Electronic Supplementary Material (ESI) for RSC Advances.

Molecular dynamics simulation of Keggin HPA doped Nafion® 117 as polymer electrolyte membrane

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Supporting Information

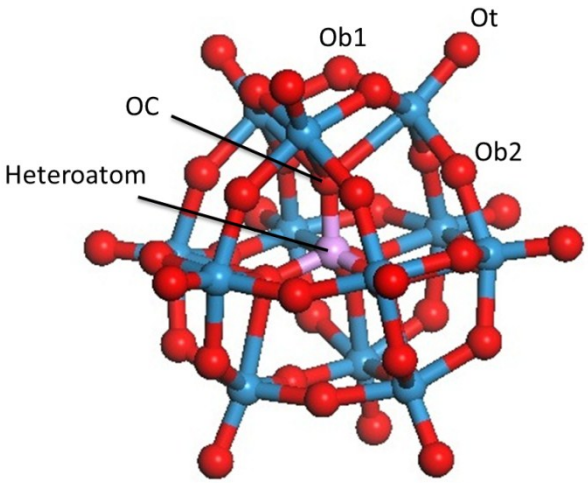

Fig. S1. The α-Keggin anion. Oxygen (red), Tungsten (blue), Phosphorus (purple).

Table S1. Partial charges for HPA anions ($PW_{12}O_{40}^{3-}$, $SiW_{12}O_{40}^{4-}$ and $AlW_{12}O_{40}^{5-}$) obtained from ChelpG method.

Atom	$PW_{12}O_{40}^{3-}$	$SiW_{12}O_{40}^{4-}$	$AlW_{12}O_{40}^{5-}$
Heteroatom(P, Si, Al)	+1.51	+3.02	+2.96
W	+3.81	+4.09	+4.26
OC	-1.25	-1.97	-2.20
Ob1	-1.37	-1.44	-1.47
Ob2	-1.55	-1.65	-1.72
Ot	-0.85	-0.93	-1.00

Table S2. Summary of simulation condition for λ=5. For each hydration total no. of water molecules can be obtain from $n_{H_2O} = n_{SO_3^-} \times \lambda - n_{H_3O^+}$.

λ	Undoped system	PW^{3-} doped system	SiW^{4-} doped sysytem	AlW^{5-} doped system
chain	40	40	40	40
H_2O	1600	1507	1476	1445
POM	0	31	31	31
H_3O^+	400	493	524	555
total	33680	35416	35447	35478

In order to compare the results of density, the experimental correlation with λ proposed by Morris and Sun[1] was applied. They have reported the following equation to estimate experimental density for membrane EW=1148.

$$\rho(\frac{g}{cm^3}) = \frac{63.7+\lambda}{31.1+\lambda}$$

Fig. S2 shows both the calculated density and the experiment data. For undoped systems, our results are in good agreement with experimental density and the study of Mabuchi et al.[2]. Note that we used same annealing procedure with Mabuchi et al.[1].

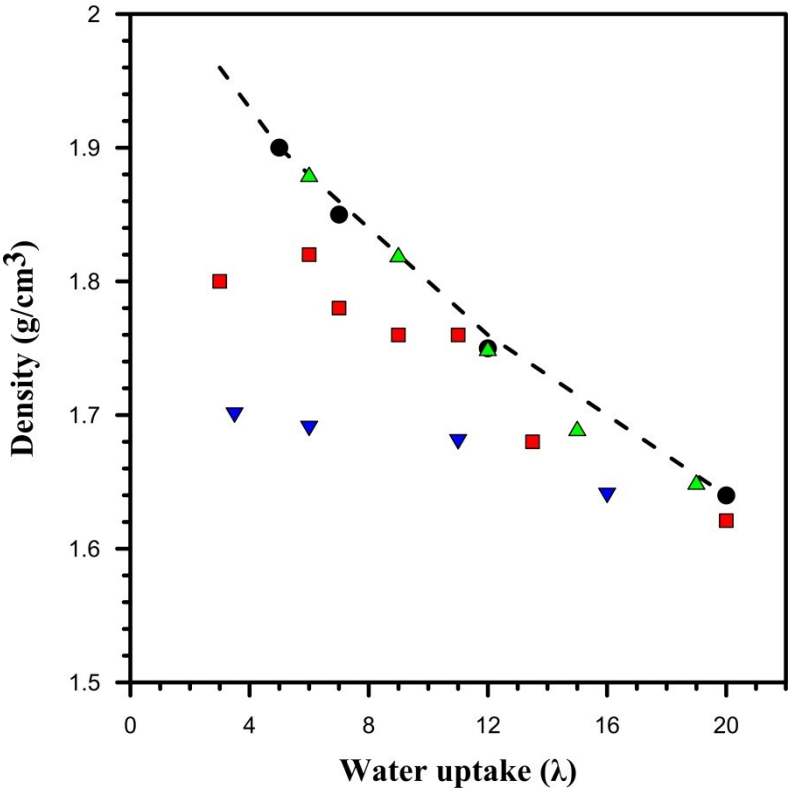

Fig. S2. The Simulated density of hydrated PFSA membranes as a function of hydration level (λ). (--) experimental data[1] (●) Our simulation (▲) Mabuchi *et al.*[2] (▼) Venkatnathan *et al.*[3] (■) Devanathan *et al.*[4].

Table S3. Final calculated density (g/cm^3) and corresponding cubic box length (Å) at different hydration levels.

λ	Undoped system	PW^{3-} doped system	SiW^{4-} doped sysytem	AlW^{5-} doped system
5	1.90 (78.06)	1.92 (79.13)	19.1 (78.86)	1.92 (78.86)
7	1.85 (78.97)	1.88 (79.09)	1.88 (79.00)	1.89 (79.20)
12	1.75 (81.00)	1.77 (83.02)	1.76 (82.50)	1.76 (82.31)
20	1.64 (83.88)	1.65 (85.00)	1.65 (84.79)	1.65 (84.60)

Table S4. Percentage of hydronium ions, which locate at outside the first solvation shell of side chains (Averaged from 20000 collected trajectories).

λ	Undoped system	PW^{3-} doped system	SiW^{4-} doped sysytem	AlW^{5-} doped system
5	12.22	17.12	18.06	20.14
7	15.02	20.49	21.09	21.62
12	22.57	27.11	29.49	30.32
20	28.41	33.78	34.50	35.62

Mean residence time

To investigate the dynamic behavior of H_2O molecules around SO_3 groups, the mean residence time (MRT) of H_2O molecules in vicinity of side chains were calculated. In according to the study of Brunne *et al*.[5] , the following time correlation function was used to evaluate MRT from all collected trajectories:

$$\tau(t_k) = \sum_{j=1}^{M-k} \sum_{i=1}^{N} \upsilon_i(t_j)\upsilon_i(t_j + t_k)$$

where the υ_{ij} is a Boolean variable that possesses a value of 1 if the *i*th oxygen of H_2O is within a distance 4.34 Å at time t and 0 otherwise. Finally, the MRT values obtain using fitting $\tau(t_k)$ with an exponential function, A exp(-t/MRT).

The MRT of water molecules in first solvation shell of sulfur atom was represented in Fig. S2 for undoped and HPA doped Nafion®. Our simulation revealed that the MRT values for HPA doped systems were lower than that of undoped systems. Among the considered dopants, the least-charged anions, PW^{3-} shows lowest MRT and the highest MRT value achieve for the most-charged anion, AlW^{5-}. In other word, the MRT of water molecules in first solvation shell of sulfur decreases when the charge of anions increases. It should be mentioned that the HPA particles do not decrease the MRT values at λ≥12.

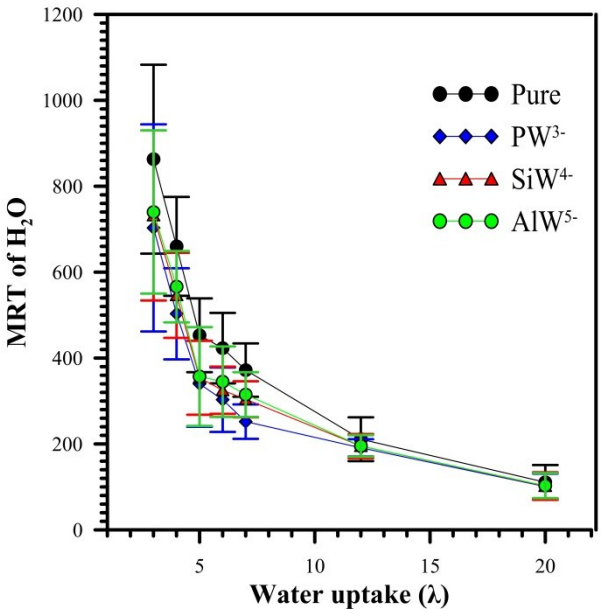

Fig. S3 Variation of mean residence time (MRT) of H2O molecules with hydration level in undoped and HPA doped Nafion®.

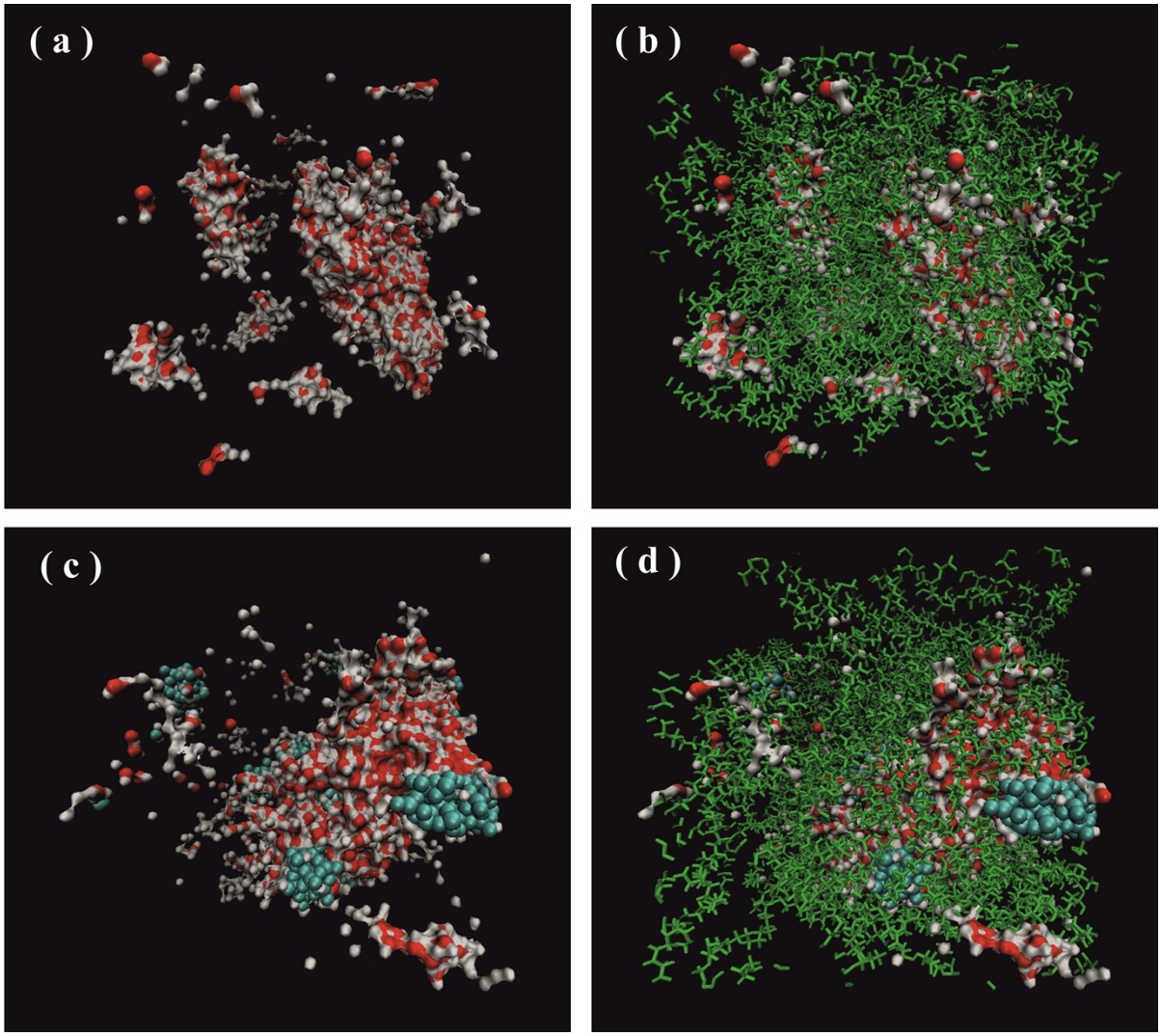

Fig. S4 Final snapshots of PW^{3-}/Nafion® membranes for λ=5 obtained at the end of production phase MD simulations. (a) and (b) undoped Nafion®, (c) and (d) HPA doped Nafion®.

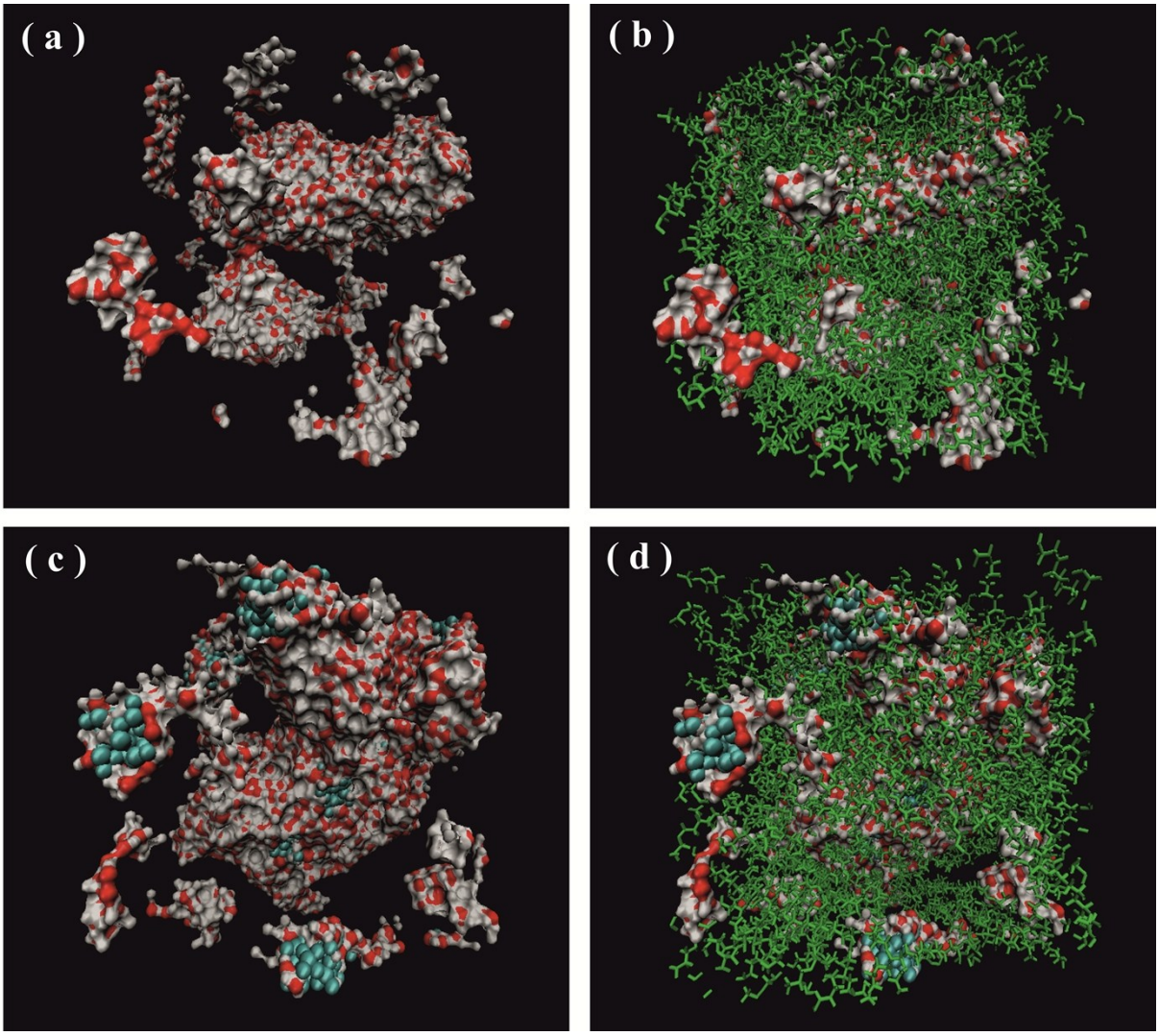

Fig. S5 Final snapshots of PW^{3-}/Nafion® membranes for λ=12 obtained at the end of production phase MD simulations. (a) and (b) undoped Nafion®, (c) and (d) HPA doped Nafion®.

Table S5. Diffusion coefficients of hydronium ions in HPA/Nafion composite membrane obtained from a 2 ns production run.

Dopants	Temp. (K)	D ($\times 10^{-6}$ cm^2 s^{-1})			
		λ=5	**λ=7**	**λ=12**	**λ=20**
PW^{3-}	300	0.880	1.480	2.120	2.790
	320	1.320	2.249	2.968	7.158
	340	2.508	3.922	5.300	9.891
	380	4.532	7.104	8.353	11.021
SiW^{4-}	300	0.940	1.530	2.170	2.910
	320	1.607	2.546	3.103	9.748
	340	2.858	4.054	5.382	8.148
	380	4.700	6.808	7.992	12.891
AlW^{5-}	300	1.020	1.610	2.280	3.140
	320	1.754	2.695	3.397	11.744
	340	2.978	4.291	5.632	12.403
	380	4.916	7.406	7.980	13.188

Table S6. Diffusion coefficients of water molecules in HPA/Nafion composite membrane obtained from a 2 ns production run.

Dopants	Temp. (K)	D ($\times 10^{-6}$ cm^2 s^{-1})			
		λ=5	**λ=7**	**λ=12**	**λ=20**
PW^{3-}	300	1.090	2.600	4.260	5.370
	320	1.864	4.269	6.347	8.893
	340	2.889	7.167	11.502	11.841
	380	5.592	12.220	17.040	19.547
SiW^{4-}	300	1.409	2.880	4.316	5.590
	320	2.369	4.793	6.172	9.447
	340	3.382	7.632	11.567	11.739
	380	6.904	12.816	16.530	19.118
AlW^{5-}	300	1.760	3.033	4.480	5.900
	320	2.746	4.451	6.272	8.555
	340	3.820	7.572	11.066	11.210
	380	8.008	12.132	16.307	18.290

References

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3 A. Venkatnathan, R. Devanathan, and M. Dupuis, The Journal of Chemical Physics B, 2007, 111, 7234.

4 R. Devanathan, A. Venkatnathan, and M. Dupuis, The Journal of Chemical Physics B, 2007, 111, 8069.

5 R. Brunne, E. Liepinsh, G. Otting, K. Wüthrich, W. Van Gunsteren, Journal of Molecular Biology, 1993, 231, 1040-1048.