Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Elucidating morphological aspects and proton dynamics in a hybrid perfluorosulfonic acid membrane for medium-temperature fuel cell applications

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Supporting Information

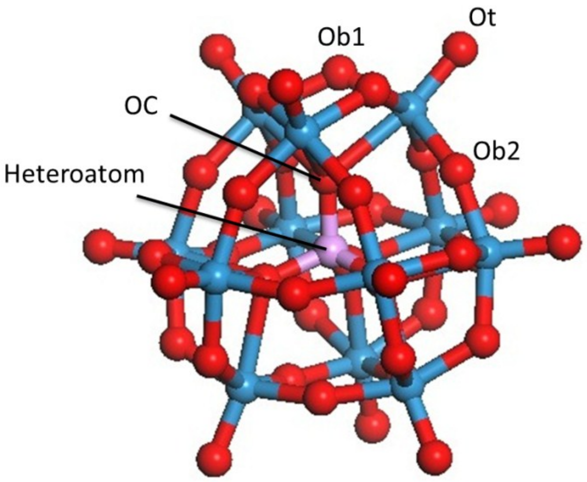

Figure S1. The α-Keggin anion. Oxygen (red), Tungsten (blue), Phosphorus (purple).

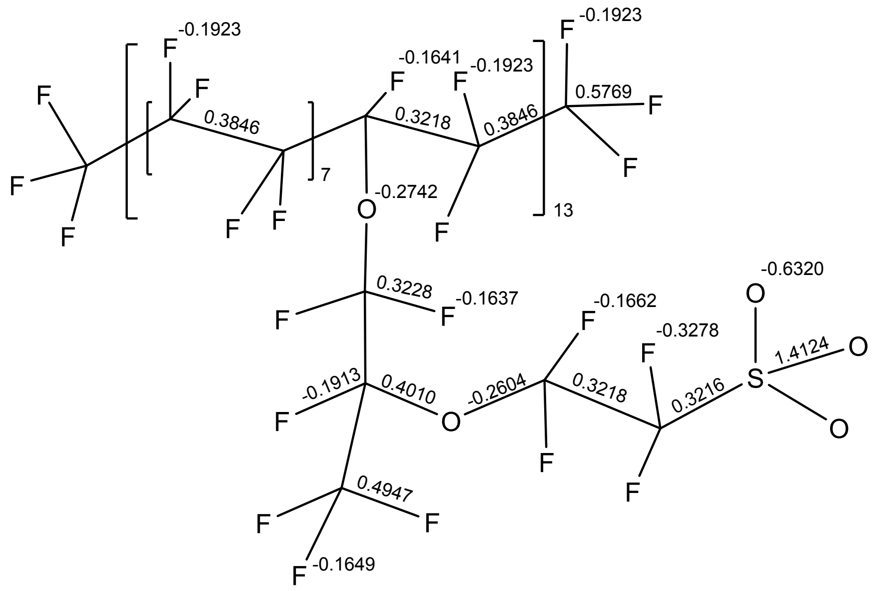

Figure S2. Chemical structure and partial charges of Nafion® polymer.

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

Atom	$PW_{12}O_{40}^{3-}$
Heteroatom(P, Si, Al)	+1.51
W	+3.81
OC	-1.25
Ob1	-1.37
Ob2	-1.55
Ot	-0.85

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.

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

Figure S3 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 the study of Mabuchi et al.).

Table S2. Final calculated density (g/cm^3) for the composite membranes and corresponding cubic box length (Å) at different hydration levels.

λ	Undoped system	$H_3PW_{12}O_{40}$ doped system	$CsH_2PW_{12}O_{40}$ doped system	$Cs_2HPW_{12}O_{40}$ doped system	$Cs_3PW_{12}O_{40}$ doped system
3	1.92 (77.97)	1.93 (78.91)	1.94 (79.6)	1.95 (79.67)	1.96 (79.68)
5	1.90 (78.06)	1.92 (79.13)	1.95 (80.13)	1.96 (80.23)	1.96 (80.41)
7	1.85 (78.97)	1.88 (79.09)	1.90 (81.45)	1.91 (81.50)	1.91 (81.57)
12	1.75 (81.00)	1.77 (83.02)	1.81 (84.32)	1.81 (84.43)	1.82 (84.53)
20	1.64 (83.88)	1.65 (85.00)	1.71 (88.34)	1.72 (88.39)	1.72 (88.56)

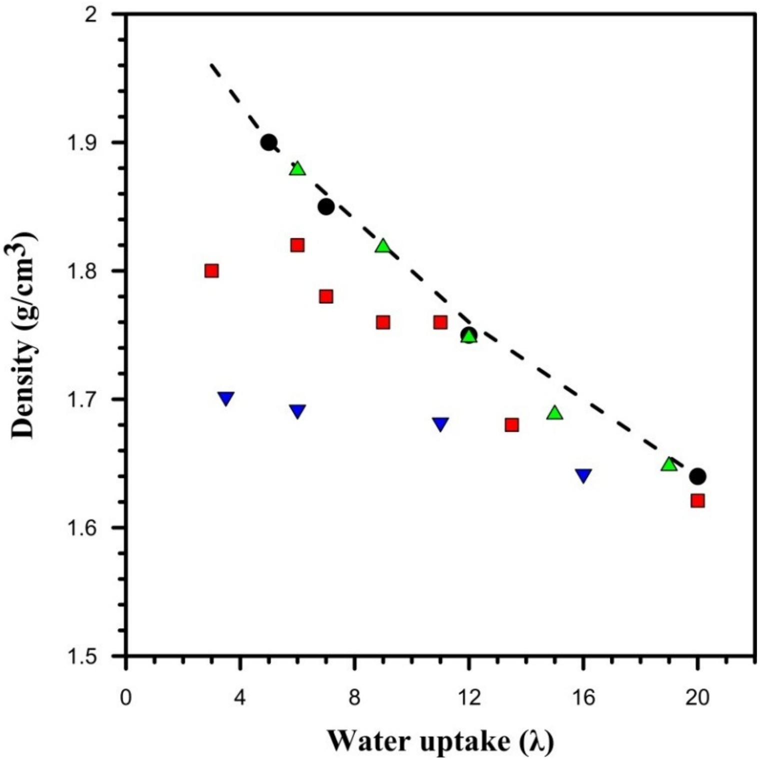

Figure S3. The Simulated density of hydrated PFSA membranes as a function of hydration level (λ). (--) experimental data[1] (●) Our simulation (▲) Mabuchi *et al.*[2] (▼) Venkatnathan *et al.* [3] (■) Devanathan *et al.*[4].

In order to evaluate the direct effect of HPA and HPS on the static properties of PEMs, radial distribution functions (RDFs) were compared. Figure S4 depicts RDF curves for sulfonic groups of side chain and oxygen of H_2O/H_3O^+ for undoped Nafion® (Ow, oxygen of water and Oh, oxygen of hydronium). The solvation of side chain increases with increasing hydration in agreement with study of Devanathan and Dupuis [5] and Sunda and Venkatnathan [6]. Figure S5 represents the S-Ow RDFs for Cs-substituted HPA doped Nafion®.

In the case of Cs-substituted HPA doped Nafion®, a dominant peak appears at a distance of 3.95 Å. For all considered hydration levels, the peak height increases as the extent of substitution of proton in HPA increases. Our results clearly show that the interaction between SO_3^- groups and H_2O molecules increases with increasing substitution cation/proton ratio. For HPS doped membrane, the

SO_3^--H_2O interaction also affected by ionic radius of the cation, so that, these interactions decreases with increasing ionic radius of cation in HPS (see Figure S7a-b).

The interactions between sulfur and oxygen of hydronium ion (Oh) are represented by S-Oh RDFs (Figure S6). The SO_3^--H_3O^+ interaction is a water mediation interaction, which decreases as water uptake increases in agreement with the study of Venkatnathan *et al.* [3]. The SO_3^--H_3O^+ interactions are affected by the extent of substitution of proton in HPA and ionic radius of the cation. For Cs-substituted HPA doped Nafion®, the peak intensity for SO_3^--H_3O^+ interaction in the $Cs_3PW_{12}O_{40}$ doped system is highest and that for $CsH_2PW_{12}O_{40}$ doped Nafion® is the lowest, at each λ value. On the other hand, the peak intensity depends on ionic radius of cation and varies similarly; i.e. ($Cs_3PW_{12}O_{40}$ doped Nafion®>$Rb_3PW_{12}O_{40}$ doped Nafion®>$(NH_4)_3PW_{12}O_{40}$ doped Nafion®).

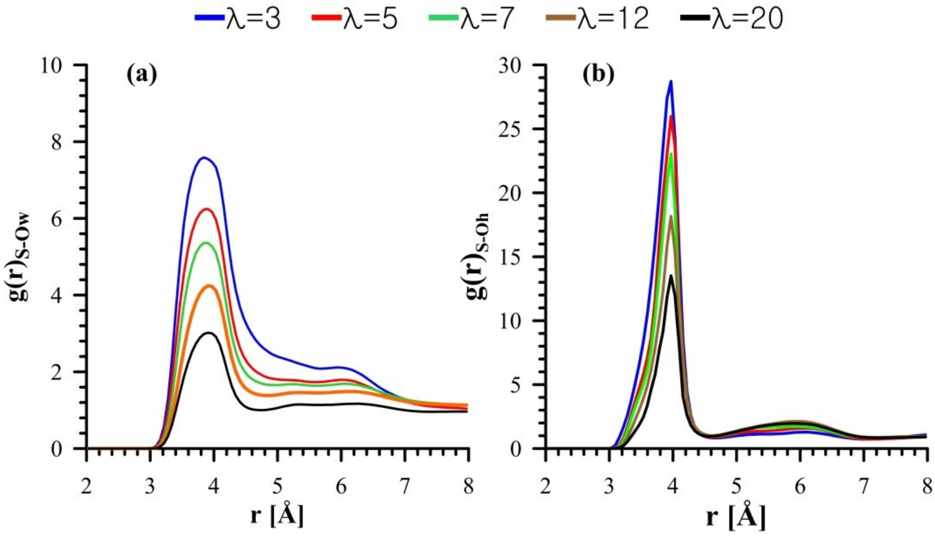

Figure S4. RDFs of atom pairs for the undoped Nafion® at various hydration levels. (a) Sulfur–Oxygen of Water molecules (Ow) RDFs, (b) Sulfur–oxygen of hydronium ion (Oh) RDFs.

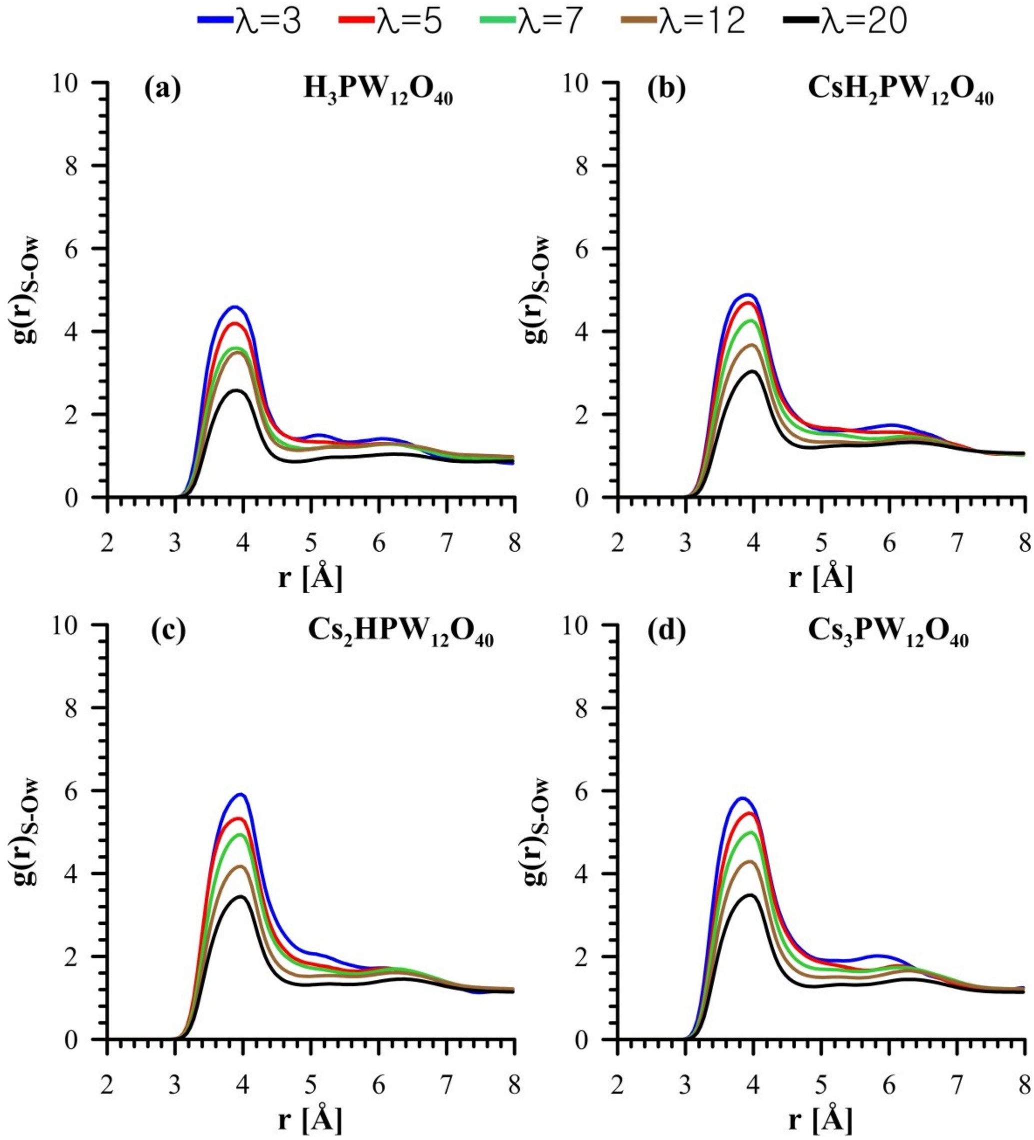

Figure S5. Representation of Sulfur-Oxygen of water molecules (Ow) RDFs for Cs-substituted HPA doped Nafion® 117.

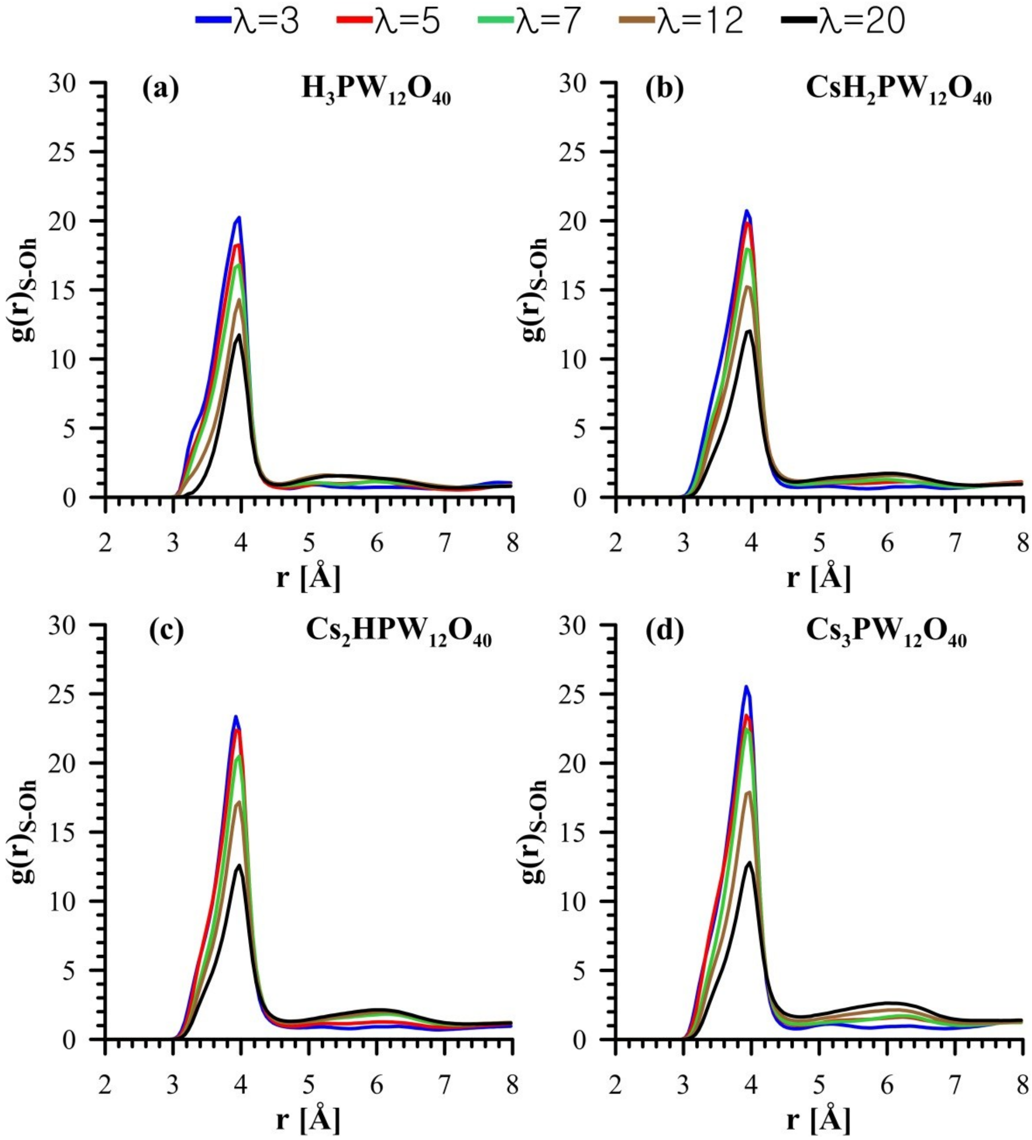

Figure S6. Representation of Sulfur-Oxygen of hydronium ions (Oh) RDFs for Cs-substituted HPA doped Nafion® 117.

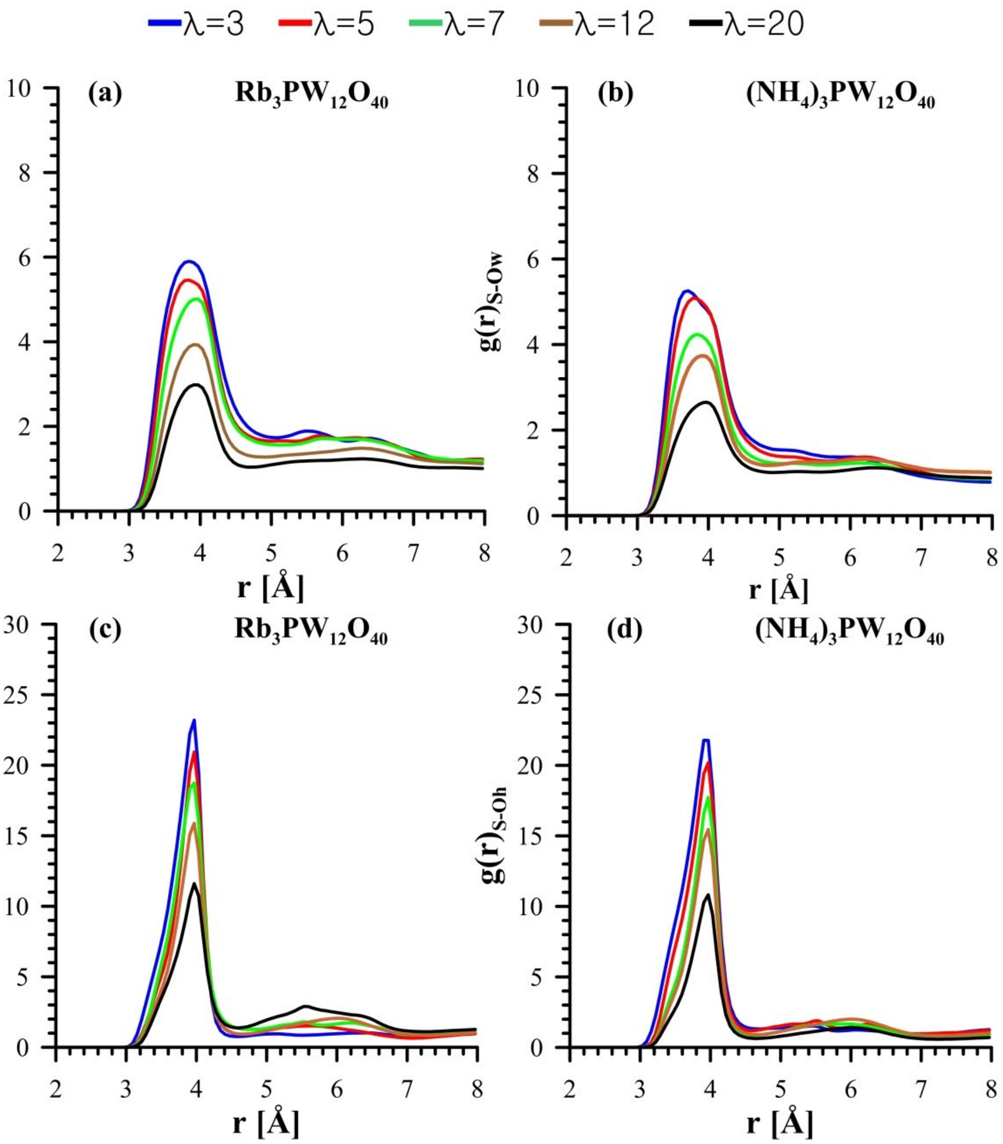

Figure S7. RDFs of atom pairs for the HPS doped Nafion® at various hydration levels. (a, b) Sulfur–Oxygen of Water molecules (Ow) RDFs, (c, d) Sulfur–oxygen of hydronium ion (Oh) RDFs.

References

[1] D.R. Morris, X. Sun, Water-sorption and transport properties of Nafion 117 H, J. Appl. Polym. Sci., 50 (1993) 1445-1452.

[2] T. Mabuchi, T. Tokumasu, Effect of bound state of water on hydronium ion mobility in hydrated Nafion using molecular dynamics simulations, The Journal of Chemical Physics, 141 (2014) 104904.

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