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

Lecture 02. Structure of Polymer Electrolyte Membranes

Dept. of Chemical & Biomolecular Engineering
Yonsei University
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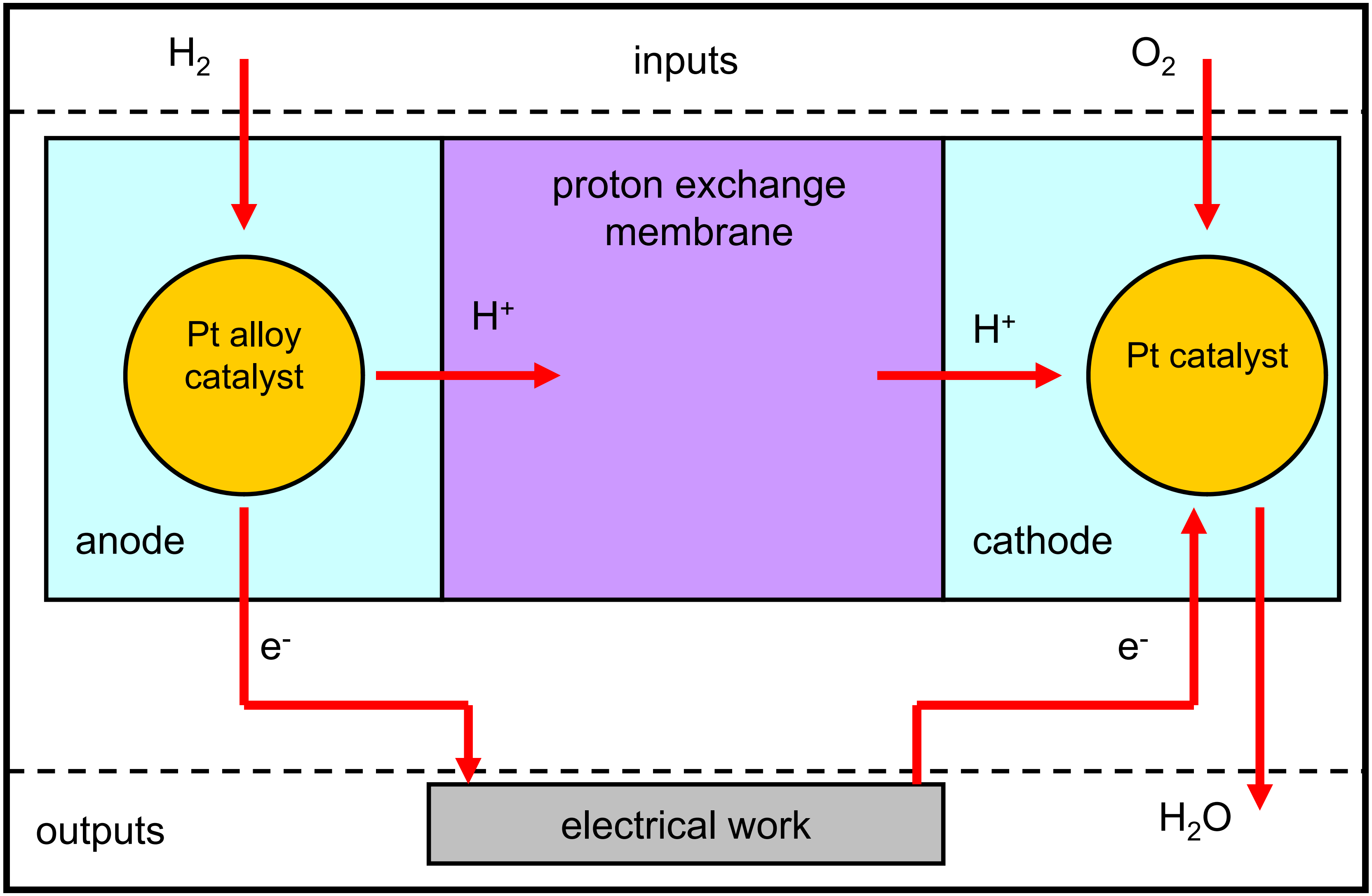
Prof. David Keffer
dkeffer@utk.edu

Lecture Outline

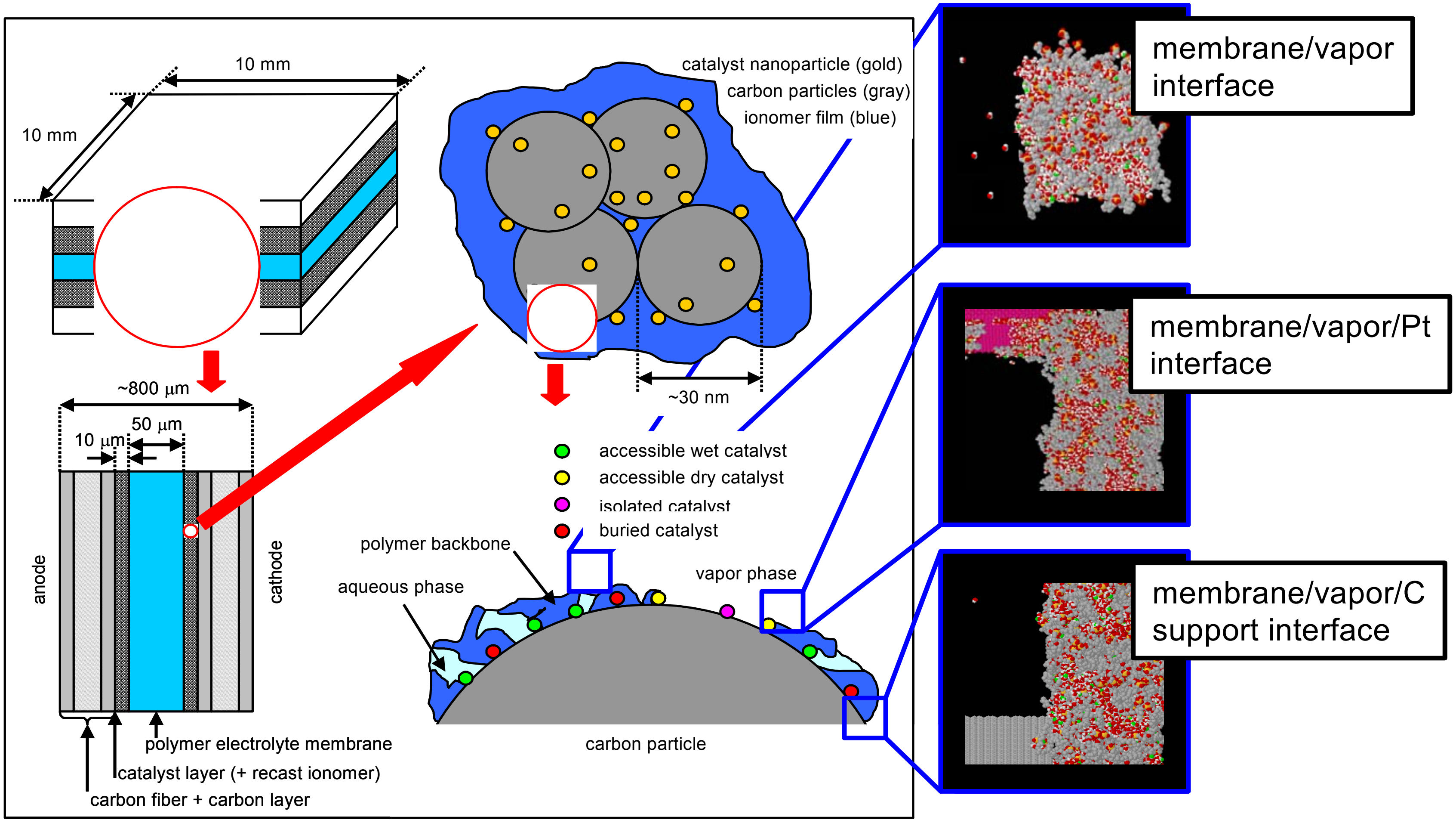
- Review of Structure
- Models of membrane morphology from the literature
- Introduction to Molecular Dynamics (MD) simulation
- Local Structure and Global Morphology of PEMs from MD simulation

how fuel cells work: conceptual level



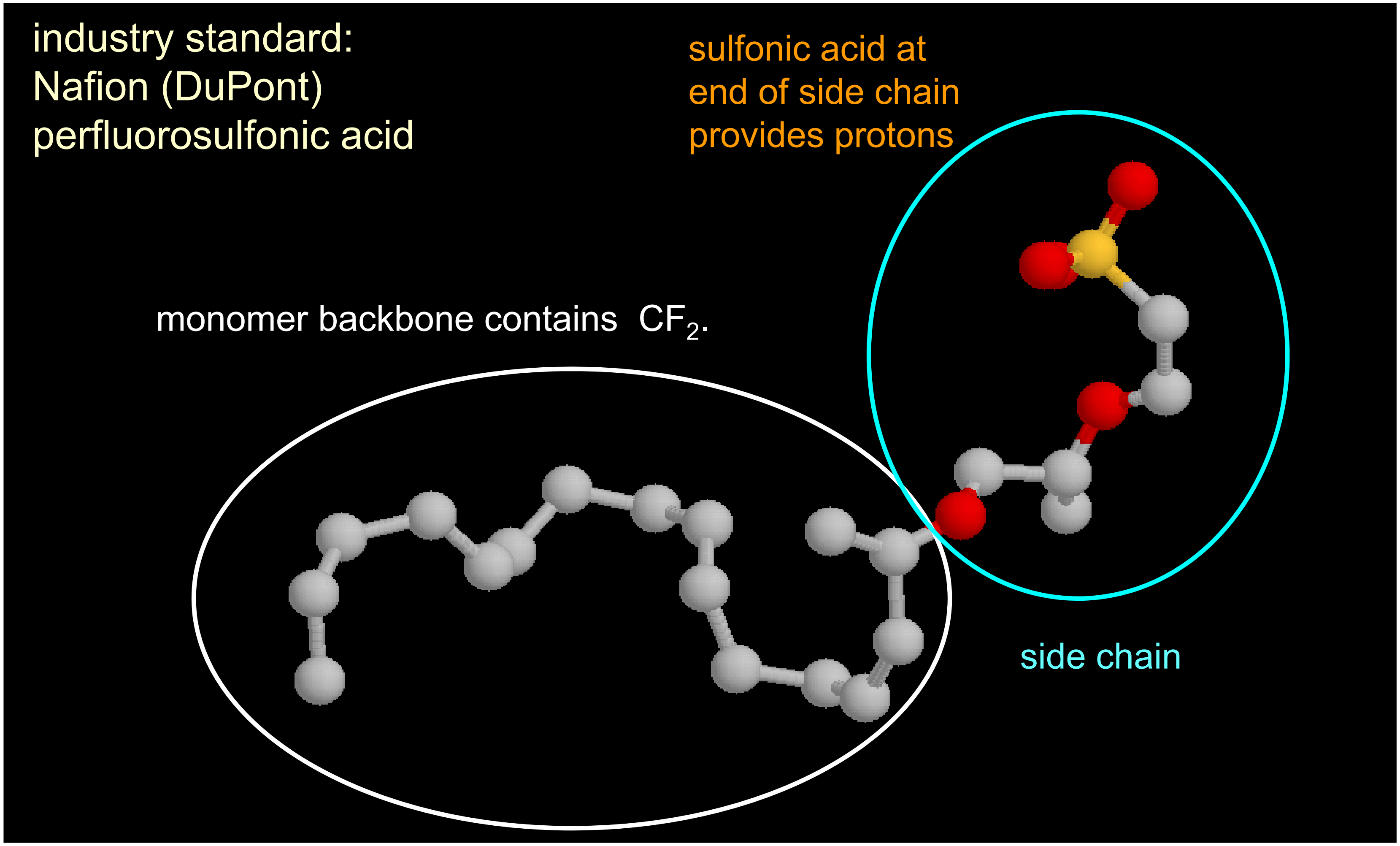
Overview of Structure

A membrane electrode assembly from the macroscale to the molecular scale



Industry Standard Membrane

proton exchange membranes are polymer electrolytes



industry standard:
Nafion (DuPont)
perfluorosulfonic acid

sulfonic acid at
end of side chain
provides protons

monomer backbone contains CF_2.

side chain

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

Industry Standard Membrane

Morphological models

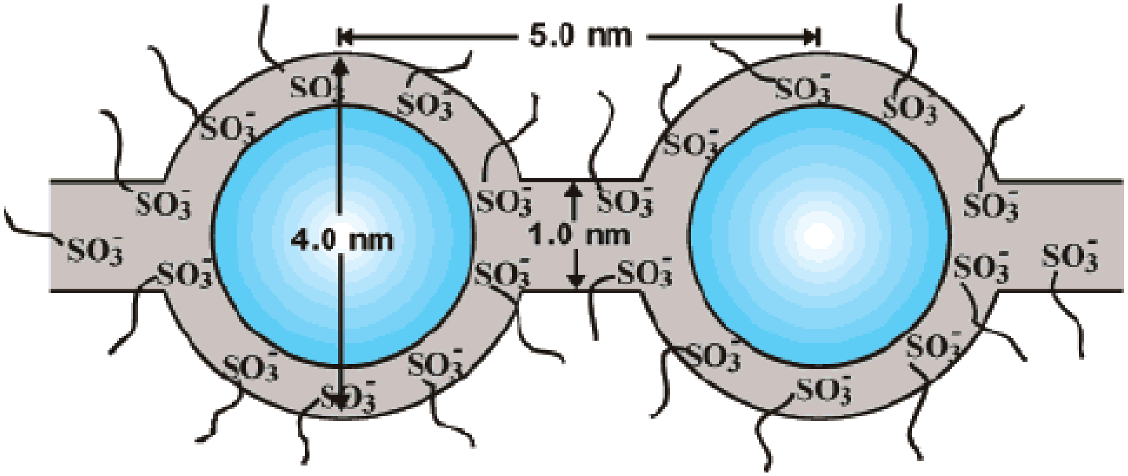
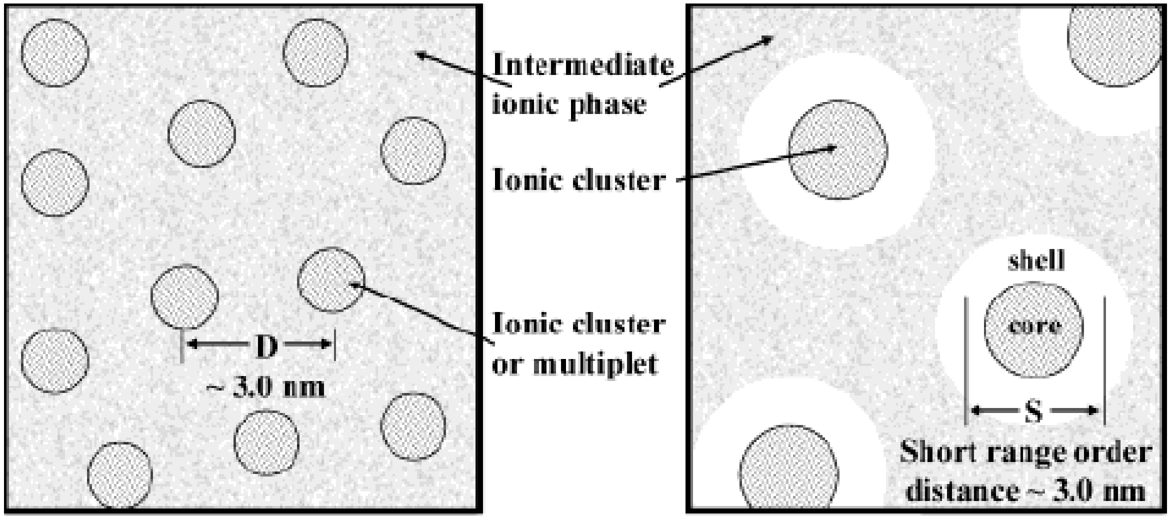


Figure 1. Cluster-network model for the morphology of hydrated Nafion. (Adapted with permission from ref 16. Copyright 1983 Elsevier.)

Mauritz & Moore, *Chem. Rev.* 2004.

Industry Standard Membrane

Morphological models



(a) (b)

Figure 2. Two morphological models used to describe the origin of the ionic SAXS maximum observed for Nafion: (a) the modified hard-sphere model depicting interparticle scattering and (b) the depleted-zone core−shell model depicting intraparticle scattering. (Adapted with permission from ref 36. Copyright 1981 American Chemical Society.)

Mauritz & Moore, *Chem. Rev.* 2004.

Industry Standard Membrane

Morphological models

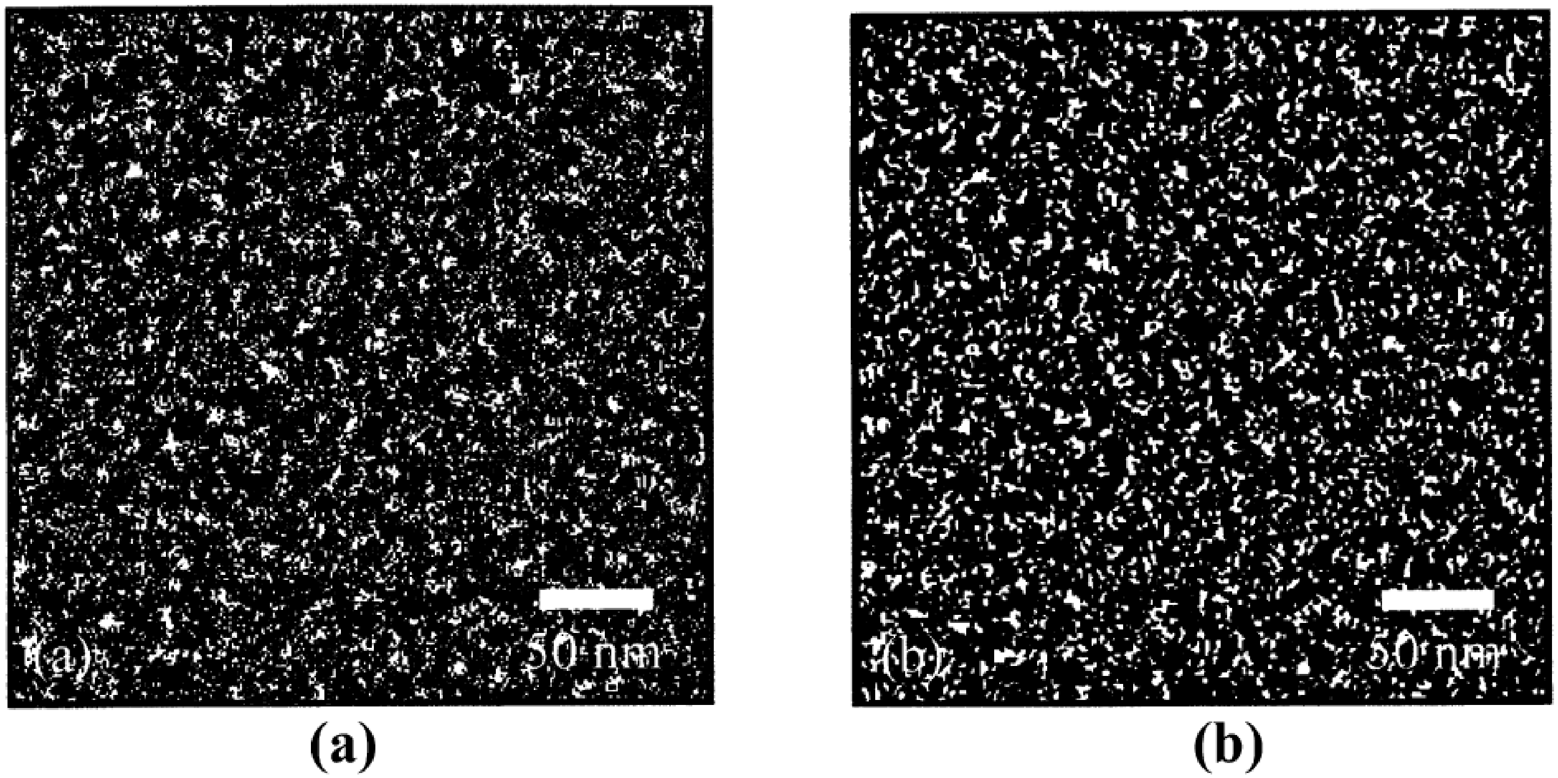


Figure 6. MaxEnt reconstruction of SAXS data from as-received Nafion equilibrated under (a) ambient humidity and (b) 100% RH. (Reprinted with permission from ref 63. Copyright 2000 American Chemical Society.)

Mauritz & Moore, *Chem. Rev.* 2004.

Industry Standard Membrane

Morphological models

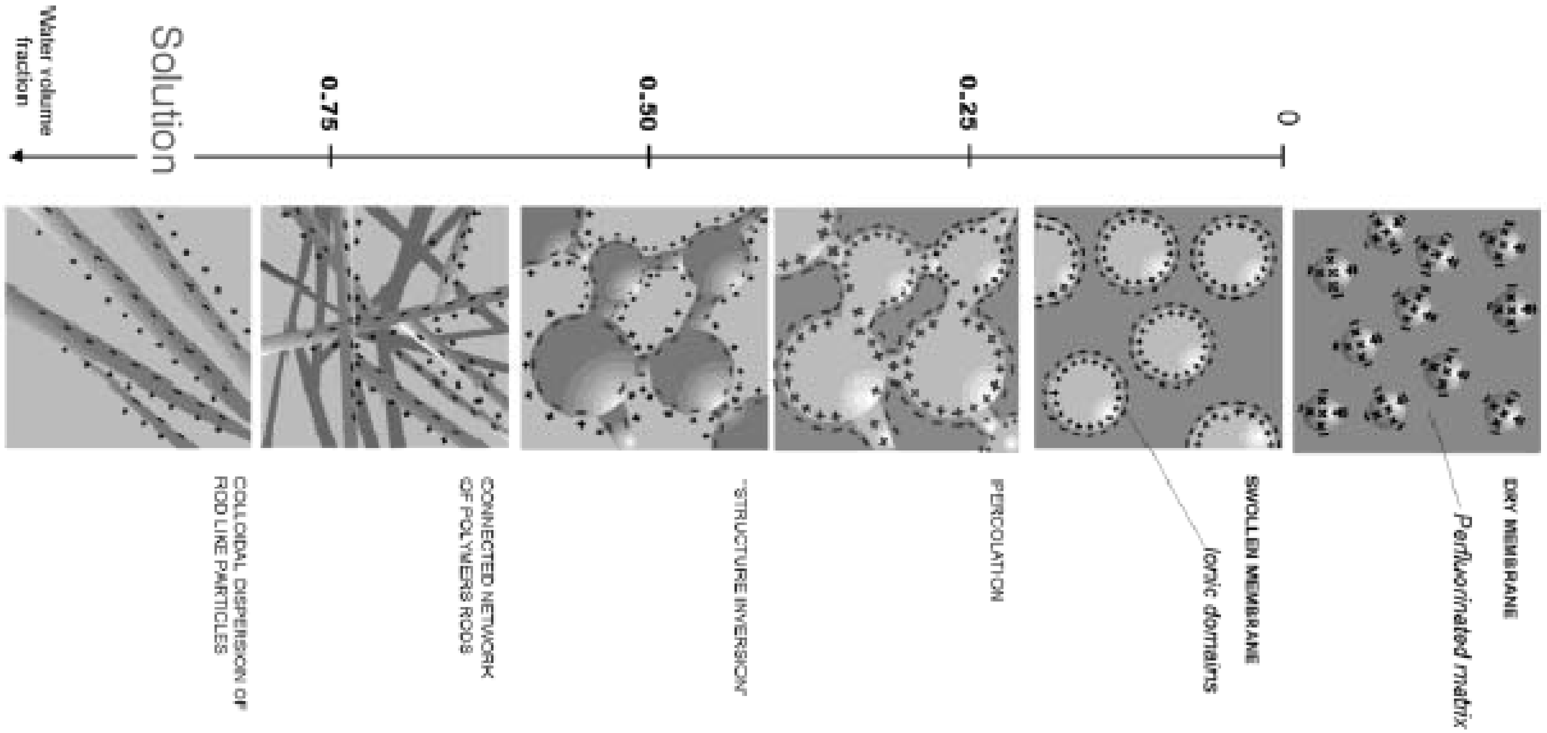


Figure 7. Conceptual model for the morphological reorganization and continuity of the ionic domains in Nafion as the dry membrane is swollen with water to the state of complete dissolution. (Reprinted with permission from ref 76. Copyright 2000 Elsevier.)

Mauritz & Moore, *Chem. Rev.* 2004.

Industry Standard Membrane

Morphological models

Figure 8. Schematic representation of an entangled network of elongated rodlike aggregates in Nafion. Long-range heterogeneities arising from bundles of locally ordered aggregates are proposed to give rise to the low angle increase in scattered intensity. (Reprinted with permission from the original author.)

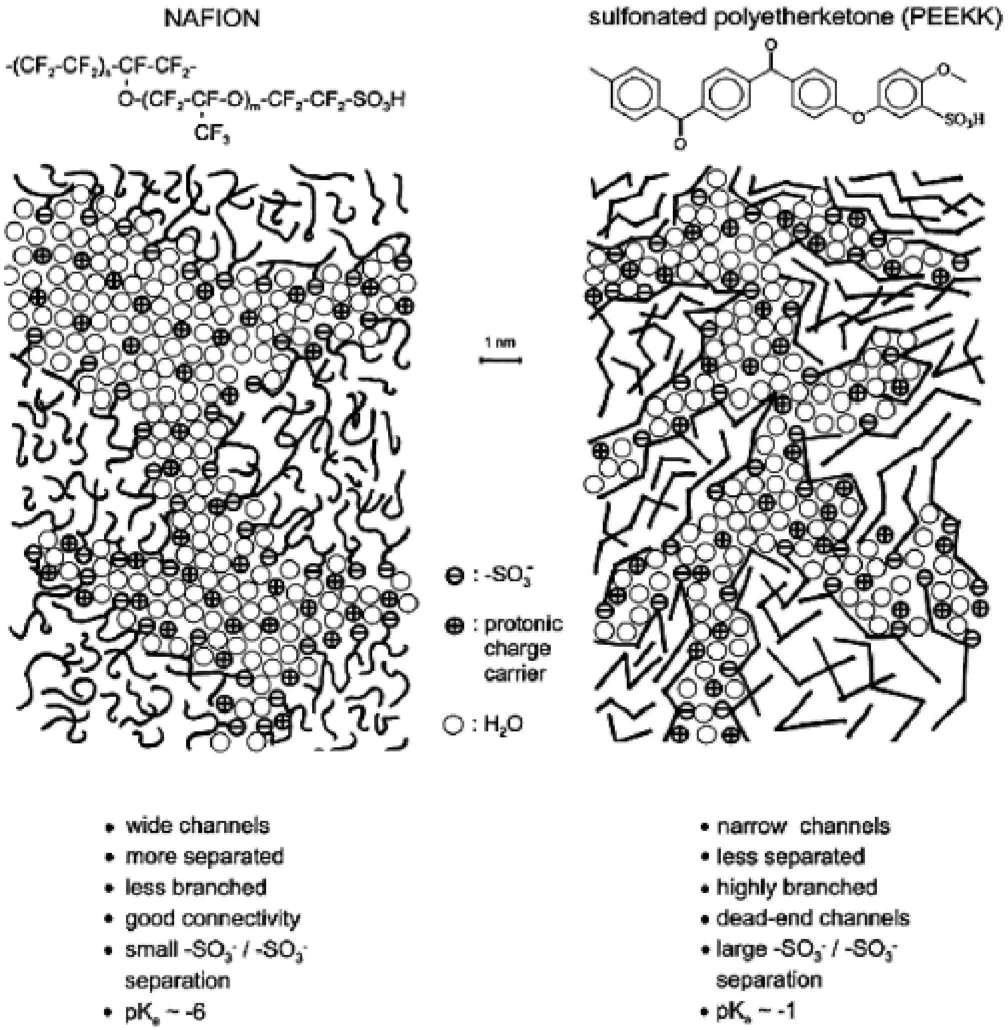
Crystalline nano-domains are hydrophobic regions.

Disordered domains are hydrated.

Mauritz & Moore, *Chem. Rev.* 2004.

Industry Standard Membrane

Morphological models



- wide channels
- more separated
- less branched
- good connectivity
- small $-SO_3^-$ / $-SO_3^-$ separation
- $pK_a \sim -6$

- narrow channels
- less separated
- highly branched
- dead-end channels
- large $-SO_3^-$ / $-SO_3^-$ separation
- $pK_a \sim -1$

Figure 11. Stylized view of Kreuer of the nanoscopic hydrated structures of Nafion and sulfonated polyetherketone. (Reprinted with permission from ref 91. Copyright 2003 Elsevier.)

Mauritz & Moore, *Chem. Rev.* 2004.

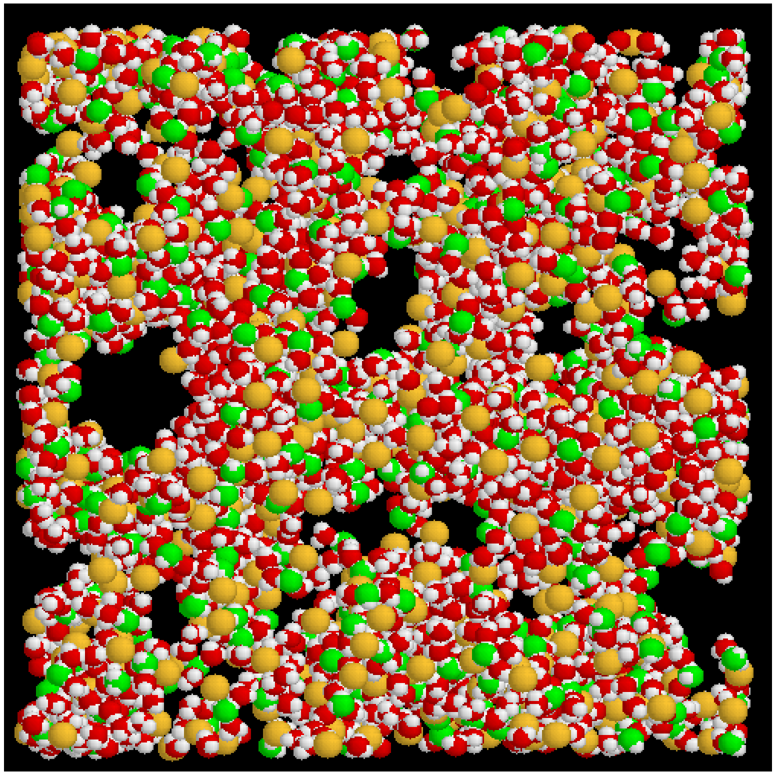
Molecular-level morphology

morphology of bulk hydrated membrane

Nafion

EW = 1144
λ= 6 H_2O/HSO_3
T = 300 K

Snapshots of the aqueous nanophase show a tortuous path.



Nafion (EW = 1144) λ = 6 H_2O/HSO_3
small aqueous channels

legend:
O of H_2O = red
H= white
O of H_3O^+ = green
S = orange
remainder of polymer electrolyte not shown

Molecular Dynamics (MD) Simulation


Newton

MD is a deterministic method.
To simulate N atoms in 3-D, you must solve a set of 3N coupled nonlinear ordinary differential equations.

$$F = ma$$

The force is completely determined by an interaction potential.

$$F \equiv -\nabla U$$

The ODE for particle *i* in dimension α is thus

$$\frac{d^2 x_{i,\alpha}}{dt^2} = -\frac{1}{m}\frac{\partial U}{\partial x_{i,\alpha}}$$

We must provide an interaction potential from either theory, quantum mechanical calculations or experiment.

- Numerically integrate the equations of motion.
- Limited to relatively small systems (10^6 particles) and short times (10 ns).
- Use MPI to parallelize code.

Molecular Dynamics

Strengths and Weaknesses of Classical MD simulation

Advantages

- The primary advantage of MD simulation is that the structure and dynamics of individual molecules can easily be tracked, giving insight into the molecular-level mechanisms governing the system.
- Materials with nanostructure and interfacial systems are particularly suited for investigation via MD simulation

Disadvantages

- small systems (less than 10^6 atoms typically)
- short simulation duration (less than 10 nanoseconds typically)
- classical MD does not model chemical reaction (needs quantum mechanics)

Requirements

- requires knowledge of atomic level interactions
- results are only as good as the interaction potential

Optimal Use

- simulation is complementary to theory and experiment
- MD simulation should be coupled with finer models (QM) and coarser models (mesocale, continuum)

Interaction Potential

Our potential model for Nafion is taken from [1-5]. Partial charges are taken from [1]. It includes bond stretching, bond bending, bond torsion, intramolecular nonbonded interactions between molecules separated by at least three bonds, and intermolecular nonbonded interactions. The nonbonded interactions themselves contain three terms intended to model electron cloud repulsion, induced-dipole/induced-dipole attraction, and Coulombic interactions. We treat the nonbonded interactions with a spherical cut-off.

Our system also includes water. We use the TIP3P model for water [6] with a flexible OH bond [5]. Our system also includes hydronium ions, H_3O^+, where the potential is taken from [3].

1. Vishnyakov and Neimark, *J. Phys. Chem. B,* 2001. 105.
2. Rivn, Meermeier, Schneider, Vishnyakov, Neimark, *J. Phys. Chem. B*, 2004: 108.
3. Urata, Irisawa, Takada, Shinnoda, Tsuzuki, Mikami, *J. Phys. Chem. B*, 2005. 109.
4. Li, McCabe, Cui, Cummings, Cochran, *Mol. Phys.,* 2003. 101.
5. Cornell et al., *J. Am. Chem. Soc.,* 1995. 117.
6. Jorgensen, Chandrasekhar, Madura, Impey, Klein, *J. Chem. Phys.,* 1983. 7.

System Size

simulation conditions

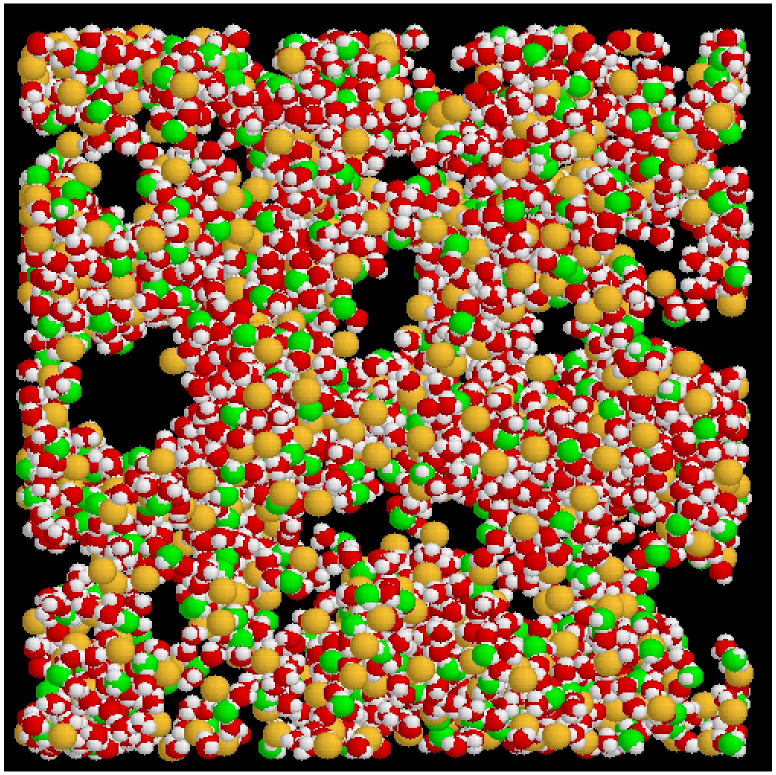
nominal H_2O content	5 wt%	10 wt%	15 wt%	20 wt%
no. of polymers	256	256	256	256
no. of H_2O molecules	2640	4160	6624	9088
no. of H_3O^+ ions	768	768	768	768
total no. of particles	31728	36288	43680	***51072***
λ (H_2O/SO_3^-)	3.44	5.42	8.63	11.83
simulation time (ns)	4.0	4.0	4.0	4.0
no. of graphite atoms	3024	3584	3584	3712
no. of Pt atoms	4872	5400	5580	6144

*51072 atoms is the largest system size we explore to date.

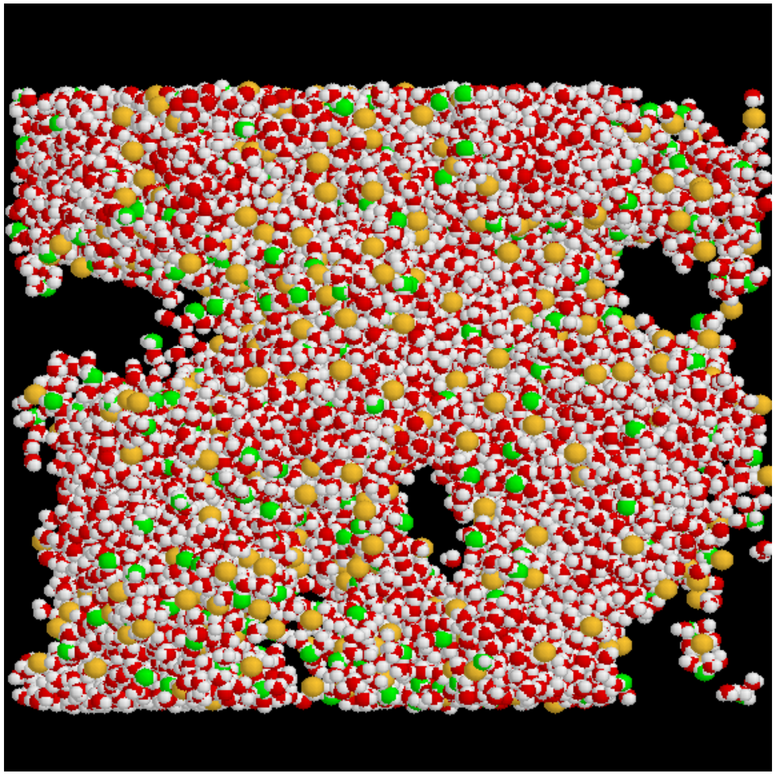
- **NVT simulations at 300K**

Molecular-level morphology

PEM morphology is a function of water content



Nafion (EW = 1144) $\lambda = 6$ H_2O/HSO_3
small aqueous channels



Nafion (EW = 1144) $\lambda = 22$ H_2O/HSO_3
much larger aqueous channels

As the membrane becomes better hydrated, the channels in the aqueous domain become larger and better connected, resulting in higher conductivity.
(The challenge to finding high-temperature membranes is to find one that can retain moisture at elevated temperatures.)

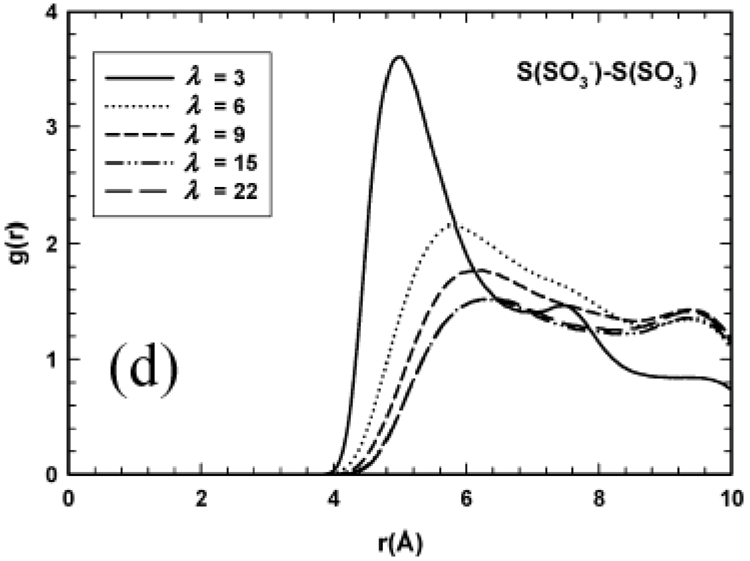
Molecular-level morphology

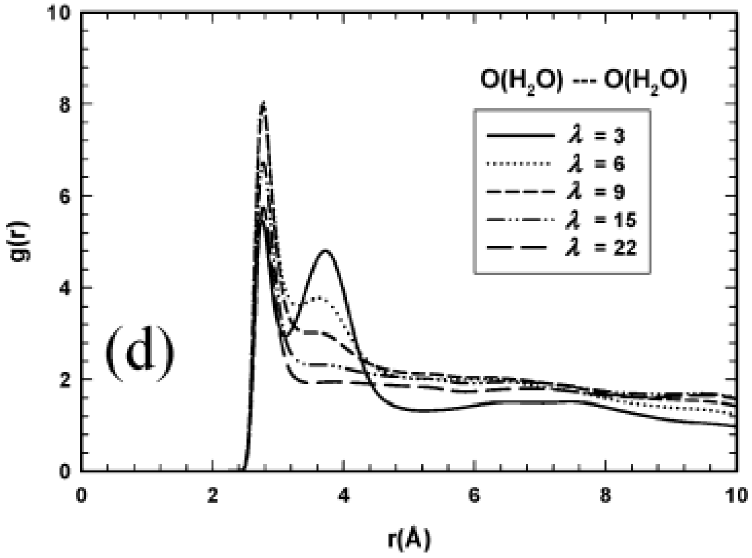
View membrane morphologies online at

https://trace.lib.utk.edu/home/davidkeffer/sites/atoms/nafion/MainPage.html

Local Structure

Pair Correlation Functions



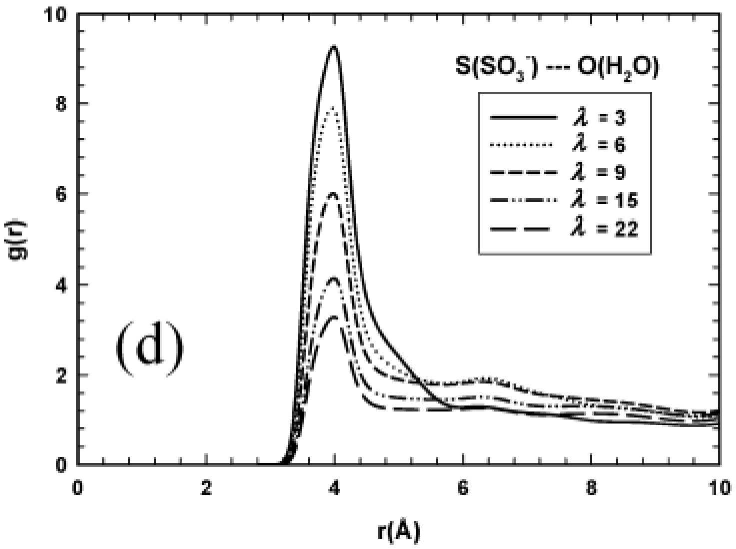


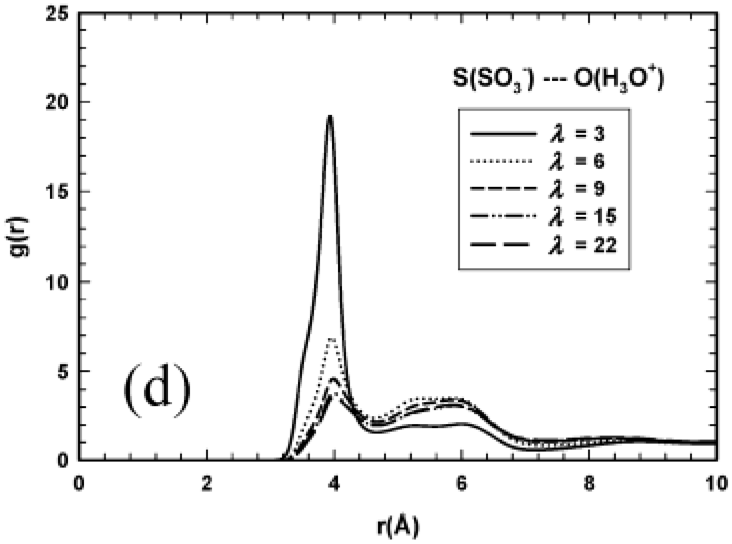
- Pair correlation functions (PCFs) are conditional probability distributions that provide the likelihood of finding another atom at a given distance.
- S-S PCFs indicate the degree of clustering of the sulfonate anions.
- O-O PCFs indicate the deviation of the water in the hydrophilic domain from a bulk water structure of a fully hydrogen-bonded network.

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

Local Structure

Pair Correlation Functions



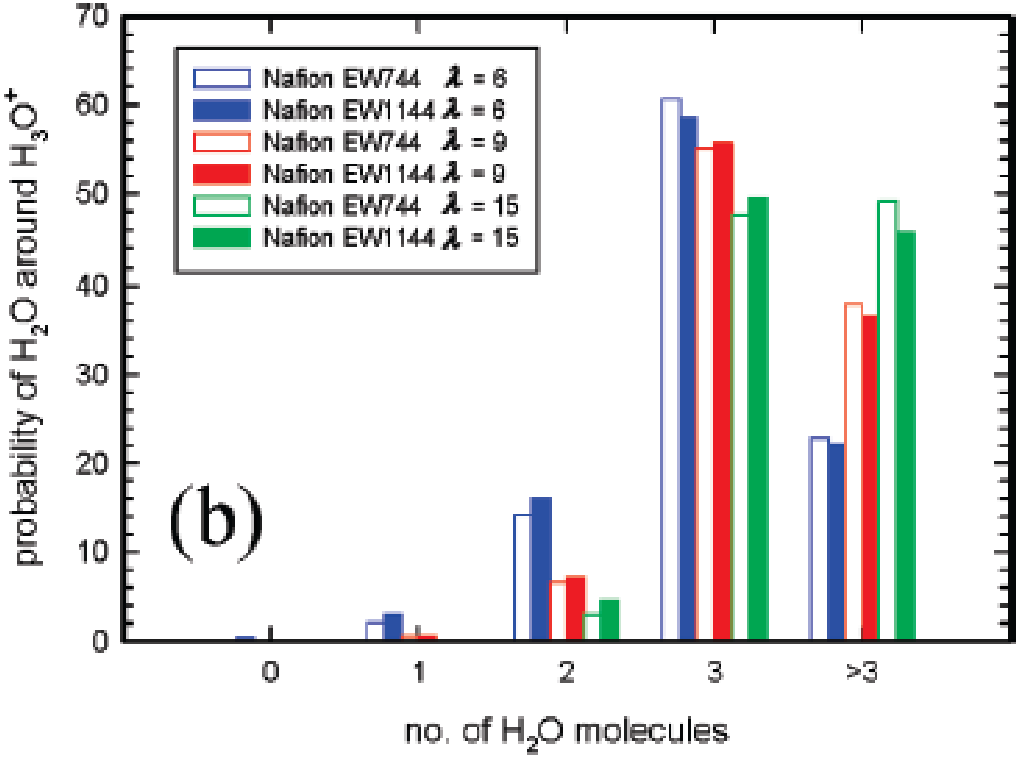


- S-O(H_2O) PCFs indicate the degree of water clustering around the anions.
- S-O(H_3O^+) PCFs indicate the degree of association between anions and cations

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

Local Structure

Hydronium Ion Hydration Distributions



- Hydronium ions are more mobile if they are better hydrated.

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

Global Structure

Water Cluster Distributions

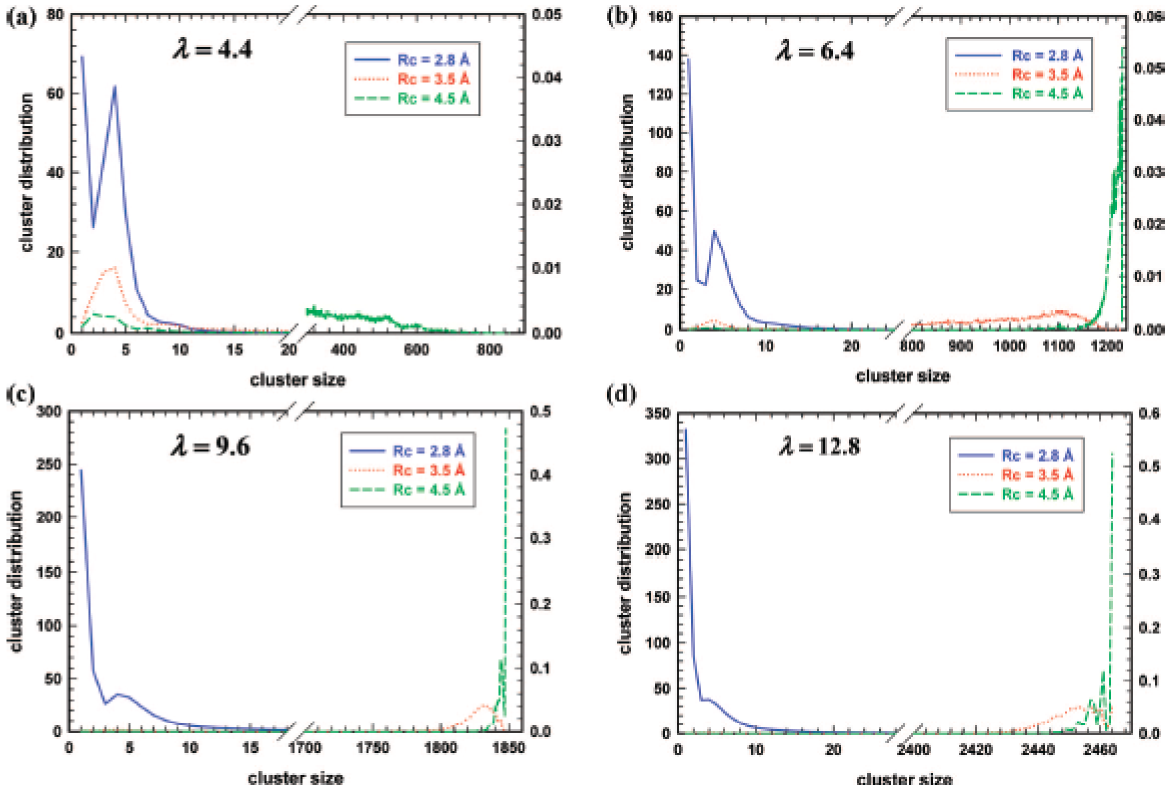


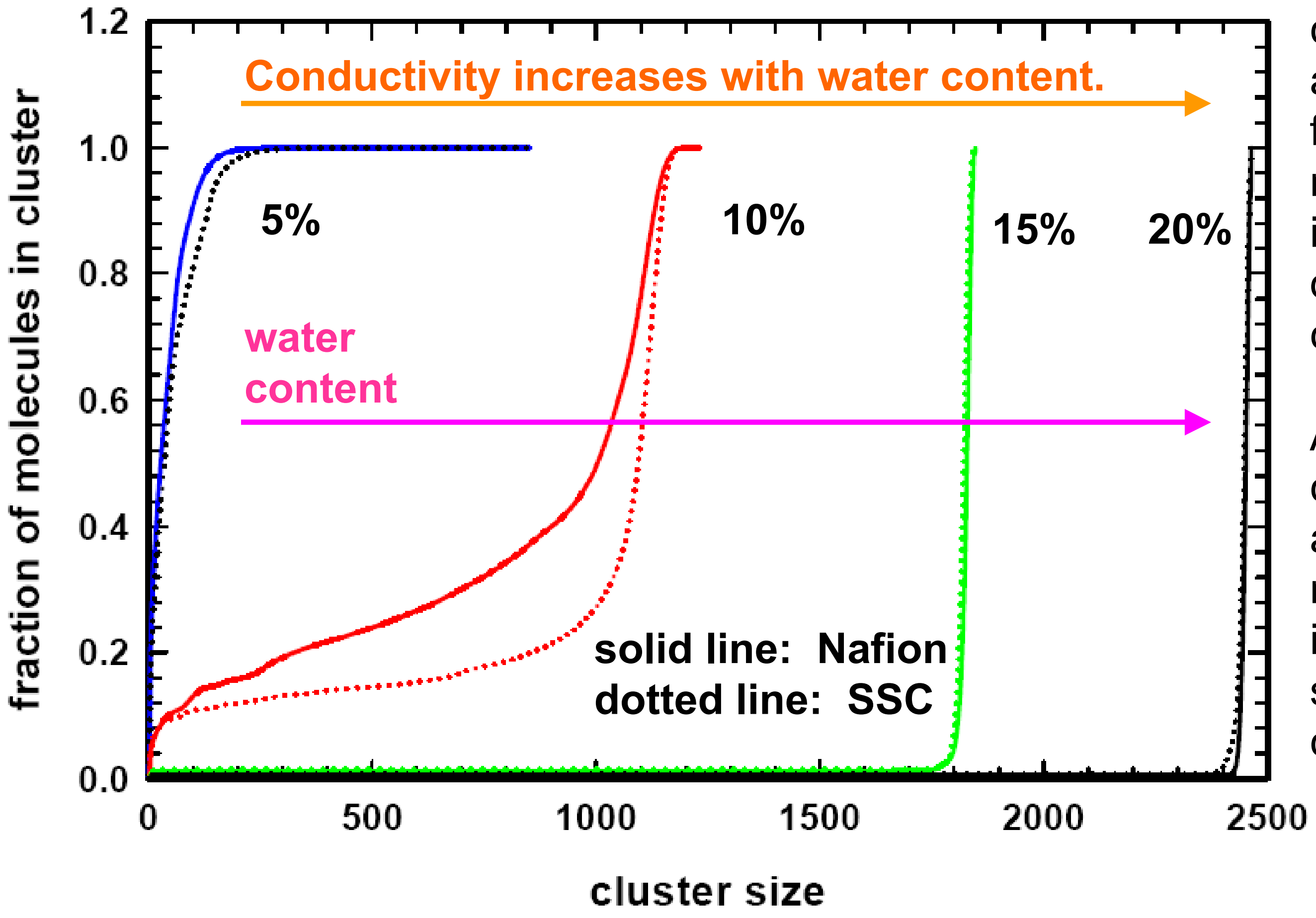
Figure 5. Cluster size distribution for hydrated Nafion at water contents corresponding to (a) λ = 4.4, (b) λ = 6.4, (c) λ = 9.6, and (d) λ = 12.8.

- Higher water contents lead to bigger water clusters

Cui et al., *J. Phys. Chem. B*, 2008.

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

Fourier Transforms of Pair Correlation Functions

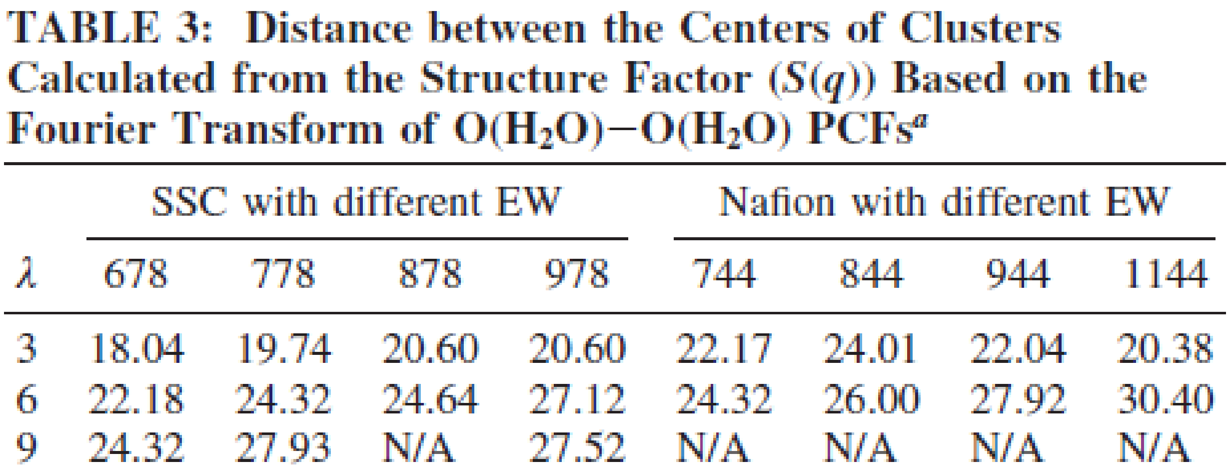


TABLE 3: Distance between the Centers of Clusters Calculated from the Structure Factor ($S(q)$) Based on the Fourier Transform of $O(H_2O)-O(H_2O)$ PCFs[a]

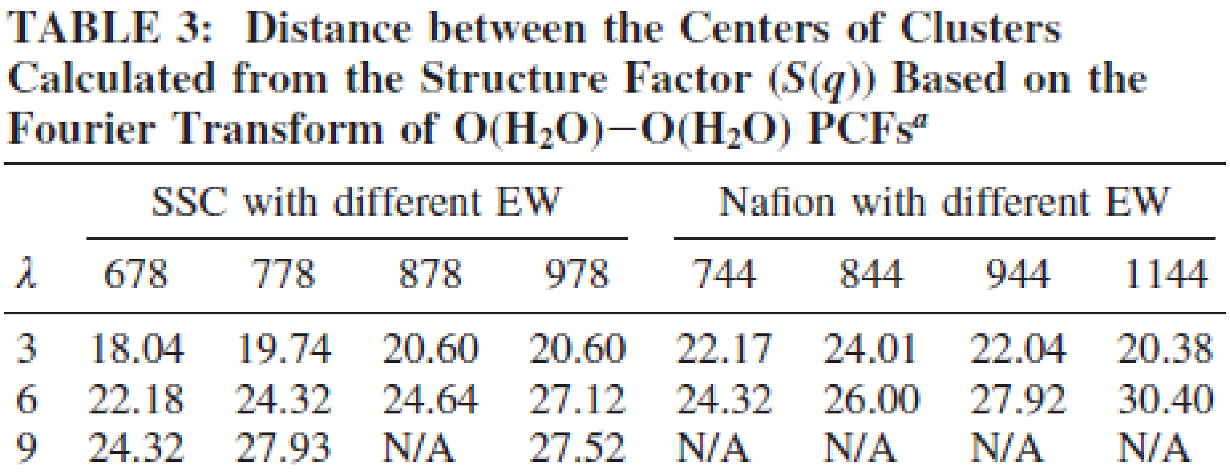
	SSC with different EW				Nafion with different EW			
λ	678	778	878	978	744	844	944	1144
3	18.04	19.74	20.60	20.60	22.17	24.01	22.04	20.38
6	22.18	24.32	24.64	27.12	24.32	26.00	27.92	30.40
9	24.32	27.93	N/A	27.52	N/A	N/A	N/A	N/A

- Characteristic water cluster size increases with increasin hydration.

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

Global Structure

Fourier Transforms of Pair Correlation Functions



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

Global Structure

Volume fraction and interfacial surface area

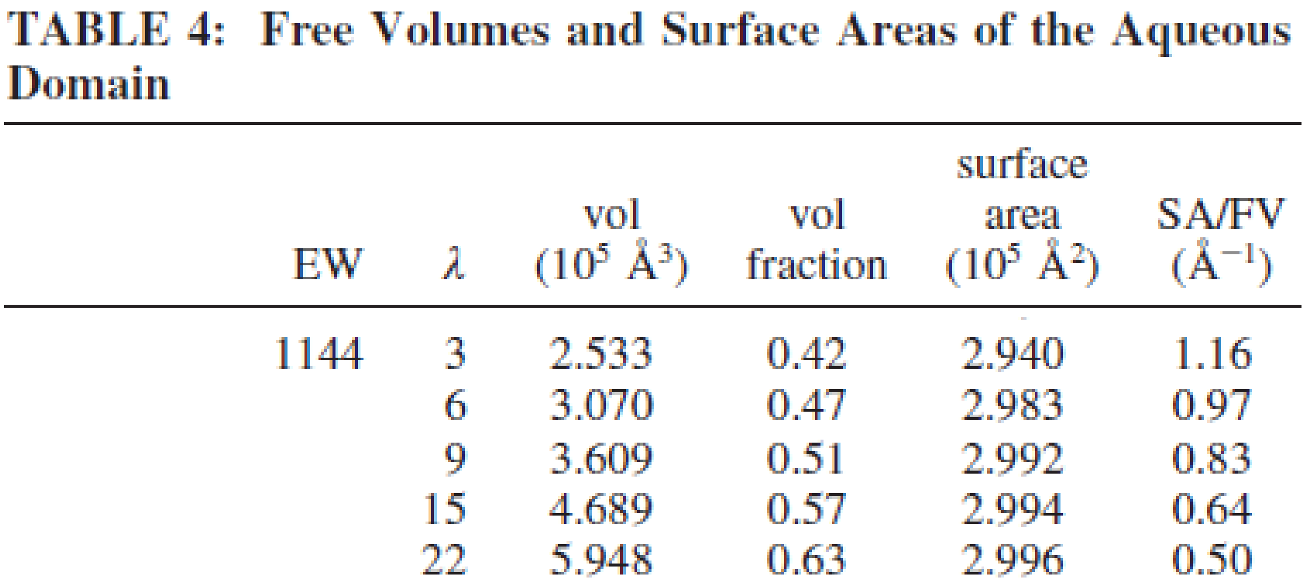

TABLE 4: Free Volumes and Surface Areas of the Aqueous Domain

EW	λ	vol (10^5 Å^3)	vol fraction	surface area (10^5 Å^2)	SA/FV (Å^{-1})
1144	3	2.533	0.42	2.940	1.16
	6	3.070	0.47	2.983	0.97
	9	3.609	0.51	2.992	0.83
	15	4.689	0.57	2.994	0.64
	22	5.948	0.63	2.996	0.50

- aqueous domain volume fraction increases with water content.
- interfacial surface area increases with water content.
- interfacial surface area per unit volume strongly decreases with water content.

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

Conclusions

Experimental and molecular simulation have given a pretty confident description of the molecular-level structure of hydrated perfluorosulfonic acid membranes.

- nanoscale segregation in aqueous and hydrophilic domains
- observed changes in local structure (pair correlation functions) and global structure (morphology of water domain) are consistent and show
  - a gradual increase in the size of the aqueous channels
  - better connectivity of the aqueous channels
  - less clustering of anions
  - movement of hydronium ions from interfacial area into center of aqueous channels