Modeling of Electrochemical Cells:
Proton Exchange Membrane Fuel Cells
HYD7007 – 01

Lecture 07. Perfluorosulfonic Acid Membranes

Dept. of Chemical & Biomolecular Engineering
Yonsei University
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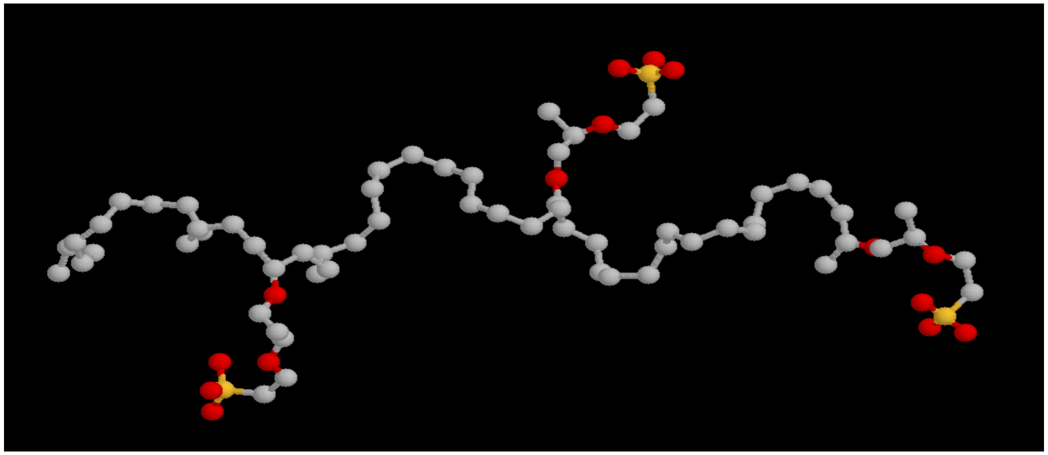
Lecture Outline

- Motivation
- Description of Polymer Chemistries
    - Molecular Weight
    - Equivalent Weight
    - Length of Side Chain
- Characterizing Structure
    - Local Structure (Pair Correlation Functions)
    - Global Structure (Water Cluster Distributions)
- Characterizing Transport Properties

Nafion

- Perfluorosulfonic acid (PFSA) electrolyte is a key component of polymer electrolyte membrane (PEM) fuel cells and functions as a separator between anode and cathode while facilitating proton conduction.

- Nafion, the archetypical PFSA electrolyte, is composed of a hydrophobic backbone (teflon) and hydrophilic side-chains terminated with sulfonate acid groups.



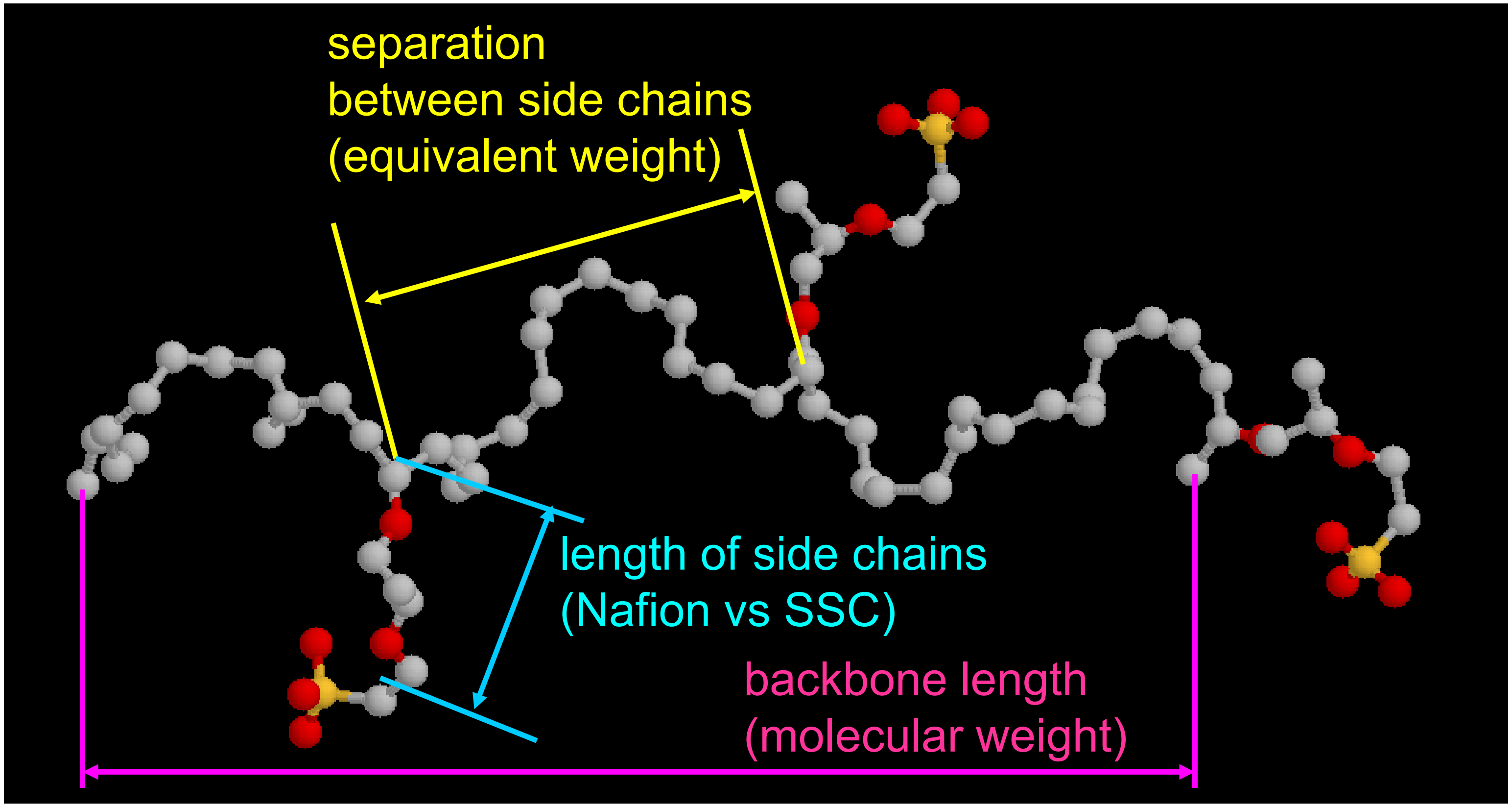
Nafion fragment

CF_2 = gray, O = red, S = orange, cations not shown.

- Design and synthesis of ideal electrolyte are tied to the understanding of proton mobility as a function of polymer structure and chemistry, and water contents, etc.

polymer electrolyte

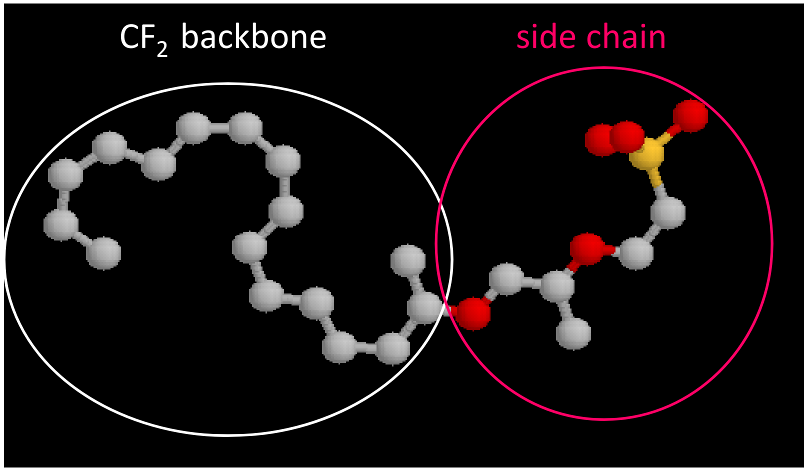
Perfluorinated sulfonic acid polymer electrolytes have a hydrophobic backbone (teflon) and hydrophilic side-chains (sulfonic acid)

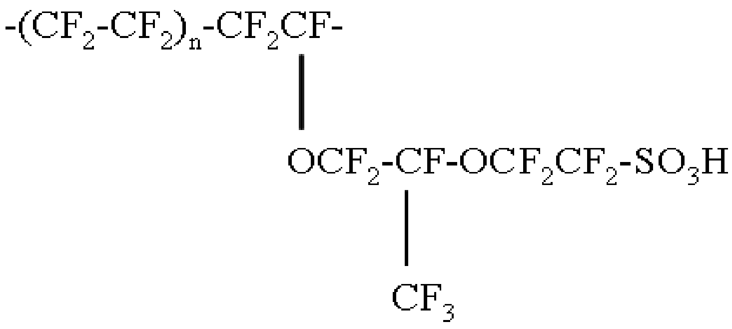


Simulated structure containing three monomer units.
CF_2 = gray, O = red, S = orange, cations not shown.

Chemical Structure of Monomer Units

Nafion®

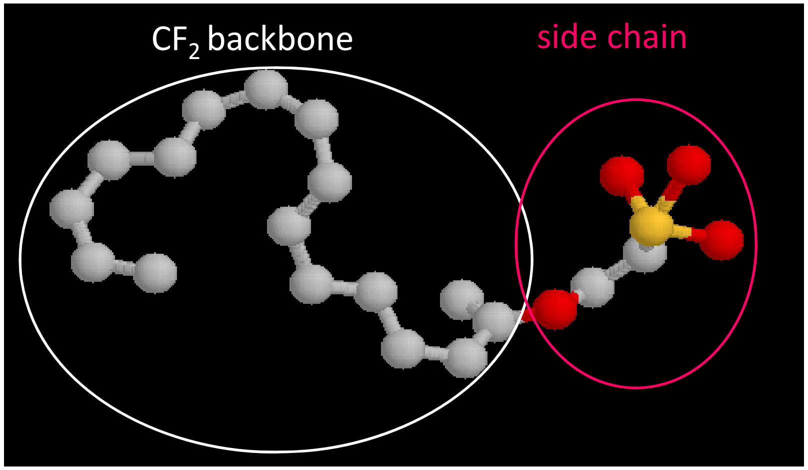


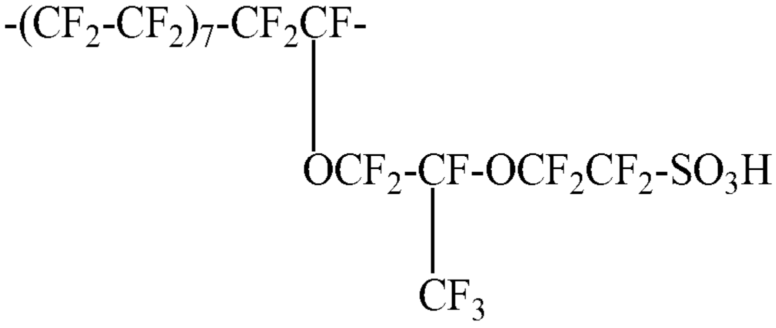


$$\begin{array}{l} \mathrm{-(CF_2\text{-}CF_2)_n\text{-}CF_2CF\text{-}} \\ \qquad\qquad\qquad\qquad | \\ \qquad\qquad\qquad\quad \mathrm{OCF_2\text{-}CF\text{-}OCF_2CF_2\text{-}SO_3H} \\ \qquad\qquad\qquad\qquad\qquad | \\ \qquad\qquad\qquad\qquad\quad \mathrm{CF_3} \end{array}$$

n = 3, 4, 5, 7
EW: 744, 844, 944, 1144

DOW Short-Side-Chain (SSC)



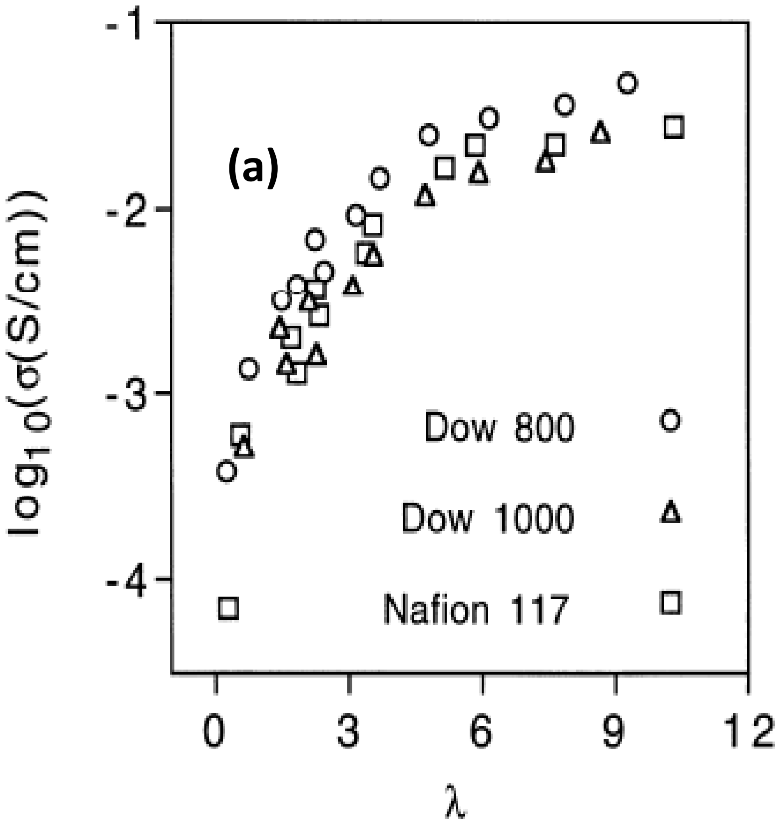


$$\begin{array}{l} \mathrm{-(CF_2\text{-}CF_2)_7\text{-}CF_2CF\text{-}} \\ \qquad\qquad\qquad\qquad | \\ \qquad\qquad\qquad\quad \mathrm{OCF_2\text{-}CF\text{-}OCF_2CF_2\text{-}SO_3H} \\ \qquad\qquad\qquad\qquad\qquad | \\ \qquad\qquad\qquad\qquad\quad \mathrm{CF_3} \end{array}$$

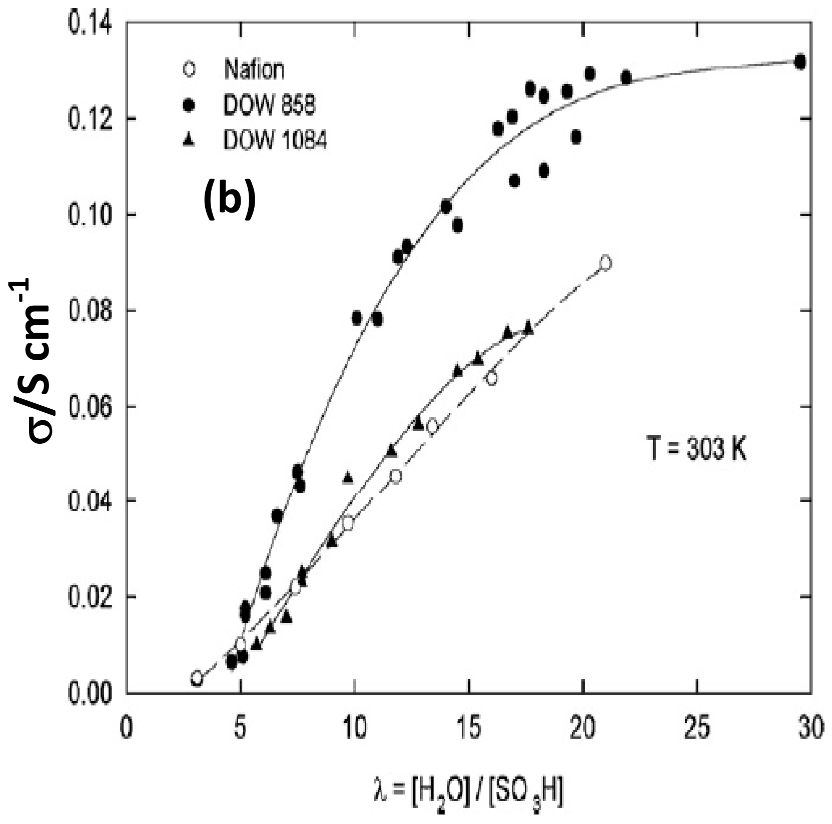
n = 4, 5, 6, 7; EW = 678, 778, 878, 978

CF_x = grey; O of SO_3^- = red; S = orange

Experimental Motivation



Edmondson *et al.,* J. Power Sources, **2000**.



Kreuer *et al.,* J. Power Sources, **2008**.

Experiment shows that the equivalent weight and side chain length impact proton mobility as a function of water contents.

Polymer Electrolytes

side chain length	degree of polymerization	equivalent weight	no. of CF_X groups on backbone between side chains
Nafion	15	1144	16
Nafion	15	944	12
Nafion	15	844	10
Nafion	15	744	8
SSC	15	978	16
SSC	15	878	14
SSC	15	778	12
SSC	15	678	10

Simulation Details

λ (H_2O/SO_3H)	3	6	9	15	22
no. of polymers	40	40	40	40	40
no. of H_2O	1200	3000	4800	8400	12600
no. of H_3O^+	600	600	600	600	600
total no. of particles	22200	27600	33000	43800	56400

- **Our potential model for Nafion is from [1]. We included bond stretching, bending, torsion, and intramolecular and intermolecular interactions via the Lennard-Jones (LJ) potential and Coulombic interactions**

- **We use TIP3P model for water [2] with a flexible OH bond [3]. The model for H_3O^+ is similar to [4]**

[1] Cui et al., *J. Phys. Chem. B* 2007, *111*
[2] Jorgensen et al., *J. Chem. Phys.* 1983, *79*
[3] Cornell et al., *J. Am. Chem. Soc.* 1995, *117*
[4] Urata et al., *J. Phys. Chem. B* 2005, *109*

Simulations run for 4 ns.

Membrane Swelling

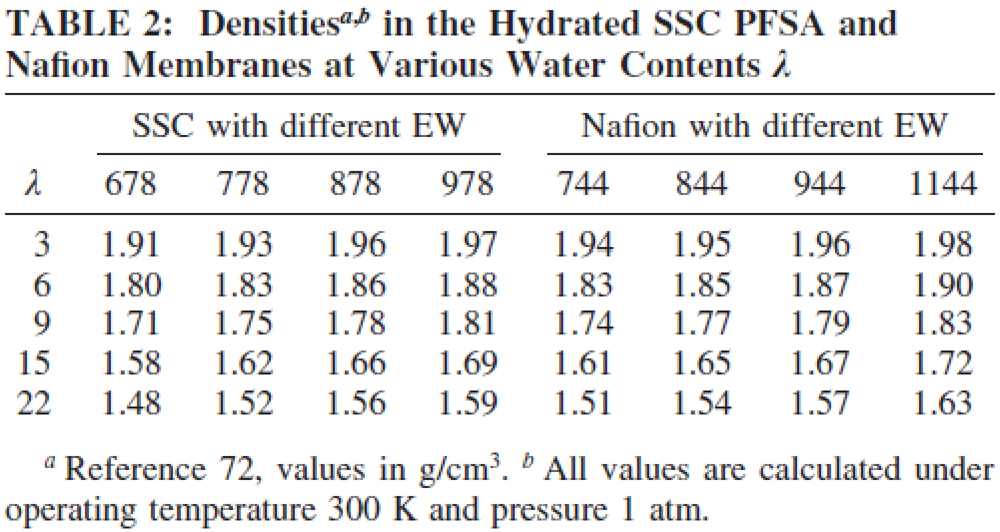


TABLE 2: Densities[a,b] in the Hydrated SSC PFSA and Nafion Membranes at Various Water Contents λ

	SSC with different EW				Nafion with different EW			
λ	678	778	878	978	744	844	944	1144
3	1.91	1.93	1.96	1.97	1.94	1.95	1.96	1.98
6	1.80	1.83	1.86	1.88	1.83	1.85	1.87	1.90
9	1.71	1.75	1.78	1.81	1.74	1.77	1.79	1.83
15	1.58	1.62	1.66	1.69	1.61	1.65	1.67	1.72
22	1.48	1.52	1.56	1.59	1.51	1.54	1.57	1.63

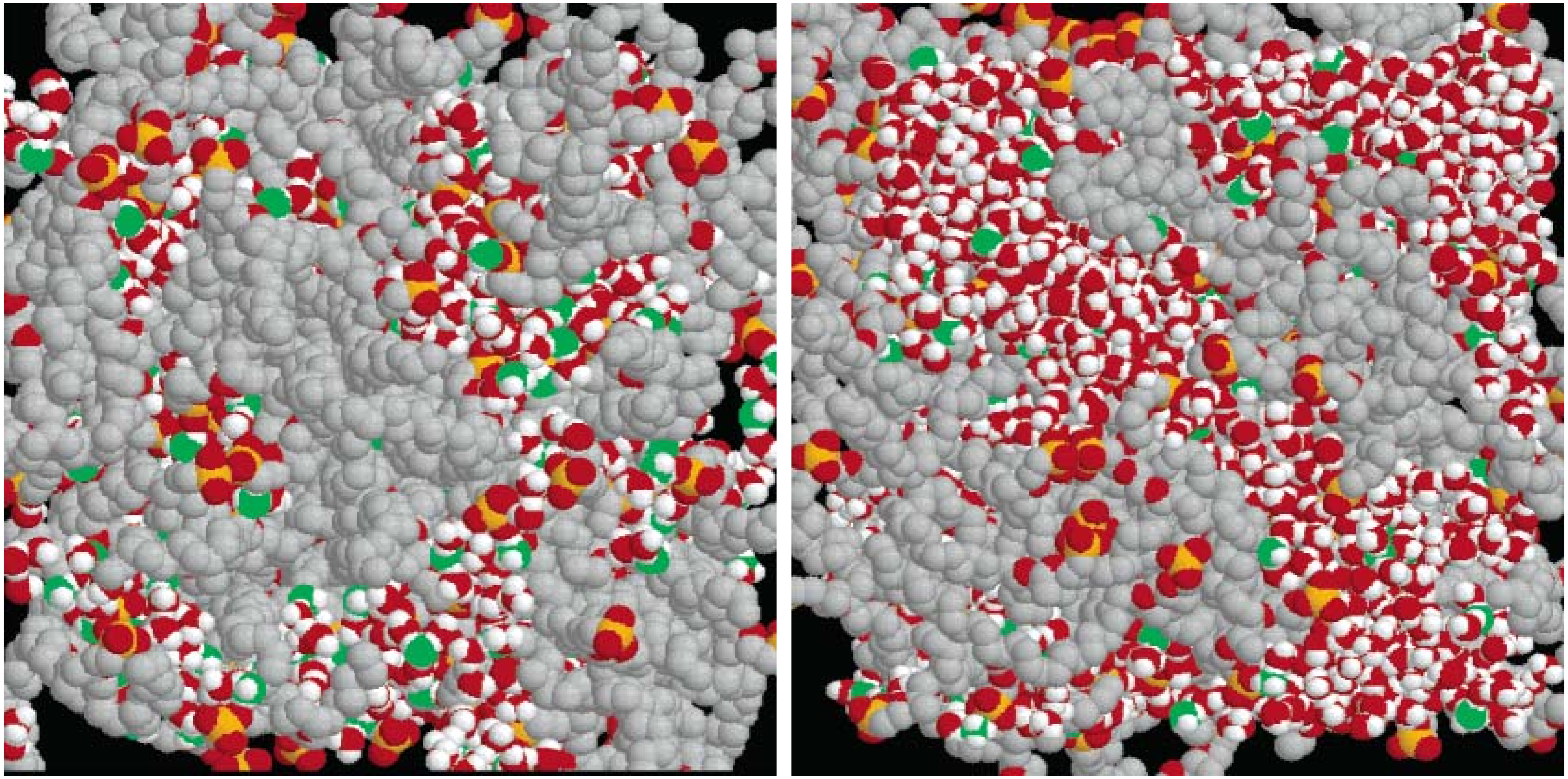
[a] Reference 72, values in g/cm^3. [b] All values are calculated under operating temperature 300 K and pressure 1 atm.

Density of the hydrated membrane varies

- **As water content increases, density decreases.**
- **As equivalent weight increases, density increases.**
- **As side chain length increases, density increases.**

Liu et al. J. Phys. Chem. C, 2010.

Molecular Dynamics Snapshots



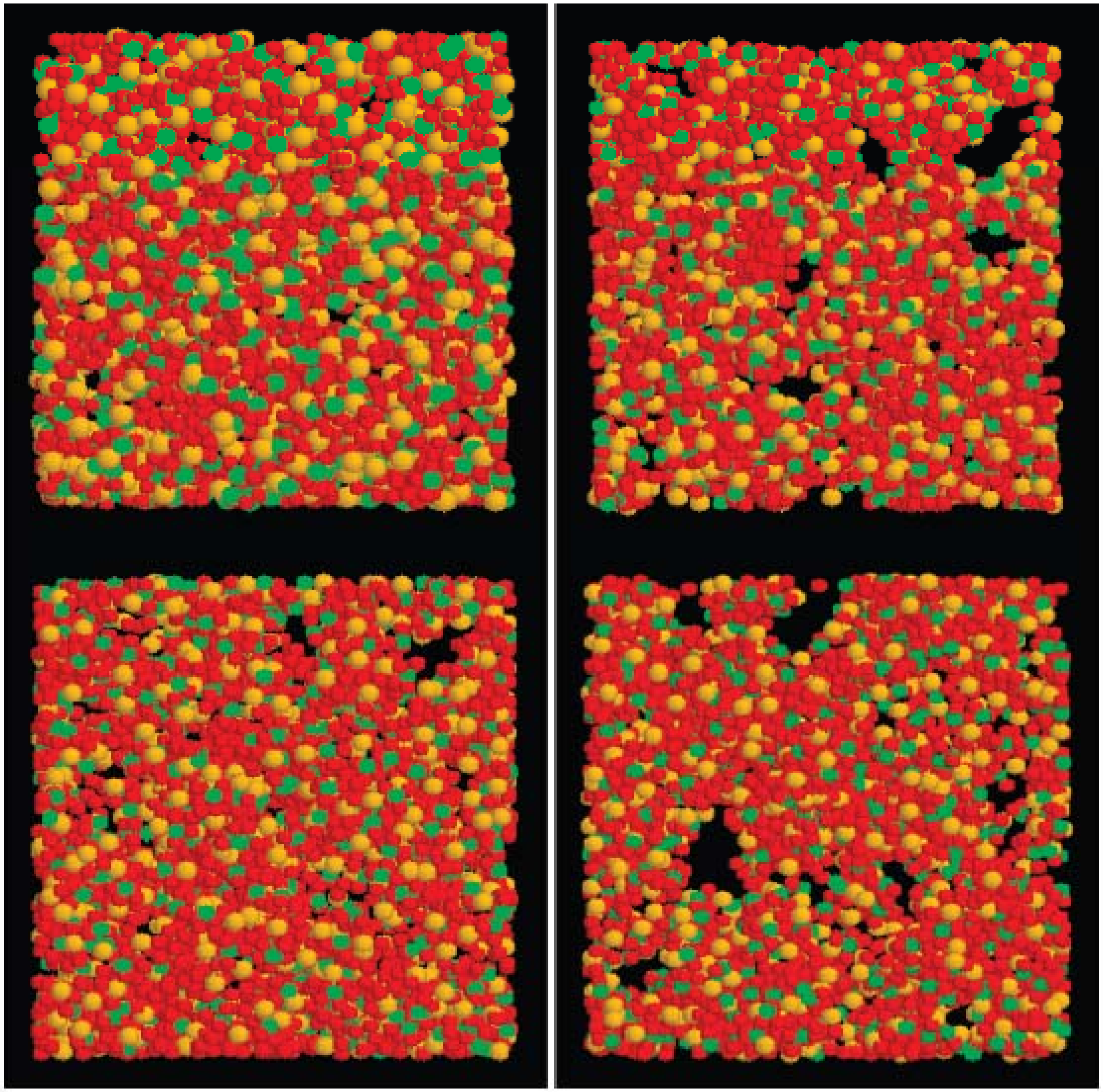
$\lambda(H_2O/SO_3H) = 4.4$ $\lambda = 12.8$

CF_x = grey; O of H_2O and SO_3^- = red; O of H_3O^+ = green; S = orange; H = white

There is nanoscale phase segregation into a hydrophobic (polymer backbone phase) and an aqueous phase.

S.T. Cui, J. Liu, M. Esai Selvan, D.J. Keffer, B.J. Edwards, and W.V. Steele, J. *Phys. Chem. B* **111** 2007.

Molecular Dynamics Snapshots



SSC PFSA EW = 678

SSC PFSA EW =978

Nafion EW = 844

Nafion EW = 1144

- **As equivalent weight increases, less uniform distribution of water.**
- **As side chain length increases, the trend is not clear from snapshots.**

Liu et al. J. Phys. Chem. C, 2010.

CF_x = grey; O of H_2O and SO_3^- = red; O of H_3O^+ = green; S = orange; H = white

Local Structure

SSC PFSA EW = 678 **SSC PFSA EW =978**

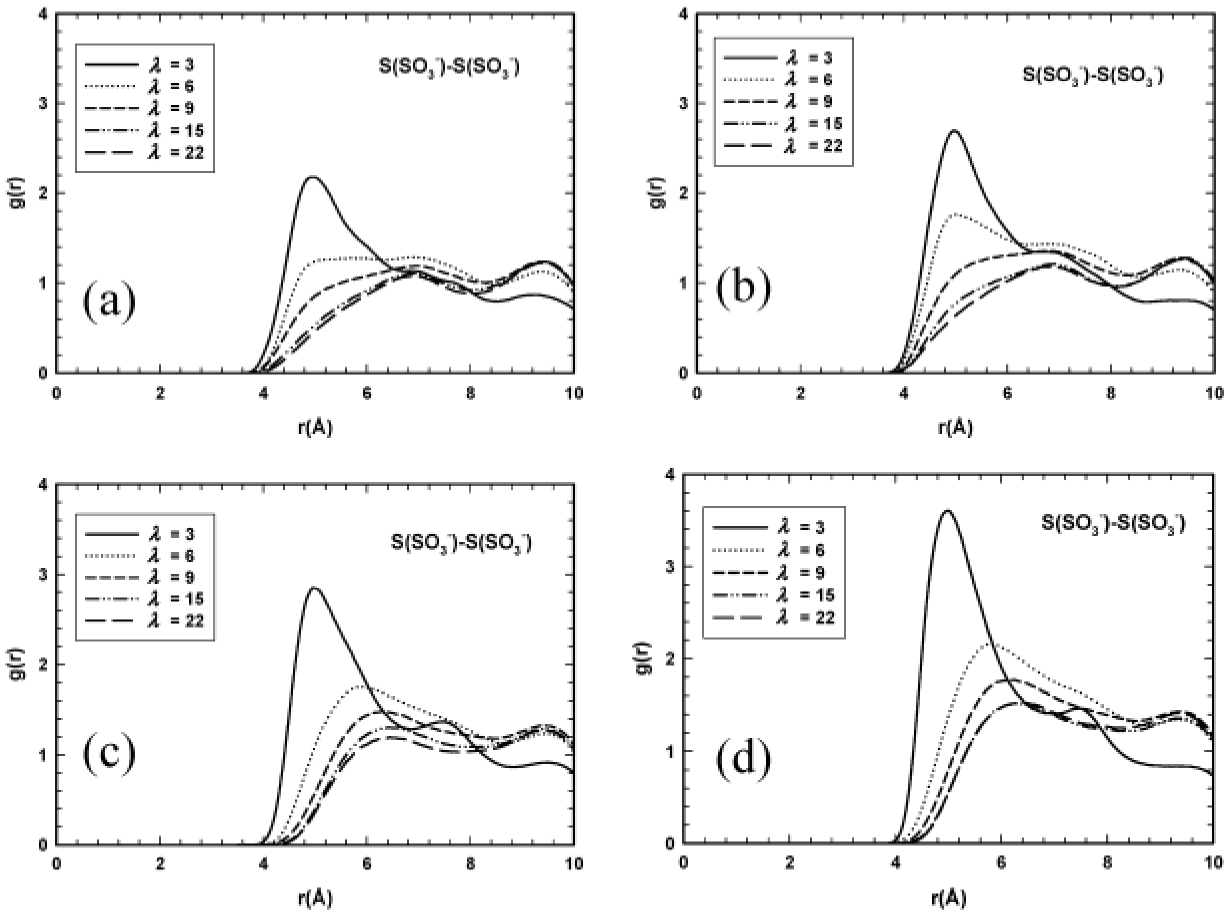


Figure 2. Sulfur−sulfur pair correlation functions for hydrated membranes: (a) SSC PFSA, EW = 678; (b) SSC PFSA, EW = 978; (c) Nafion, EW = 844; and (d) Nafion, EW = 1144.

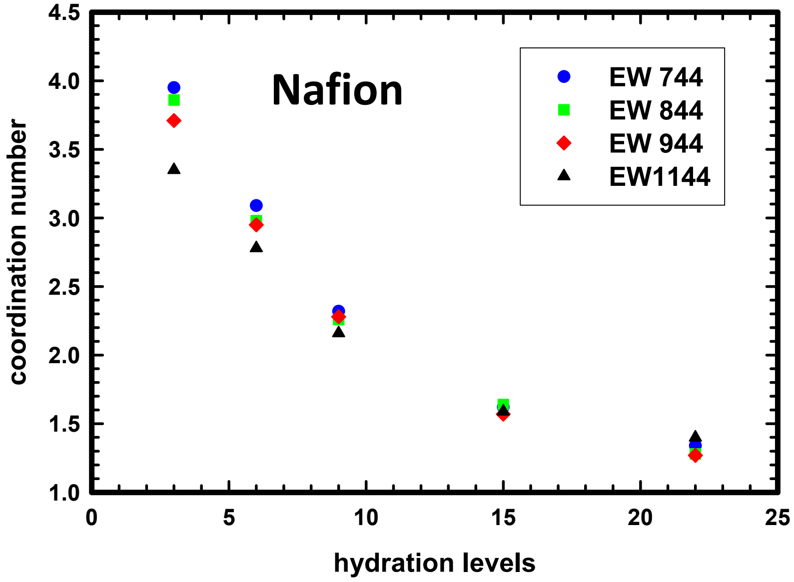
Nafion EW = 844 **Nafion EW = 1144**

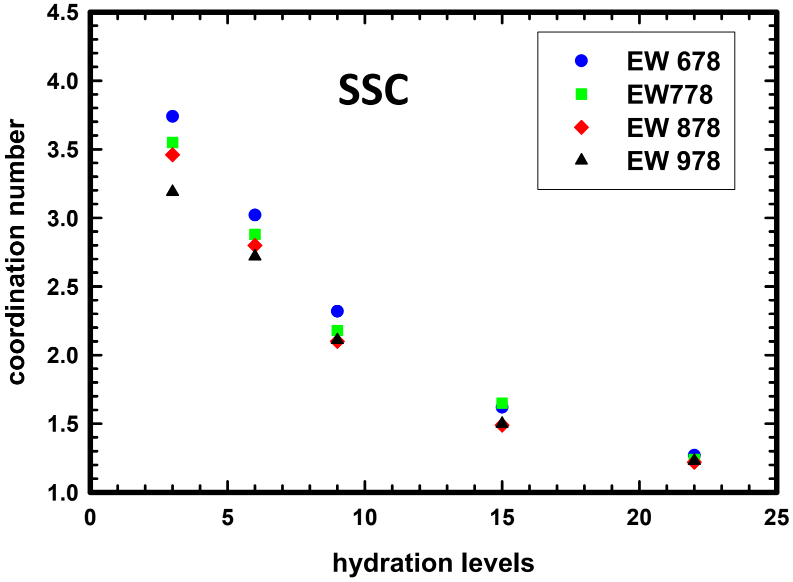
S-S Pair Correlation functions show more clustering of sulfur groups at low EW, low water content and longer side chains.

Liu et al. J. Phys. Chem. C, 2010.

S-S Coordination Numbers

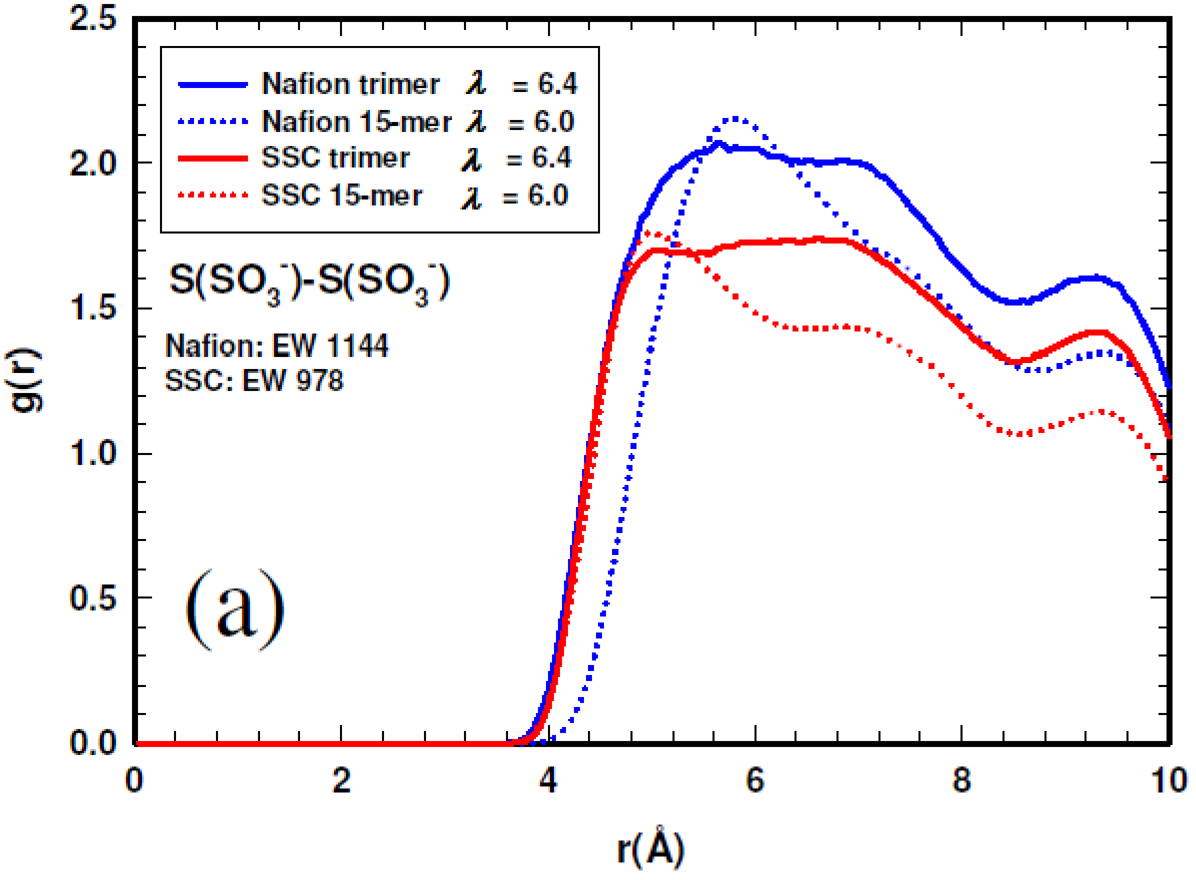
PCFs can be integrated to yield coordination numbers.





- **Sulfonate groups aggregate more easily in low EW materials.**
- **Sulfonate groups aggregate more easily in Nafion.**
- **Effect is observed most at low water content.**

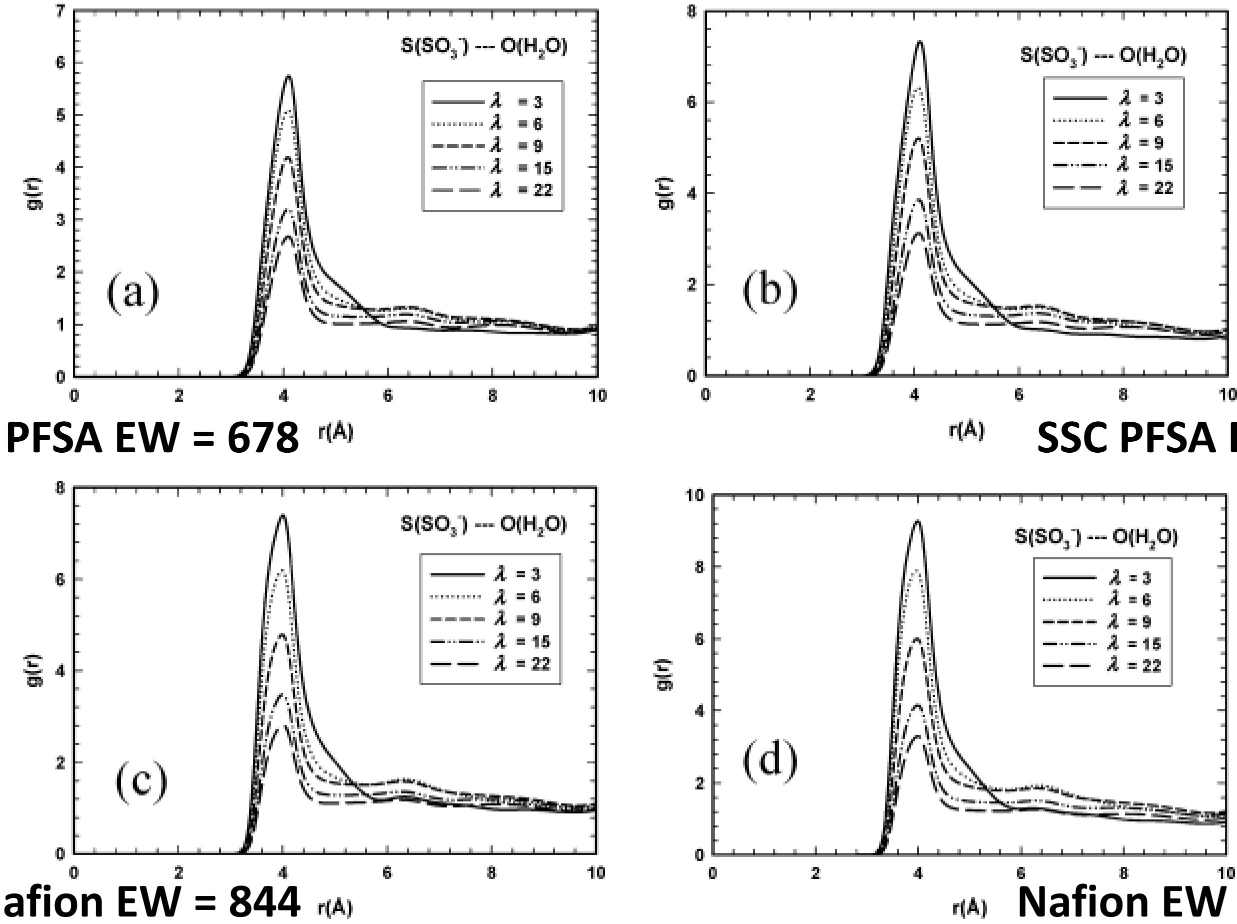
Local Structure



S-S Pair Correlation functions show the same trends independent of molecular weight.

Liu et al. J. Phys. Chem. C, 2010.

Local Structure



SSC PFSA EW = 678

SSC PFSA EW =978

Nafion EW = 844

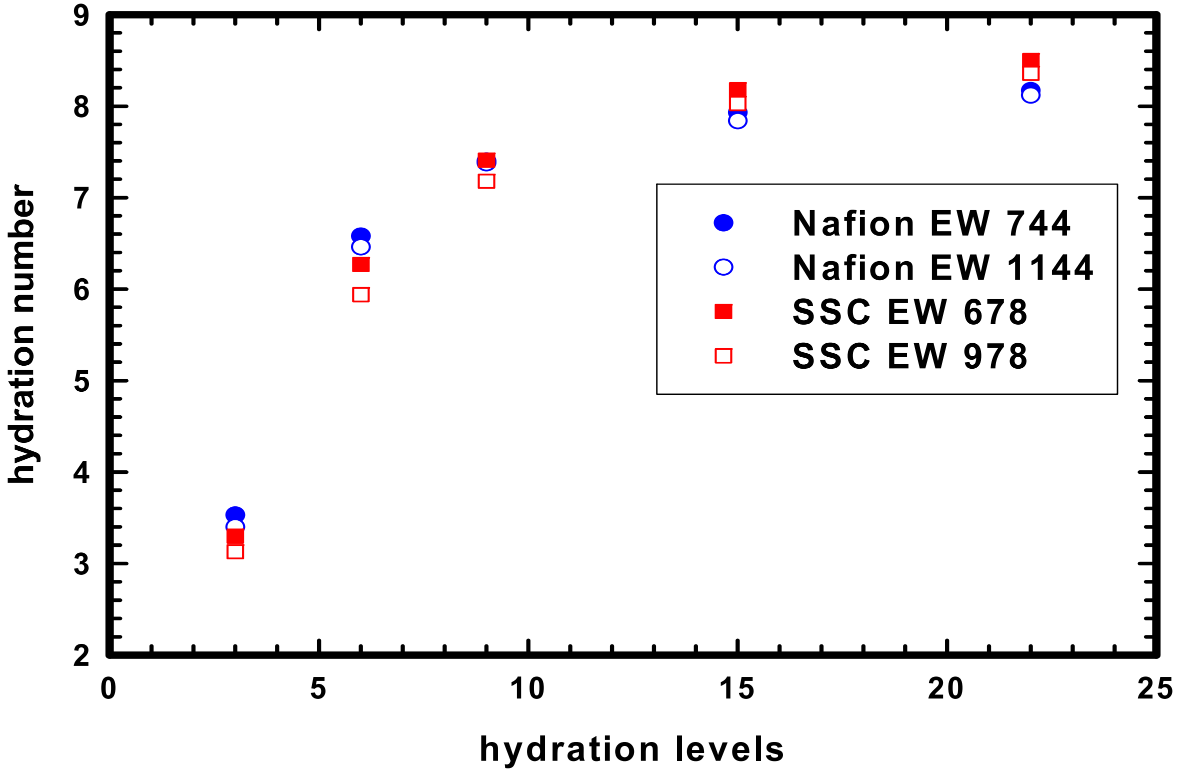
Nafion EW = 1144

Figure 3. Sulfur−water (oxgen atom of water) pair correlation functions for hydrated membranes: (a) SSC PFSA, EW = 678; (b) SSC PFSA, EW = 978; (c) Nafion, EW = 844; and (d) Nafion, EW = 1144.

Liu et al. J. Phys. Chem. C, 2010.

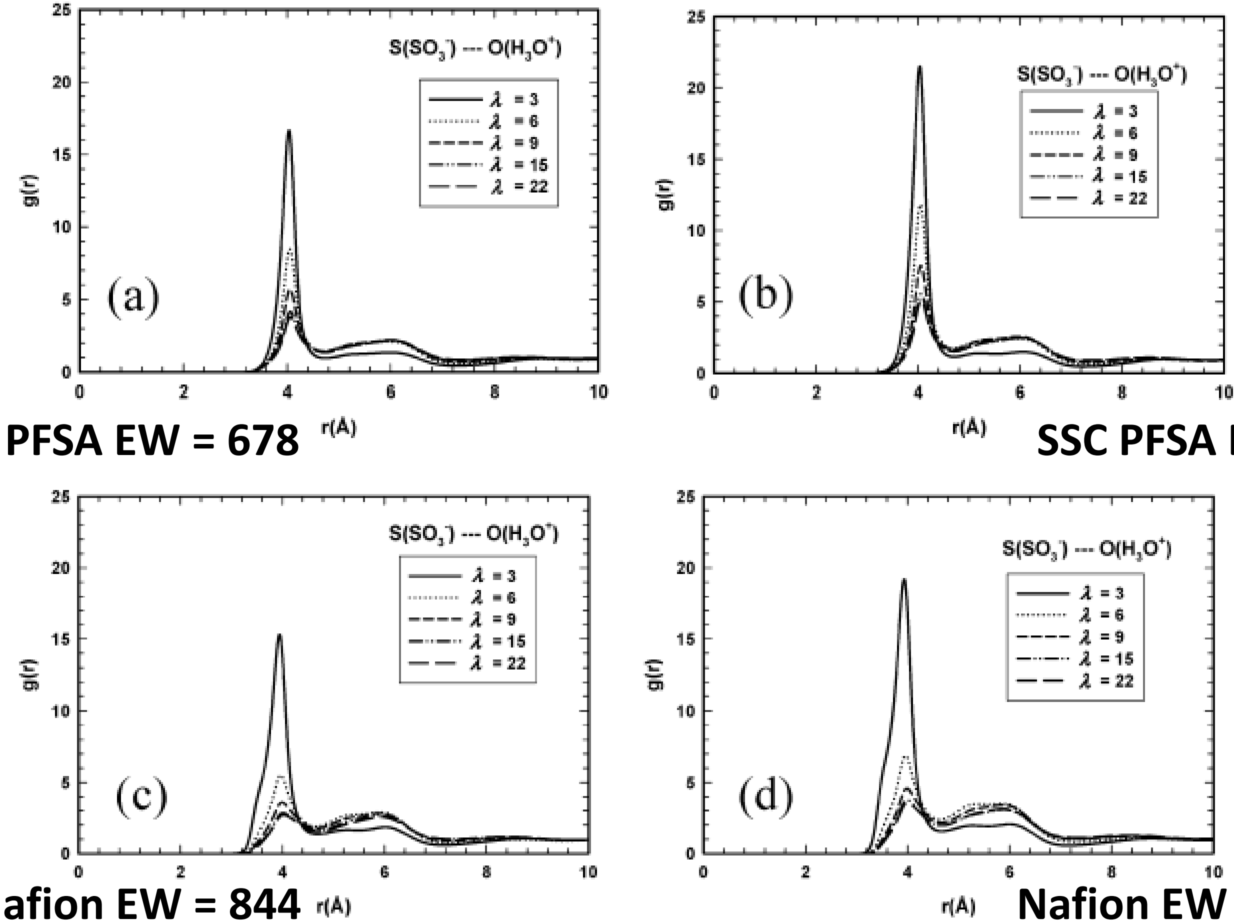
S-O_{H2O} PCFs show that low EW membrane tends to better hydrate sulfonate.
More water molecules tend to surround the sulfonate group with the longer side chain at low water cotnent, but the situation is opposite at the high hydration.

Hydration of Sulfonate Groups



- Sulfonate groups are more hydrated in low EW materials.
- Sulfonate groups are more hydrated in Nafion at low water content and more hydrated in SSC at high water contents. Previously seen.

Local Structure



SSC PFSA EW = 678

SSC PFSA EW =978

Nafion EW = 844

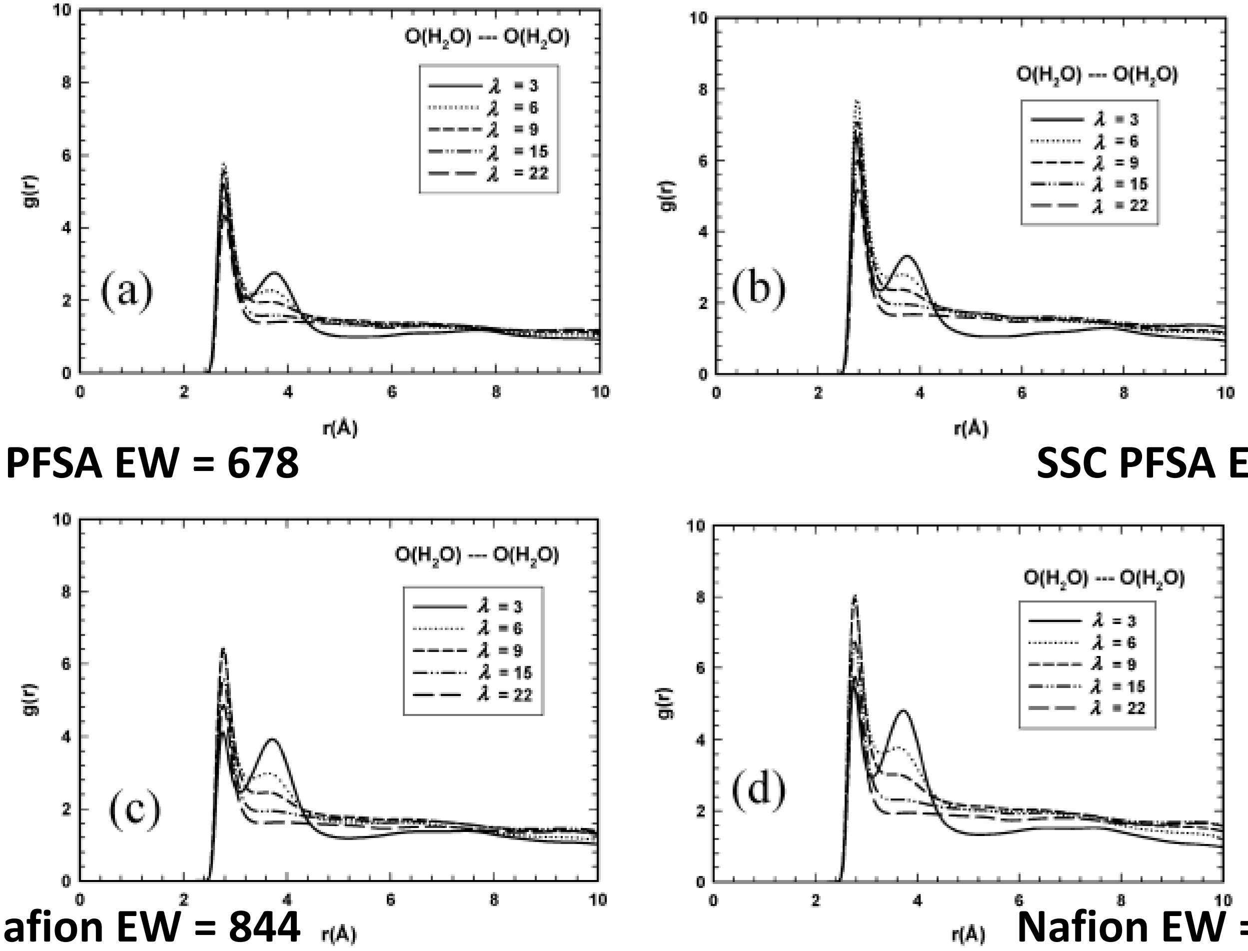
Nafion EW = 1144

Figure 4. Sulfur−hydronium ion (oxgen atom of hydronium ion) pair correlation functions for hydrated membranes: (a) SSC PFSA, EW = 678; (b) SSC PFSA, EW = 978; (c) Nafion, EW = 844; and (d) Nafion, EW = 1144.

Liu et al. J. Phys. Chem. C, 2010.

S-O_{H3O+} PCFs show more association in Nafion.
Association diminishes with increasing water content.

Local Structure



SSC PFSA EW = 678

SSC PFSA EW =978

Nafion EW = 844

Nafion EW = 1144

Figure 6. Water−water ion pair correlation functions for hydrated membranes: (a) SSC PFSA, EW = 678; (b) SSC PFSA, EW = 978; (c) Nafion, EW = 844; and (d) Nafion, EW = 1144.

Liu et al. J. Phys. Chem. C, 2010.

O_{H2O} -O_{H3O+} PCFs show better hydration of hydronium with an decrease in EW and an increase in side chain length.

Local Structure

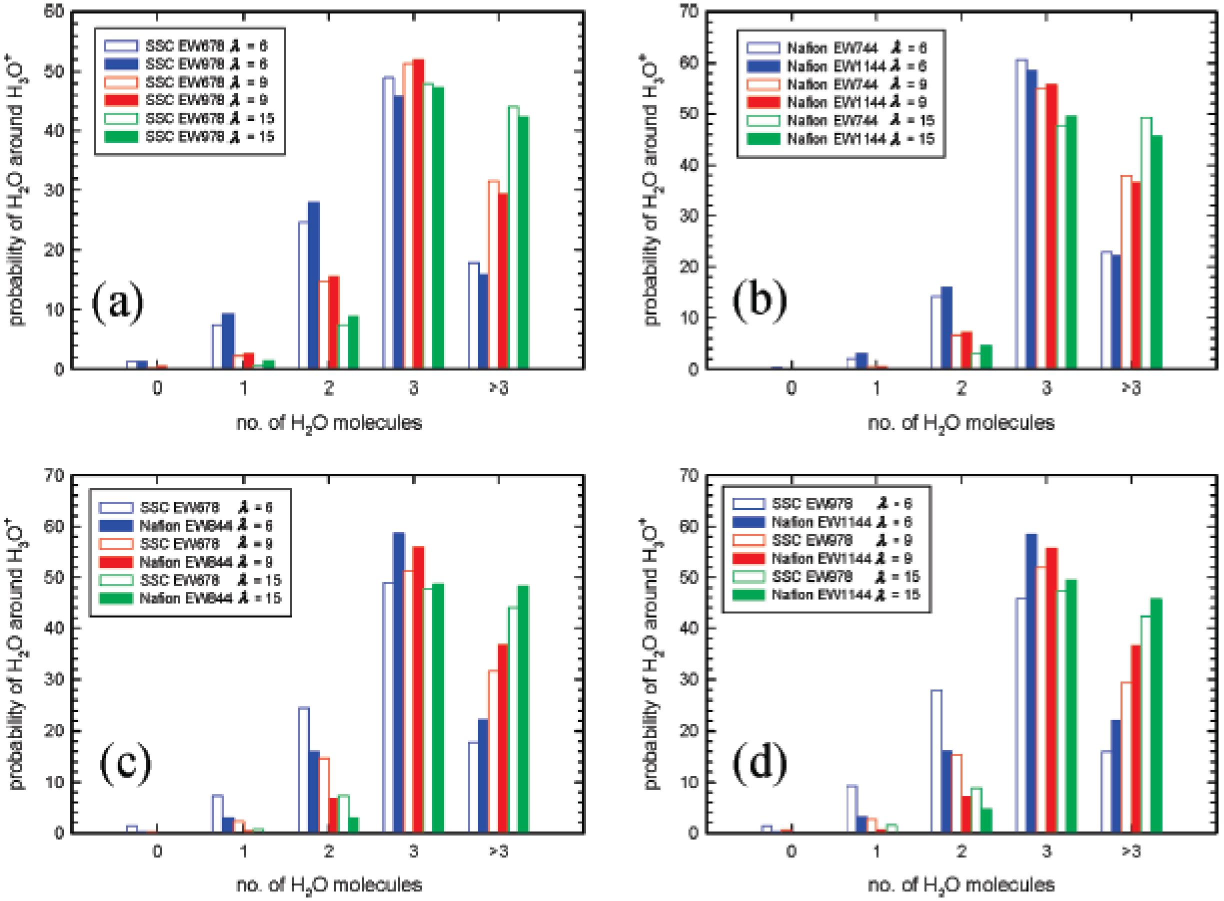
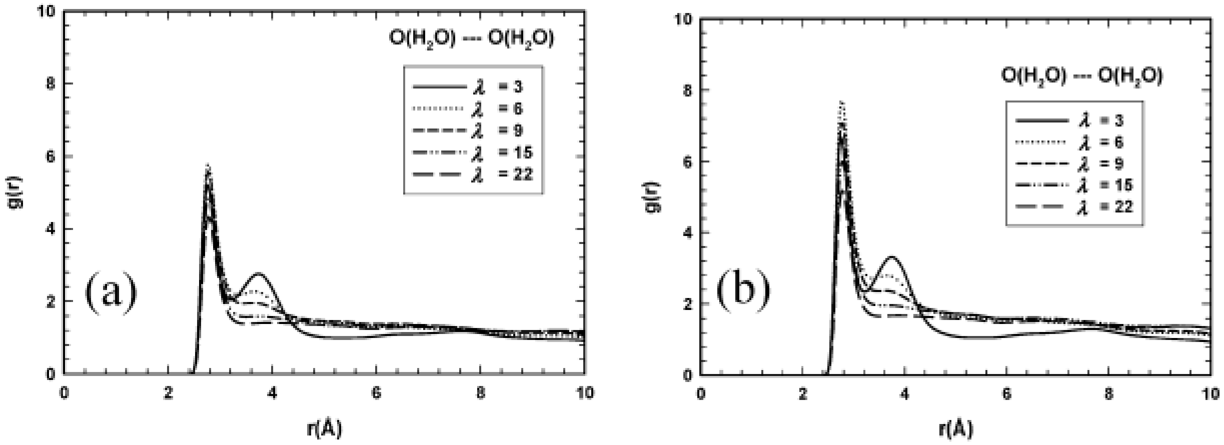


Figure 7. Histograms for hydration of hydronium ions at the three intermediate water contents: (a) SSC PFSA as a function of EW; (b) Nafion as a function of EW; (c) comparison of SSC PFSA and Nafion at low EW; and (d) comparison of SSC PFSA and Nafion at high EW.

Liu et al. J. Phys. Chem. C, 2010.

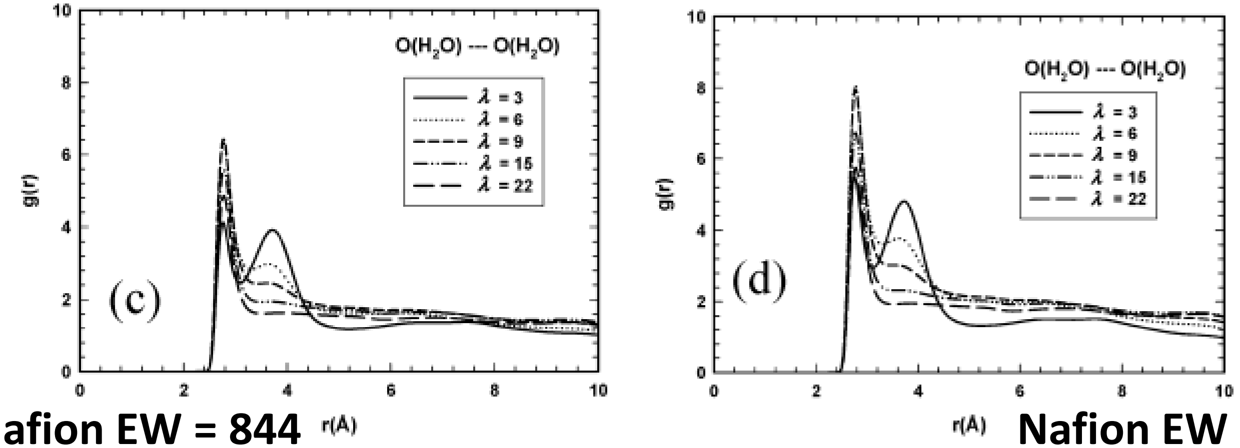
O_{H2O} -O_{H3O+} hydration histograms show better hydration of hydronium with an decrease in EW and an increase in side chain length.

Local Structure



SSC PFSA EW = 678

SSC PFSA EW =978



Nafion EW = 844

Nafion EW = 1144

Figure 6. Water−water ion pair correlation functions for hydrated membranes: (a) SSC PFSA, EW = 678; (b) SSC PFSA, EW = 978; (c) Nafion, EW = 844; and (d) Nafion, EW = 1144.

Liu et al. J. Phys. Chem. C, 2010.

O_{H2O} –O_{H2O} PCFs show better more aggregation of water with a decrease in EW and an increase in side chain length.

Distance Between Centers of Clusters

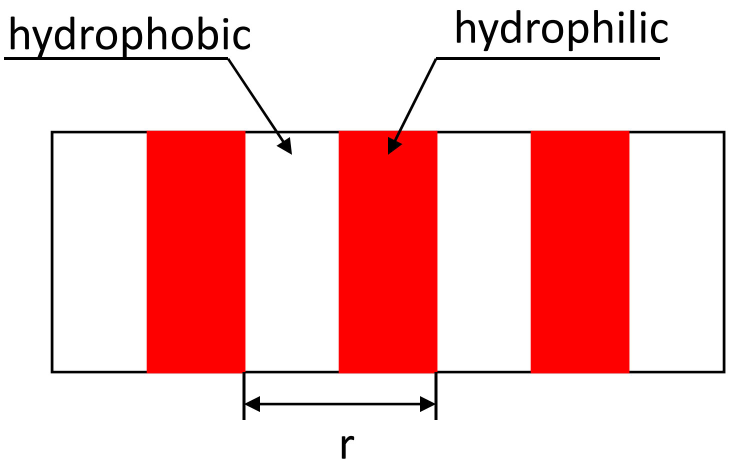
λ	SSC with different EW				Nafion with different EW			
	678	778	878	978	744	844	944	1144
3	18.04	19.74	20.60	20.60	22.17	24.01	22.04	20.38
6	22.18	24.32	24.64	27.12	24.32	26.00	27.92	30.40
9	24.32	27.93	N/A	27.52	N/A	N/A	N/A	N/A

*Cutoff distance is 30 Å.

- Structure factor is calculated as the Fourier transform of the water-water pair correlation function:

$$S(q) = 1 + 4\pi \frac{N}{V} \int [g(r) - 1)] \frac{\sin(qr)}{q} r dr$$

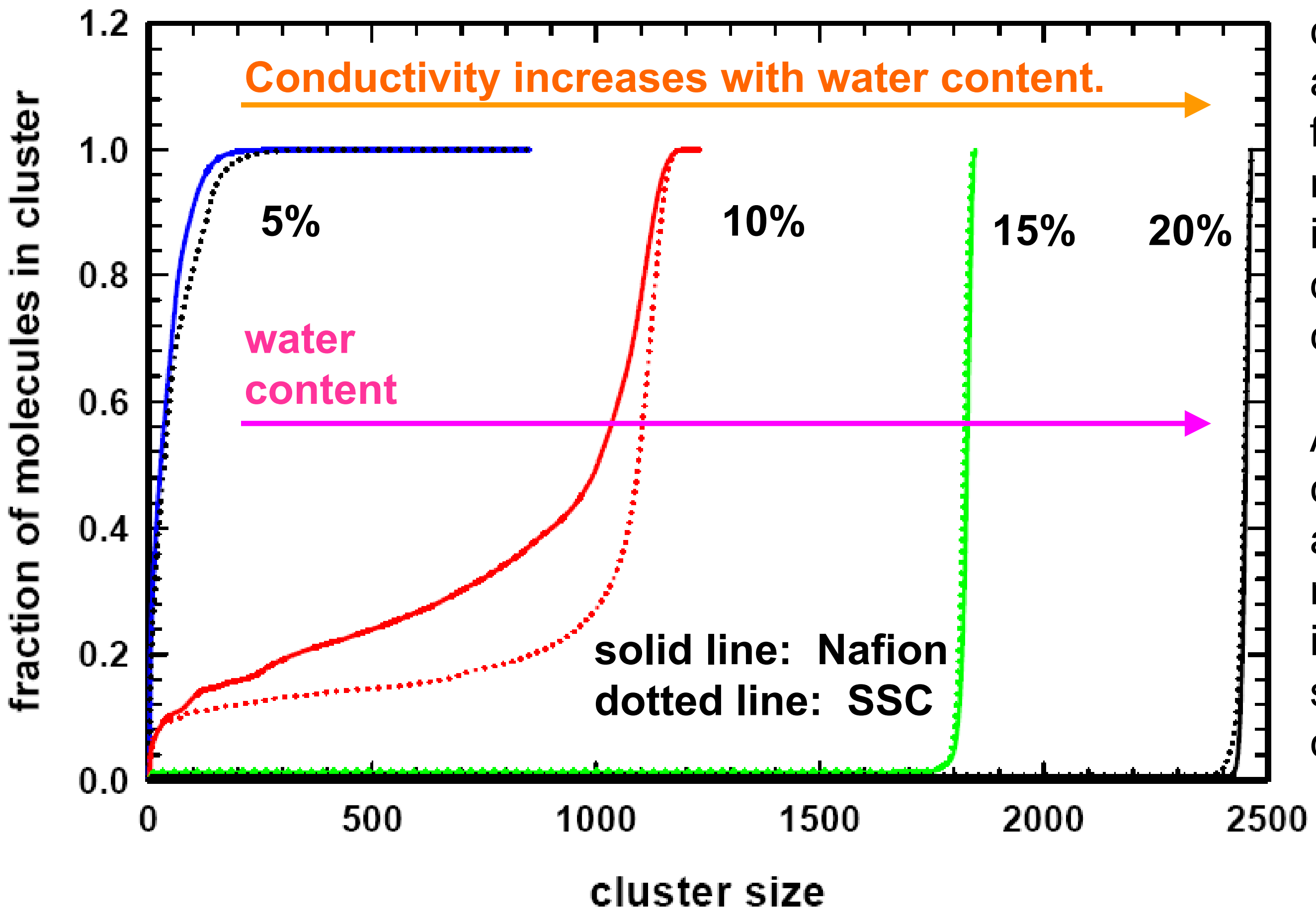
- Intercluster distance r = 2π/q Å



Fourier Transform of O_{H2O} –O_{H2O} PCFs shows bigger clusters characteristic dimensions in larger EW system (more polymer) and with Nafion.

global structure: water clusters

cumulative probability distributions

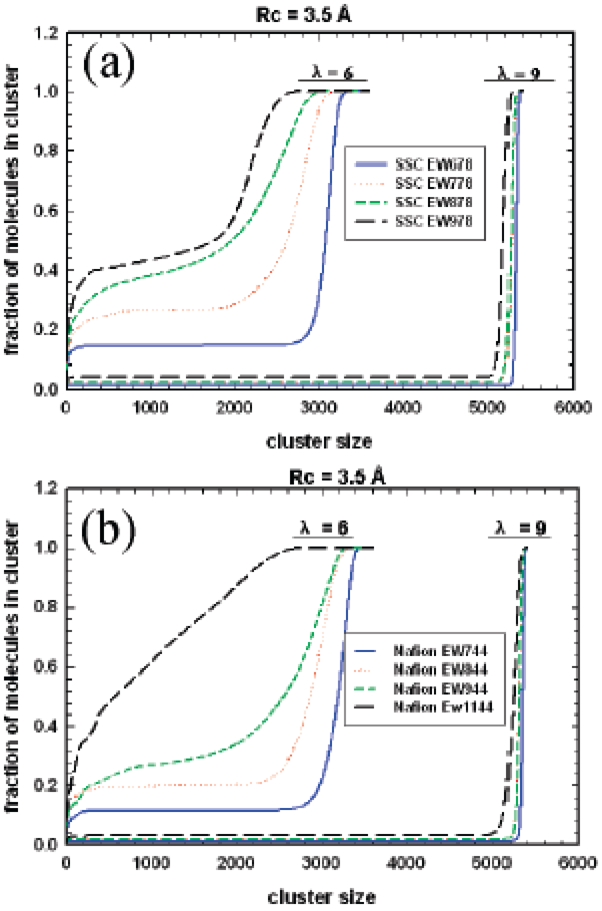


At low water content, an appreciable fraction of water molecules exist in many small discontinuous clusters. (bad)

At high water content, virtually all water molecules exist in a single sample-spanning cluster. (good)

At intermediate water contents, SSC provides a better connected aqueous network.

global structure: water clusters



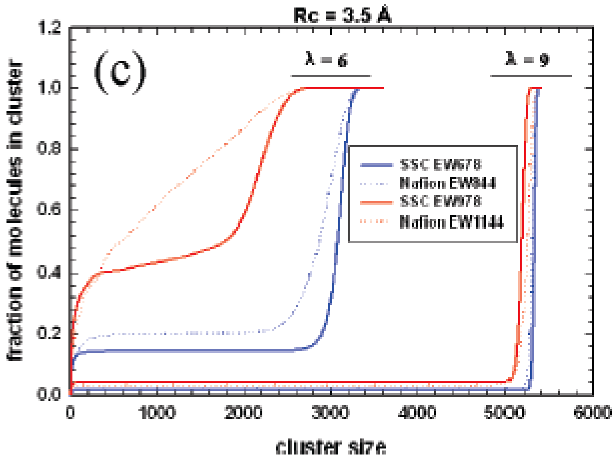
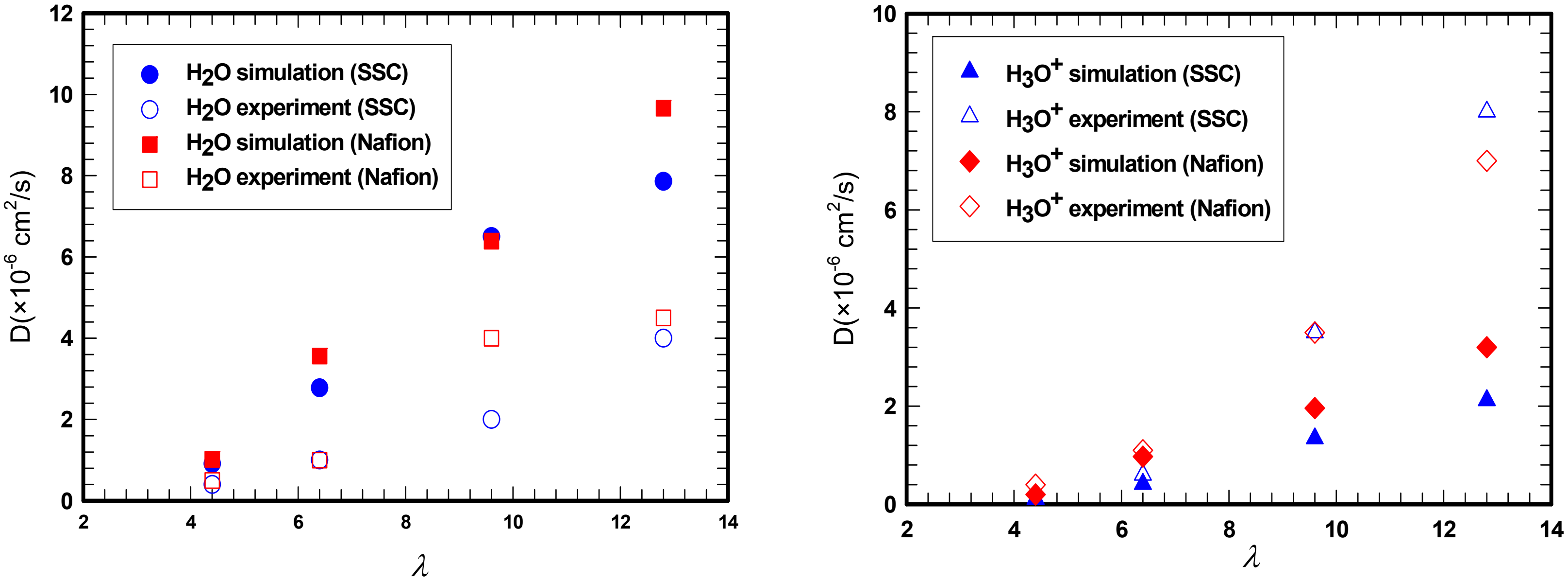


Figure 8. Cumulative probability distribution functions for number of water molecules in a cluster for a cutoff distance of 3.5 Å at intermediate water contents: (a) SSC PFSA as a function of EW; (b) Nafion as a function of EW; and (c) comparison of SSC and Nafion.

Better connectivity at smaller EW and better connectivty in SSC.

Diffusion coefficients
Comparison with Experiment

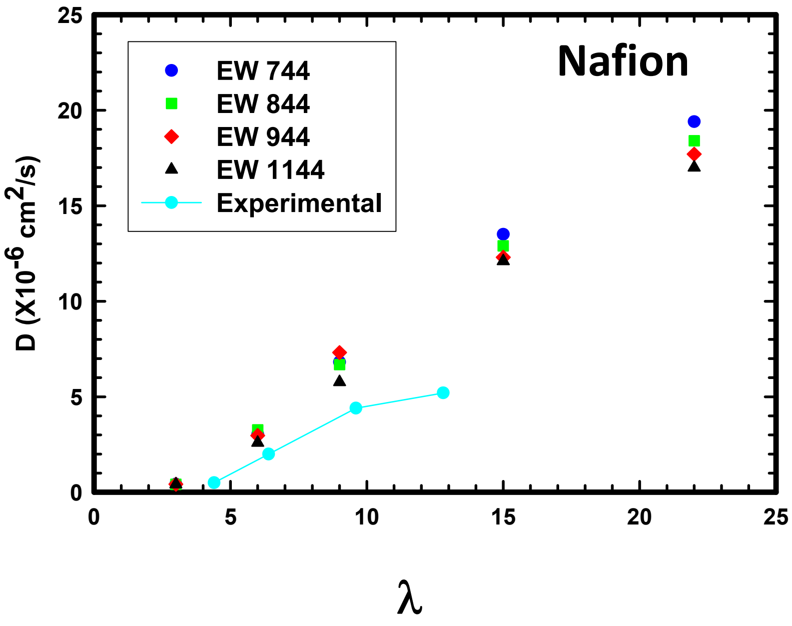
Diffusion coefficients for H_2O & H_3O^+: Simulated vs. Experiment

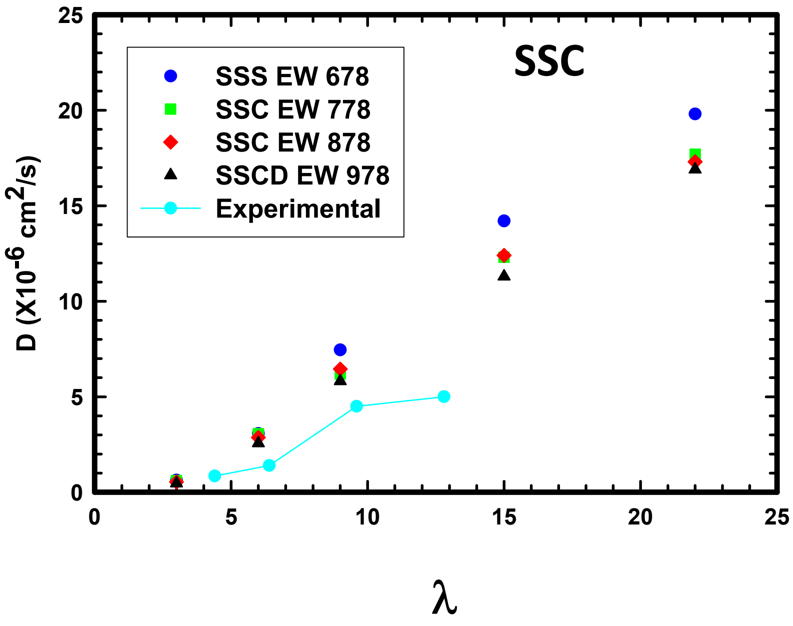


- The H_2O diffusion coefficients are higher than experimental values because we use TIP3P water model, which yields high diffusivities relative to experiment.
- The H_3O^+ diffusion coefficients are lower than experimental data because our simulations neglect structural diffusion.

S.T. Cui, J. Liu, M. Esai Selvan, S.J. Paddison, D.J. Keffer, B.J. Edwards, *J. Phys. Chem. B* **112**, 13273, 2008.

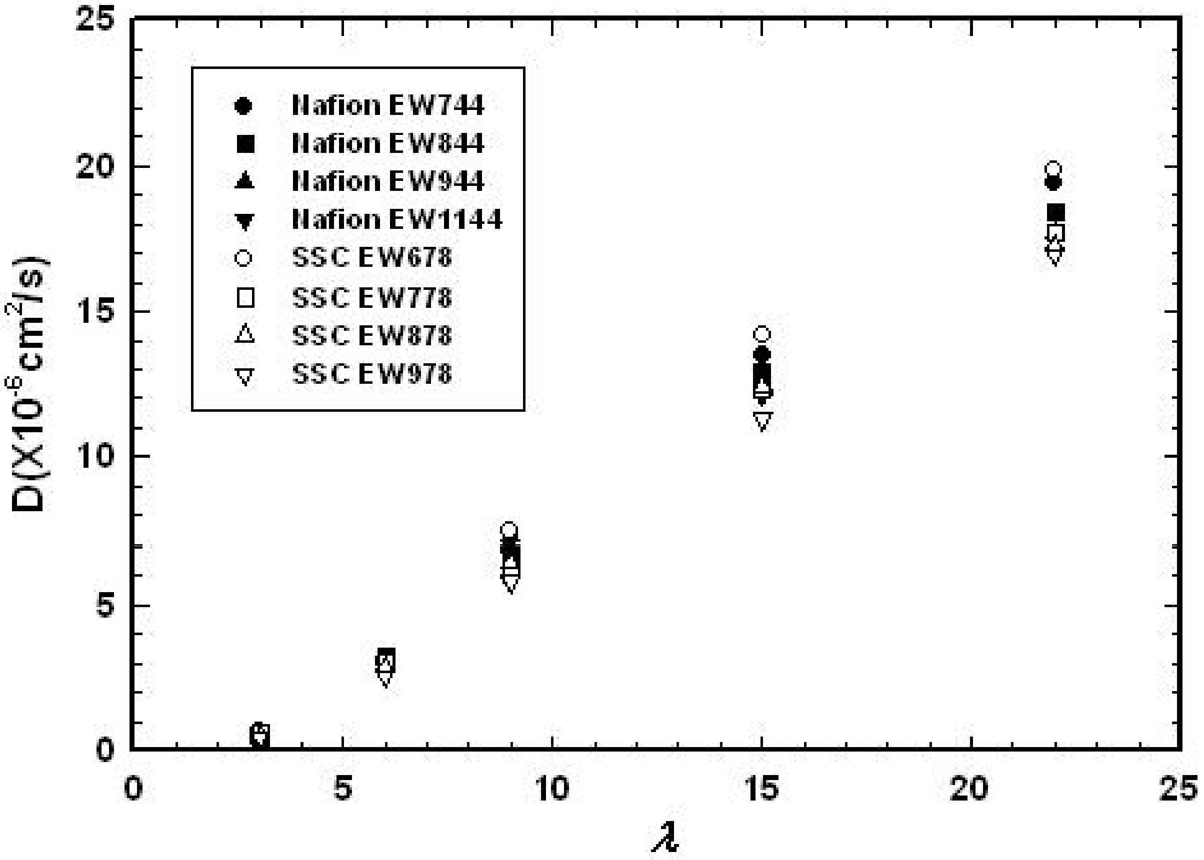
Water Diffusion Coefficients





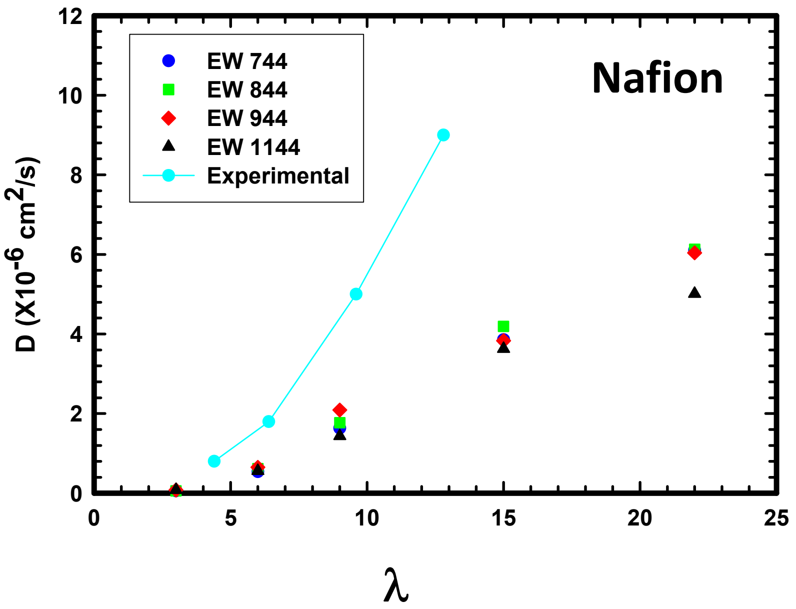
- The diffusivity of water increases with increasing water content in all materials.
- Simulated diffusivities are higher than experimental diffusivities due to TIP3P model, which gives a high bulk water diffusivity.
- Little dependence on EW at low water content and little dependence on side chain length at all water contents.

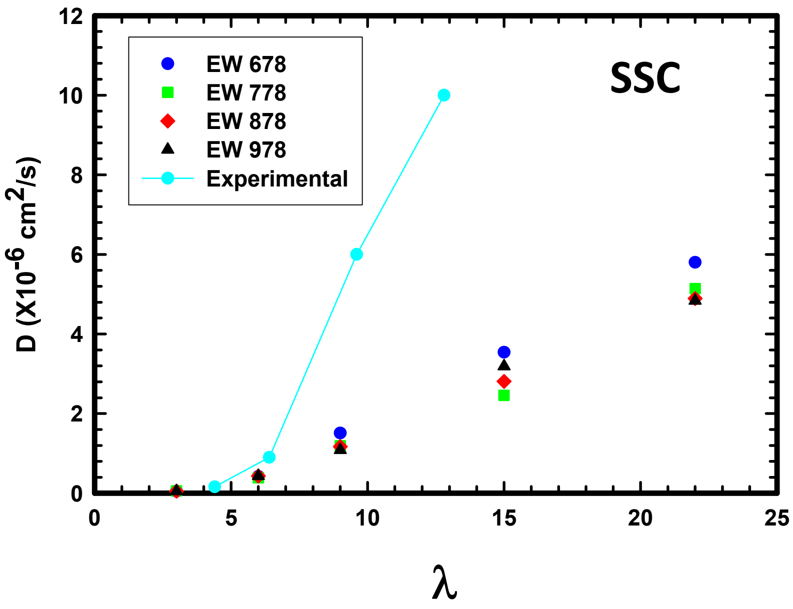
Diffusion coefficients as a function of polymer chemistry



- Modest dependence of water diffusivity on polymer chemistry. Consistent with recent experimental work showing superior performance of SSC is largely due to enhanced mechanical properties.

H_3O^+ Diffusion Coefficients





- Charge diffusivities are well below experimental data at high water content since the simulations do not include structural diffusion.
- Weak dependence on EW and side chain length.

Conclusions

Impact of Side Chain Length: in Nafion, there is
(1) more clustering of the sulfonate groups,
(2) more clustering of water around the sulfonate groups at low water contents, but less clustering of water around the sulfonate groups at high water contents,
(3) less clustering of the hydronium ions around the sulfonate groups,
(4) more clustering of water around the hydronium ions,
(5) more local water-water clustering,
(6) a more poorly connected aqueous domain,
(7) a larger characteristic dimension from the structure factor,
(8) a larger interfacial surface area to aqueous volume ratio.

Taken collectively, these observations paint a picture of the morphology of the hydrated membrane in which an increase in side chain length results in more poorly connected aqueous domains. The aqueous domains allow for better clustering of the species (sulfonate groups, water, and hydronium ions) in the aqueous phase. These changes in morphology due to the difference in side chain length do not yield an appreciable difference in water diffusivity. We do observe a slightly higher diffusivity for the hydronium ion in Nafion than in the SSC PFSA.

Conclusions

Impact of Equivalent Weight: When one decreases the equivalent weight (EW) in either SSC PFSA or Nafion, there is
(1) more clustering of the sulfonate groups,
(2) more clustering of water around the sulfonate groups,
(3) little change in the clustering of the hydronium ions around the sulfonate groups,
(4) more clustering of water around the hydronium ions,
(5) more local water-water clustering,
(6) a better connected aqueous domain,
(7) a smaller characteristic dimension from the structure factor, and
(8) A smaller interfacial surface area to aqueous volume ratio.

These changes in morphology due to the difference in EW result in a higher diffusivity for water at lower EW. We also observe higher diffusivities for the hydronium ion at lower EW for intermediate and high water contents. The diffusivity of water is controlled by a balance between connectivity and confinement. The lower EW enhances connectivity and reduces confinement, both of which favor an increase in diffusivity. The longer side chain reduces connectivity and reduces confinement, which are in opposition to each other, and result in no significant change in the diffusivity.

Conclusions

Impact of molecular weight:
Finally, we compared SSC PFSA and Nation chains composed of 3 and 15 monomeric units and found that the qualitative observations given above are independent of the MW, at least in the low range studied herein.

Structural differences do not lead to great transport differences. So what is causing the difference in behavior:

From: Kreuer et al. J. Power Sources, 2008.

“No distinct differences in water and proton transport and in the hydrophobic/hydrophilic separation as a function of water volume fraction were observed for SSC PFSA ionomers (Dow) compared to Nafion of the same equivalent weight. The significantly higher elastic modulus of Dow may be the sole reason for its superior performance as the electrolyte in a fuel cell. The better mechanical properties allow for the formation of membranes with higher IEC (lower equivalent weight) which leads to an increased concentration of protonic charge carriers and a reduction in hydrophobic/hydrophilic separation.”

IEC = ion exchange capacity