIA was simulated for four different hydration levels ($\lambda = 5, 10, 15$ and 20) and at two different temperatures of $T=300$ K and $T=353$ K. The hydration level (λ) is defined as the number of water molecules per side chain of PFIA. As observed in a previous DFT study [19], the sulfonate group loses its hydrogen at $\lambda \geq 3$ and the sulfonyl imide group loses its hydrogen at $\lambda \geq 7$. Hydronium ions were introduced into the simulation box to account for the dissociated hydrogen from these protogenic groups.

The number of PFIA chains inside a simulation box was 14. There were four different simulation boxes corresponding to the four different hydration levels. Some simulations were also run with 7 chains of PFIA in a simulation box to check for finite size effects. The simulations were run for 5.85 ns and the trajectory from last 2 ns of production was used

for analysis. A detailed description of the model construction, force field and simulation protocol has been presented in the Supplementary Material (Sections I, II and III).

3. Calculation methods

From the production runs, structural and dynamic characteristics like RDFs, cluster distribution of water molecules and/or hydronium ions, accessible volumes for water molecules inside the polymer bulk systems and diffusion coefficients of water molecules and hydronium ions were calculated.

The radial distribution function ($g(r)$) is proportional to the probability of finding an atom B at a distance r from reference atom A inside a shell of thickness dr [29]. The average radius of gyration ($\langle R_g \rangle$) of the PFIA/Nafion chains is calculated for different hydration levels and temperatures [33].

The cluster distribution for water molecules and hydronium ions was computed for the different hydration levels (λ) using the OVITO software [76]. A cluster is defined as a group of atoms in which each atom is within a particular pre-defined cut-off distance of at least another atom within that group. The oxygen atom in the water molecule and hydronium ion was used for computing cluster sizes containing water molecules and hydronium ions (i.e. cluster of 10 oxygen atoms is assumed to represent the cluster of 10 water molecules and/or hydronium ions). The cluster distribution plots number of clusters, averaged over a time interval, versus the cluster size.

The accessible volumes were computed using the ZEO++ software [77] for the hydrated PFIA systems for two different probe radii values. The translational diffusion coefficients for water molecules and hydronium ions were computed by analysing the mean square displacement (MSD) using the Einstein relation in the diffusive regime [33].

The conductivity (C) was calculated using the Nernst-Einstein equation as

$$C = \frac{Nz^2e^2D}{Vk_BT} \dots\dots\dots (1)$$

where N is the total number of charge carrying ions, z is the charge number, e is the elementary charge, D is the diffusion coefficient, V is the volume of the simulation cell, k_B is the Boltzmann constant and T is the temperature.

All the analysis mentioned in the paper has been shown for the PFIA 14-chain system unless mentioned otherwise. There were negligible differences between the 14-chain system and the 7-chain system which meant that finite size effects were negligible.

4. Results and discussion

4.1 Density

The Table 1 (columns 2 and 4) shows the simulated density values for PFIA for different temperatures and for four different hydration levels. These simulated density values are the final equilibrium density values during the production runs.

The simulated density decreases with increasing hydration level due to increased size of the water phase which leads to the swelling of the sample. The simulated density is also decreasing with temperature in the simulations which is to be expected. The simulated density is within 7% of the experimental density [78] of 625-EW PFIA measured at 300 K. The experimental densities are from a single data set with no error values provided.

λ	Density ($T=300$ K) (g/cc)	Density ($T=300$ K) (Experimental) (g/cc)	Density ($T=353$ K) (g/cc)
5	2.03	1.98	2.00
10	1.96	1.85	1.91
15	1.85	1.73	1.80
20	1.76	NA	1.72

Table 1. Simulated density of PFIA at $T=300$ K and $T=353$ K and experimental [78] density at $T=300$ K. The errors values of the simulated density are very small (order of 10^{-5}) and hence not shown here.

Simulated density values have been used as a criteria for judging the accuracy of the force field for classical MD simulations of PEMs [26][28][38][39][68][71]. Therefore, the choice of force field for our simulations are well suited for analysing PFIA since the simulated density values are close to the experimental values.

4.2 Hydration and temperature effects on the hydrated nanostructure

Fig. 2. Snapshots for PFIA simulations at the end of production runs for (a) $\lambda=5$ (b) $\lambda=10$ (c) $\lambda=15$ (d) $\lambda=20$ at $T=300$ K. Orange- PFIA backbone atoms, Pink- PFIA side chain atoms, Black- hydronium ions, Blue- water molecules

The Fig. 2 shows the snapshots at the end of the simulation for the four different hydration levels at 300 K. The orange spheres represent the backbone atoms of the PFIA

molecule, the pink spheres represent the side chain atoms, the black spheres represent the hydronium ions and the blue spheres represent the water molecules. The atoms of the water molecules can be seen to form larger water phase domains as the hydration level increases and the hydronium ions are dispersed in these water phase domains. The PFIA molecules can be seen to form a separate phase different from the water phase. This phase separation occurs due to the hydrophilic nature of PFIA side chain and hydrophobic nature of PFIA backbone. Due to the hydrophilic nature of the side chain in PFIA, the side chain atoms can be seen to be in contact with the water phase and aligned away from the polymer backbone.

Hydration of the PFIA membrane causes swelling, as seen in the decrease of density in Table 1, due to formation of water phase clusters as shown in Fig. 2. This phenomenon can also be observed in the S-S (S- sulfur of sulfonate group) and N-N (N- nitrogen of sulfonyl imide group) RDF's as shown in Fig. S2 (Supplementary Material). Peaks in the S-S and N-N RDF's are more prominent at lower $\lambda=5, 10$ as compared to higher $\lambda=15, 20$. Small water phase cluster formation (Fig. 7) and low accessible water volumes (Table 3) are seen at $\lambda=5, 10$ as compared to higher hydration levels indicating small water phase domain sizes at $\lambda=5, 10$. These small water phase domain sizes lead to reduced distance between the side chain protogenic groups which is reflected in the prominent RDF peaks at lower hydration levels.

The $g(r)$ values for different hydration levels at $T=353$ K are slightly less for both N-N (Fig. S2 (d) of Supplementary Material) and S-S RDFs (Fig. S2 (b) of Supplementary Material) as compared to the values at $T=300$ K at any particular distance. Similar behaviour has also been observed for other PFIA RDFs analysed in this paper and also for Nafion simulations [29]. This should be due to a sparser system and larger homogeneity at a higher temperature.

Fig. 3. PFIA RDFs at different hydration levels at $T=300$ K for (a) S-Ow (b) N-Ow; S- Sulfur in sulfonate group, N-Nitrogen in sulfonyl imide group, Ow- Oxygen in water molecule

The sulfonate and the sulfonyl imide groups in PFIA make the side chain hydrophilic. These groups interact strongly with the water molecules and hydronium ions. Hence, studying the RDF plots of S and N with oxygen atom of water molecule (Ow) and oxygen atom of hydronium ion (Oh) provides some important information about these interactions. Fig. 3 shows the RDFs for S-Ow and N-Ow at 300 K. The first peak of the S-Ow RDFs is at 4.1 Å which is quite close to the values observed in previous simulations for Nafion [26][28]. The first peak of the N-Ow RDF for $\lambda=5$ is at 2.8 Å while the first peak of N-Ow RDF for higher hydration levels has shifted slightly to a greater distance of 3 Å. This shift is due to the dissociation of the sulfonyl imide group for $\lambda=10, 15$ and 20 , but not for $\lambda=5$. The dissociated sulfonyl imide group has a net negative charge which repels another dissociated sulfonyl imide group having the same charge. The magnitude of the first peak of S-Ow and N-Ow RDF decreases as λ keeps on increasing. This is because bigger water phase domains are formed at higher hydration levels as can be seen from the visualizations (Fig. 2) and from the cluster distributions which have been described later. The bigger water

phase domains allows more space for the water molecules to move around, which weakens the interactions between sulfonate group and water molecules.

λ	CN (S-Ow)	CN (N-Ow)	CN (Oh-Ow)
5	4.37	0.84	2.36
10	5.90	1.38	3.08
15	7.73	1.69	4.15
20	8.80	1.83	4.51

Table 2. PFIA Coordination Numbers (CN) inside the first coordination shell at $T=300$ K for Ow around S, Ow around N and Ow around Oh in PFIA. 5 Å, 3.6 Å, 3.5 Å are the sizes of the first coordination shells of S-Ow, N-Ow and Oh-Ow respectively. S- Sulfur of sulfonate group, N-Nitrogen of sulfonyl imide group, Ow- Oxygen of water molecule, Oh-Oxygen of hydronium ion

The coordination number (CN) is the average number of a particular atom type around a reference atom type at a defined distance. Therefore, CN can provide some extra quantitative insight into the interactions of side chain protogenic groups and water molecules. Table 2 (columns 2 and 3) shows the CN of S-Ow for PFIA and CN of N-Ow for PFIA inside the respective first coordination shells at $T=300$ K. The first coordination shell for S-Ow extends from 0 Å to 5 Å which is similar to Nafion S-Ow coordination shells [27][29]. The first coordination shell for N-Ow extends from 0 Å to the first local minima (3.6 Å) in the N-Ow RDFs. The number of water molecules increases around both the side chain protogenic groups as the hydration level increases.

The total number of water molecules in the first coordination shell around the side chain protogenic groups in PFIA is higher than that in Nafion [27][29] due to the presence of two side chain protogenic groups in PFIA as compared to only one in Nafion. The water molecules in the first coordination shell around the protogenic groups are usually in a bound state in Nafion [27][29]. We can expect an occurrence of a similar bound state of water molecules in PFIA. As a result, the percentage of bound water molecules in PFIA could be higher than that in Nafion due to the higher total coordination number in PFIA.

Fig. 4. PFIA RDFs at different hydration levels at $T=300$ K (a) S-Oh (b) N-Oh; S- Sulfur in Sulfonate, N- Nitrogen in Sulfonyl imide, Oh- Oxygen in hydronium ion

The RDFs in the Fig. 4 provide information about the interactions of hydronium ions with the protogenic groups. The first peak of S-Oh RDFs occurs around 4.1- 4.2 Å which is similar to what has been observed for previous simulations of Nafion [28] and Aciplex [79]. The magnitude of the first peak for S-Oh RDF decreases with increasing hydration levels. The reason for this same trend is also due to the increasing domain sizes of the water phase. The $g(r)$ values for S-Oh is significantly higher than the $g(r)$ values for S-Ow at any particular distance. This is because of the net positive charge on the hydronium ion which results in a stronger attraction to the sulfonate group as compared to the water molecule.

A slightly different trend is observed for N-Oh RDF. The first peak of the N-Oh RDF for $\lambda=5$ has moved to a larger distance as compared to the peaks for other higher hydration levels. This is because the nitrogen of the sulfonyl imide group was not ionized at $\lambda=5$ and hence the nitrogen, which is negatively charged in the ionized state, did not attract the positively charged hydronium ions as strongly as compared to higher hydration levels. Unlike the N-Oh RDF, the first peak of the N-Ow RDF for $\lambda=5$ is almost at the same distance as that of the peaks for higher hydration levels. This is because a water molecule

has a net charge of 0, while a hydronium ion has a +1 net charge, and hence electrostatic forces do not play as large a role for water molecules as for hydronium ions. At around 7.5 Å, the peak for $\lambda=5$ is sharper than the peaks for higher hydration levels. This should be due to the low phase separation at $\lambda=5$ which leads to hydronium ions being confined in a small space.

Fig. 5. PFIA RDFs at different hydration levels at $T=300$ K (a) Ow-Ow; (b) Oh-Ow; Oh- Oxygen in hydronium ion, Ow- Oxygen in water molecule

The water molecules are a part of the water phase clusters inside the hydrated nanostructure of PFIA membranes. Studying the RDF between Ow-Ow provides insights into the interactions in these water phase clusters. Fig. 5(a) shows the RDF plots for Ow-Ow at various hydration levels in PFIA. The first peak in these RDFs occur at 2.9 Å which is quite close to previous simulations of PFSA membranes [28][33] and experimental data [80]. The water domains increase in size as the hydration levels increase which causes a subsequent decrease in the magnitude of the first peak of the Ow-Ow RDF with increasing hydration.

The hydronium ions bind with the water molecules through hydrogen bonding which plays a role in proton transport. The Fig. 5(b) shows the RDF for the Oh-Ow for PFIA a

$T=300$ K. The first peak in Fig. 5(b) occurs at $2.7 \text{ \AA}$ which is very close to the first peak of Oh-Ow RDFs in previous simulations of PFSA membranes like Nafion [28] and Aciplex [33]. There is a second broad peak in between $4.7 \text{ \AA}$ to $5 \text{ \AA}$ which corresponds to the second solvation shell. The first peak magnitude of the Oh-Ow RDF decreases with increasing hydration levels because the hydronium ions are more dispersed in bigger water domains. This phenomenon can also be seen in Fig. 2.

Table 2 (column 4) shows the average number of water molecules around a hydronium ion inside the first coordination shell of hydronium ion and water molecule. The first coordination shell extends from 0 to the first minima ($3.5 \text{ \AA}$) in the Oh-Ow RDFs. The CN of Ow around Oh in PFIA is comparable to what has been observed in previous simulations of Nafion [28][31]. The water molecules in the first coordination shell around hydronium ions forms hydrogen bonded structures [28][31] with the hydronium ions.

In our simulations, the total number of hydronium ions in PFIA is double that of Nafion at $\lambda=10, 15$ and 20 . Therefore, the total number of water molecules in the first coordination shell around hydronium ions would be significantly higher in PFIA as compared to that in Nafion at these hydration levels. This should promote much more hydrogen bonding in between the hydronium ions and water molecules in PFIA as compared to Nafion.

4.3 PFIA chain length statistics

The average radius of gyration (Fig. 6(a)) for PFIA does not show any trend with respect to hydration levels. It could be due to a low dispersive force between membrane and water molecules leading to a relatively less chain expansion even at higher λ [33]. The radius of gyration also does not change much at a higher temperature ($T=353$ K, Fig. S6 of Supplementary Material) which means that the polymer structure is not affected much by

increasing temperature. This would make PFIA suitable for fuel cell operating temperatures which are around 353 K.

Fig. 6. (a) Averaged PFIA chain radius of gyration vs λ (b) PFIA side chain length vs λ at $T=300\text{ K}$

The side chain length in PFIA is calculated as the average distance between the backbone carbon atom, which attaches to the side chain, and the sulfur in the sulfonate group averaged over the total number of side chains and simulation timesteps. The side chain length (Fig. 6(b)) does not show any correlation with hydration levels.

4.4 Cluster distribution and accessible volume

The cluster distribution is computed for water molecules and hydronium ions at two different cut-off distances of $3\text{ \AA}$ and $4\text{ \AA}$. The $3\text{ \AA}$ cut-off distance is near the first peak distance of the Ow-Ow RDF (Fig. 5(a)) and, hence, will encompass some of the water molecules. Mostly, small clusters should be seen at this cut-off distance. The $4\text{ \AA}$ distance is near the first coordination shell of the Ow-Ow RDF and well beyond the first coordination shell of the Oh-Ow RDF. Therefore, it will encompass most of the water molecules and hydronium ions and should show large cluster formation. The Fig. 7 shows the cluster distributions for these two different cut-off distances.

The cluster distribution for the smaller cut-off distance of 3 Å (Fig. 7(a), (b)) shows that all the cluster sizes at different hydration levels are below 100. Henceforth, small clusters shall denote cluster sizes <100 and large clusters shall denote cluster sizes >1400. When the cut-off distance is increased to 4 Å, the number of small clusters reduce (Fig. 7(c)) and large clusters are seen forming for $\lambda=15$ and 20 which indicates the formation of a single large continuous water phase (Fig. 7(d)). This continuous phase can also be seen in the visualization shown before in Fig. 2. A continuous hydrophilic phase has also been reported to have formed at high hydration levels in experimental studies of PFIA [20].

Fig. 7. PFIA Cluster distribution for different hydration levels at $T=300$ K for (a) cut-off =3 Å (b) cut-off =3 Å (Magnified view) (c) cut-off =4 Å and small cluster sizes (d) cut-off =4 Å and large cluster sizes. Cluster size is the number of water molecules and/or hydronium ions in one cluster. Note- In part (d) the y axis numbers are below 1 because it represents the average number of clusters. For any particular timestep, there is only one large cluster for $\lambda=15$ and 20.

The Table 3 (columns 2 and 3) shows the continuous cluster fraction (CCF) at two different cut-off distances. The CCF has been defined as the fraction of the total number of water molecules and hydronium ions present in a single large cluster. The cluster size used to compute CCF is the mean size of large cluster distribution at a particular hydration level (Fig. 7d). For the bigger cutoff distance of 4 Å, a large fraction of water molecules and hydronium ions are contained in a single large cluster at higher hydration levels ($\lambda=15, 20$). This single large cluster is the continuous water phase which facilitates diffusion of hydronium ions and water molecules. This facile diffusion is reflected in the significant increase in the diffusivity coefficients of water molecules and hydronium ions at higher hydration levels ($\lambda=15, 20$) as compared to lower hydration levels ($\lambda=5, 10$) (Fig. 9).

λ	CCF (cut-off=3 Å)	CCF (cut-off=4 Å)	AVF (1.4 Å probe radius)	AVF (1.7 Å probe radius)
5	0	0	0	0
10	0	0	0.047	0
15	0	0.7	0.105	0.051
20	0	0.85	0.172	0.061

Table 3. PFIA Continuous cluster fractions (CCF) at two different cut-off distances and PFIA accessible volume fractions (AVF) for two different probe radii at $T=300$ K.

The Table 3 (columns 4 and 5) shows the accessible volume fractions (AVF) in PFIA at different hydration levels for two different probe radii values. Hydronium ions bind to the water molecules diffusing through the accessible volumes and charge transport via the vehicular mechanism [56]. The average van der Waals radius for a water molecule is 1.4 Å [81] and accessible volumes were computed for a probe radius of 1.4 Å. PFIA shows non-zero accessible volumes at $\lambda=10, 15$ and 20 through which water molecules can move in all three dimensions.

A problem in fuel cells is the crossover of oxygen gas through the PEM which reduces the efficiency [82][83]. We have computed the amounts of accessible volume existing

inside the PFIA hydrated nanostructure for a probe radius of 1.7 Å, which is the kinetic radius of oxygen gas molecule [84]. The kinetic radius has been used previously as a criterion for checking the permeability of materials to various gases [84][85]. The amounts of accessible volume (Table 3 column 5) is zero except for high hydration levels of $\lambda=15$, 20. This implies that the channels inside the PFIA hydrated structure would not be sufficiently big to allow oxygen gas to pass through except at high hydration levels, which would make PFIA well suited for PEMFCs.

4.5 Translational diffusion

Fig. 8. PFIA MSDs at $T=300$ K for (a) water molecules in linear representation (b) water molecules in log-log representation (c),(d) the same but for hydronium ions. Dashed line is for slope=1 indicating diffusive regime

The Fig. 8 shows the mean square displacements (MSD) for the water molecules and hydronium ions in PFIA at $T=300$ K. The MSD values were computed as averages of all the water molecule atoms and separately for all the hydronium ion atoms. The calculations were also done by

considering the oxygen and hydrogen atoms separately for both water molecules and hydronium ions. The difference between the former and latter calculations for both water molecules and hydronium ions was negligible. The MSD values for PFIA at $T=353$ K (Fig. S7(a), (b) of Supplementary Material) is approximately twice the MSD values at $T=300$ K for both hydronium ions and water molecules. Similar amount of increase in MSD with temperature has also been observed in previous simulations of PFSA membranes like Nafion [29][30] and Aciplex[33].

The MSD vs time plots show a linear trend which indicates diffusive regime. The slope of the log-log plots (Fig. 8 (b), (d)) for PFIA is almost unity, which indicates diffusive regime, except for hydronium ion at $\lambda=5$. The reason for this sub-diffusive behaviour at $\lambda=5$ could be due to the strong attraction of hydronium ions to side chain protogenic groups at lower hydration levels [79] and/or due to the negligible water accessible volumes at $\lambda=5$ (Table-3 column 4).

The MSD for water molecules (Fig. 8(a), (b)) and hydronium ions (Fig. 8(c), (d)) keeps increasing with increasing hydration levels due to larger water phase cluster formation with increasing λ . The MSD values for hydronium ions are quite low as compared to those for the water molecules. This is due to the fact that hydronium ion is positively charged and is strongly attracted to the negatively charged protogenic groups of PFIA which restricts the movement of the hydronium ions.

The Fig. 9 shows the simulated vehicular diffusion coefficients of water molecules and hydronium ions in PFIA, which were calculated from the last 1 ns of the MSD plots (Fig. 8) of the present simulations, and previously published simulated vehicular diffusion coefficients of Nafion [26][29][30]. For every λ , the vehicular diffusion coefficients for hydronium ions are almost an order of magnitude smaller than those for water at both $T=300$ K and $T=353$ K because of the reasons mentioned in the previous paragraph. The vehicular

diffusion coefficient for water molecules and hydronium ions are very low at $\lambda=5$ because of the presence of negligible accessible volume for water molecules (Table 3 column 4) which, in turn, restricts the diffusion of water molecules. The vehicular diffusion coefficients for water molecules and hydronium ions in PFIA shows a significant increase for $\lambda=15$ as compared to that for $\lambda=10$ at both $T=300$ K and $T=353$ K. This can be explained due to the emergence of a large continuous water phase cluster at $\lambda=15$ (Fig. 7(d) and Table 3 column 3) which helps in the enhanced diffusion of water molecules and hydronium ions. The vehicular diffusion coefficients of PFIA are comparable to the previously published vehicular diffusion coefficients for Nafion for both water molecules and hydronium ions at $T=300$ K and $T=353$ K.

Fig. 9. PFIA and Nafion vehicular diffusion coefficients at $T=300$ K and $T=353$ K for (a) water molecules (b) hydronium ions; Nafion1 [30], Nafion2 [26], Nafion3 [29] are values from Nafion simulations published previously

The Fig. 10 shows the simulated vehicular proton conductivity values of PFIA and Nafion at $T=300$ K and $T=353$ K which were calculated by using the Nernst-Einstein equation (Equation 1). The PFIA vehicular proton conductivity values were calculated using the simulated vehicular diffusion coefficients of hydronium ions in PFIA. The Nafion vehicular proton conductivity values were calculated by using the previously published

Nafion simulated vehicular diffusivities for hydronium ions [26][29][30]. The PFIA vehicular proton conductivities are observed to be higher than those of Nafion at both $T=300$ K and $T=353$ K. This agrees qualitatively with the experimental trends seen at $T=300$ K [20] and $T=353$ K [22].

Fig. 10. PFIA and Nafion vehicular proton conductivity values at $T=300$ K and $T=353$ K. Nafion1 [30], Nafion2 [26], Nafion3 [29] are values from Nafion simulations published previously

The Nernst-Einstein equation states that the conductivity is proportional to the concentration of the charge carrying ions and the diffusion constants of the charge carrying ions, which are hydronium ions in the present study. The concentration of hydronium ions in PFIA for $\lambda=10, 15$ and 20 is significantly higher to that in Nafion at the corresponding hydration levels due to the dissociation of the extra protogenic group (sulfonyl imide) at these hydration levels in PFIA. Since the simulated vehicular diffusion coefficients for hydronium ions in PFIA are comparable to those for hydronium ions in Nafion, the simulated vehicular proton conductivity values for PFIA are higher than those for Nafion.

The simulated vehicular proton conductivity values for PFIA at $T=353$ K are smaller than the experimental proton conductivity⁴ values for PFIA at $T=353$ K [22]. A limitation of classical MD simulations is that it cannot account for proton hopping or the Grotthuss mechanism. The Grotthuss mechanism aids in diffusion of protons inside the water phase in addition to the vehicular diffusion of protons. Therefore, the difference between simulated and experimental proton conductivity values could be due to this limitation of classical MD simulations which has also been observed in previous simulations of PEMs [29][30][38][47].

5. Conclusions

PFIA, which belongs to a new class of PEMs known as MASC membranes, has been studied using classical MD simulations and *pcff* force field for a range of hydration levels ($\lambda=5-20$) and for two different temperatures, $T=300$ K and 353 K. The simulated densities were observed to be close to the experimental density values. The peak distances for RDFs in PFIA were similar to the corresponding RDFs for Nafion. The RDFs showed negligible change with temperature. The number of water molecules in the first coordination shell around the side chain protogenic groups in PFIA was found to be higher than that in Nafion due to the presence of the extra side chain protogenic group in PFIA. This could lead to a higher percentage of bound water in PFIA. The total number of water molecules in the first coordination shell around the hydronium ions was also observed to be higher in PFIA than that in Nafion due to the dissociation of two side chain protogenic groups at $\lambda=10, 15$ and 20 in PFIA as opposed to the dissociation of only one side chain protogenic group in Nafion.

⁴ The experimental proton conductivity values for PFIA are not available as a function of λ .

This could lead to more hydrogen bonding among hydronium ions and water molecules in PFIA.

The average radius of gyration of the PFIA chains did not have any correlation with temperature which makes PFIA suitable for high temperatures in fuel cells. The side chain length of PFIA was also not varying much with varying levels of hydration.

The hydrated PFIA nanostructure showed a separate water phase made up of water molecules and hydronium ions. The water phase clusters increased in size with increasing hydration and a large continuous water phase cluster was seen to be formed at high hydration levels of $\lambda=15$ and 20. Such large continuous water phase clusters at high hydration levels have also been observed in experimental studies [20]. The water accessible volumes also increased with increasing hydration. The emergence of a single large continuous water phase cluster at $\lambda=15$ led to a significant increase in the vehicular diffusion for hydronium ions and water molecules at $\lambda=15$ as compared to those at $\lambda=10$. The vehicular diffusion for hydronium ions and water molecules in PFIA increased with temperature and increasing hydration levels.

The vehicular proton conductivities were observed to be higher for PFIA than those for Nafion at both $T=300$ K and $T=353$ K which agrees qualitatively with the experimental trends of proton conductivity [20][22]. The higher vehicular proton conductivities in PFIA combined with crystallinity comparable to Nafion makes PFIA suitable for fuel cell usage. However, the simulated vehicular proton conductivities for PFIA were smaller than the experimental proton conductivities at $T=353$ K⁵ [22]. This has also been observed in other previous classical MD simulation studies [29][30][38][47] possibly because classical MD

⁵ Proton conductivity values were not available at $T=300$ K. Current values were available at $T=300$ K

simulations cannot take into account the diffusion of protons due to Grotthuss mechanism. The inclusion of Grotthuss mechanism implies the description of interactions to observe proton hopping which can provide a quantitative agreement of diffusion coefficients with experimental data [62][65]. The study of Grotthuss diffusion in hydrated PFIA membrane will be the focus of future studies like it has been done for Nafion previously [59][61].

In conclusion, we have successfully characterized the hydrated morphology and the concomitant effects on vehicular transport of protons inside the hydrated nanostructure for a new MASC PEM material (PFIA).

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