Mechanical/Chemical Energy Balance in Perfluorinated Sulfonic Acid Membranes

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Outline

- **General overview and results**
  - Mechanical/chemical energy balance
    - Model overview

      Small angle X-ray scattering (SAXS)
    - Pretreatment (internal)
    - Compression (external)
  - Interfacial aspects
    - Liquid vs. vapor

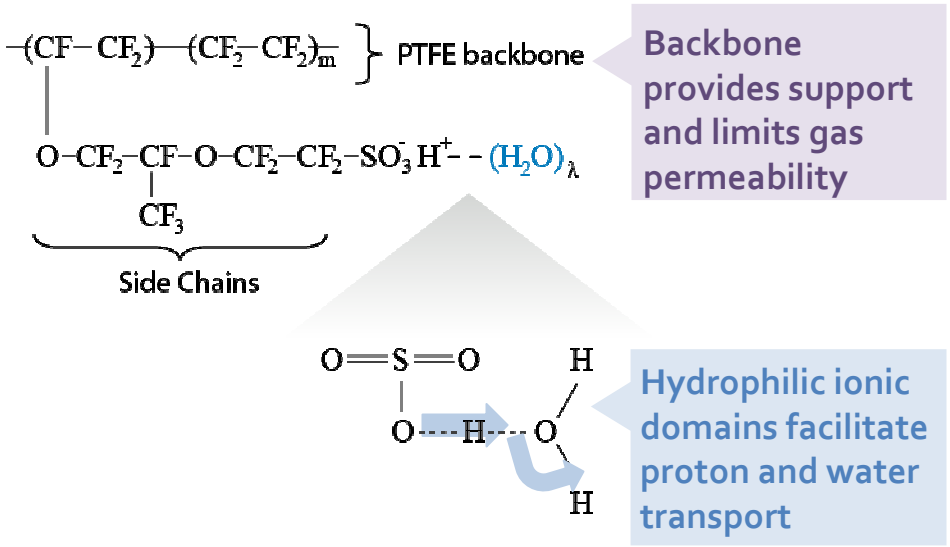
- **Thin films**
  - Grazing incidence (GI) SAXS
  - Water uptake
  - Thin(ner) films
    - Structure
    - Conductivity

- **Summary**

Sulfonated Polymers

- **Ion conductive & mechanically robust**
  - Multiple functionalities
- **Perfluorinated Sulfonic Acid (PFSA)**

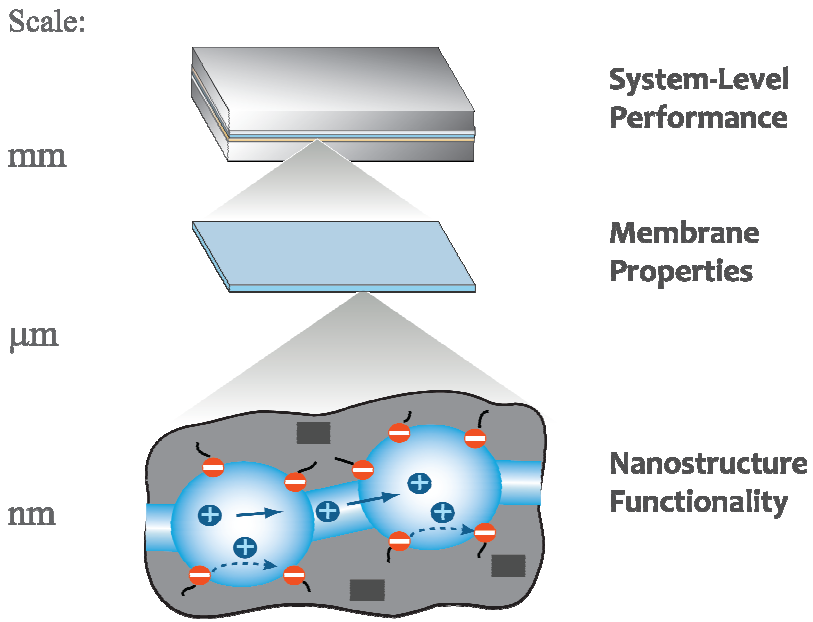
Chemical Structure of PFSA



Backbone provides support and limits gas permeability

Hydrophilic ionic domains facilitate proton and water transport

- It is of great interest to gain a fundamental understanding of (nano)structure-function relationship
- Role of Chemical/Mechanical Balance



Phase-separated nanostructure is key to the functionality of membrane in fuel cell

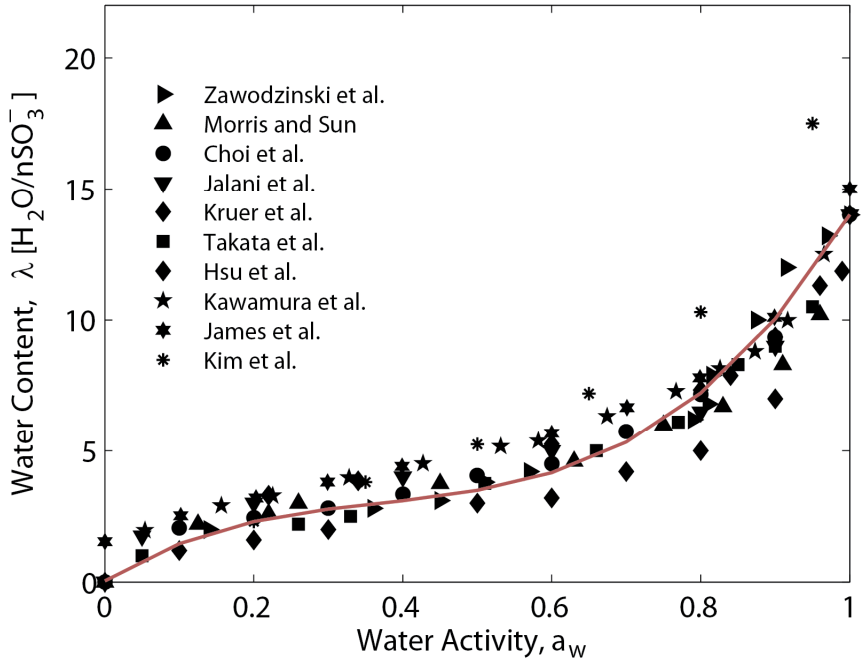
Water Uptake in Nafion: Literature

- **Water content**

$$\lambda = \frac{\mathrm{mol}(H_2O)}{SO_3} = \frac{W_w / M_w}{W_m^{dry} / EW}$$

Springer, T. E., T. A. Zawodzinski, et al. "Polymer Electrolyte Fuel-Cell Model." J. Electrochem Soc., 138, 2334. (1991)

- **Literature sorption isotherms**



- **Transport properties are highly dependent on water content**

Chemical/Mechanical Energy-Balance Model

Modeling Sorption

- Swelling equilibrium

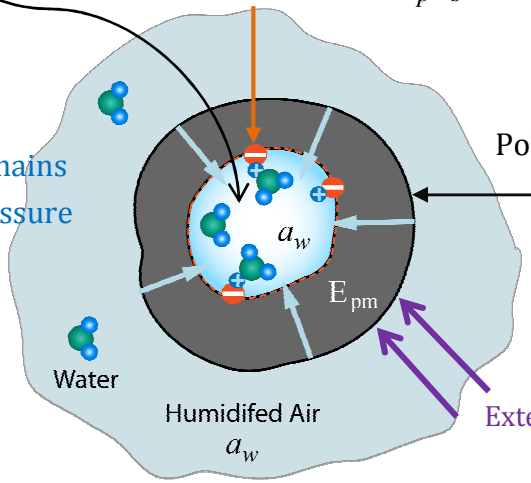
$$\mu_w^{ext} = \mu_w^{int} \Rightarrow \begin{cases} \mu_w^{ext} = RT \ln a_w \\ \mu_w^{int} = RT \ln a_w^p + \bar{V}_w P \end{cases}$$

- Flory-Huggins theory

$$\ln a_w = \ln \phi_w + \left(1 - \frac{1}{\bar{V}_p / \bar{V}_w}\right)\phi_p + \underbrace{\chi}_{\text{Interaction Energy}} \phi_p^2 + \frac{1}{RT} \underbrace{P_s}_{\text{Swelling Pressure}}$$

Polymer-Water Interactions
Control mixing *(ENTHALPIC)* χ_{p-s}

Water goes to ionic domains
to increase osmotic pressure
(ENTROPIC) $a_w \rightarrow \phi_w$



Polymer matrix applies
counter pressure
$E_{pm} \rightarrow P_s$

External Load:
$P_e \rightarrow P_s$

Swelling Equilibrium

- Membrane absorbs water
  - Entropic effects
  - Polymer-Solvent interactions
- Polymer matrix limits expansion
  - Deformation of matrix
  - Structural organization
  - External Loads

Swelling Pressure

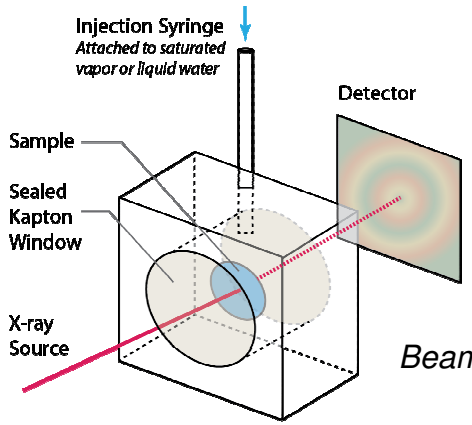
$$P_s = E_{pm} \times \underbrace{f(\phi_w, \text{geometry})}_{\text{MatrixDeformation}}$$

Backbone

Domain Growth

See Poster 2-31

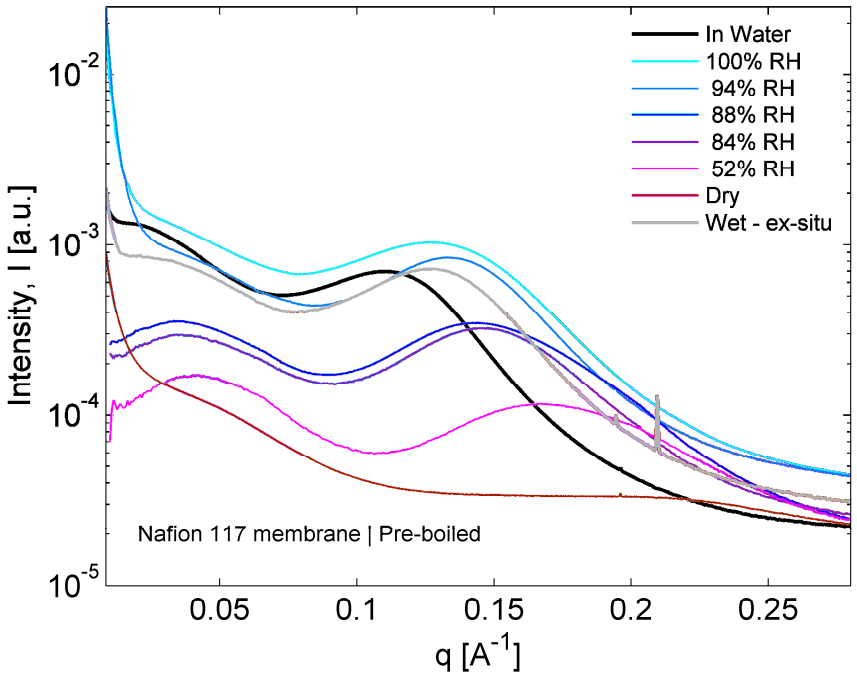
Nanostructure of Nafion (SAXS)



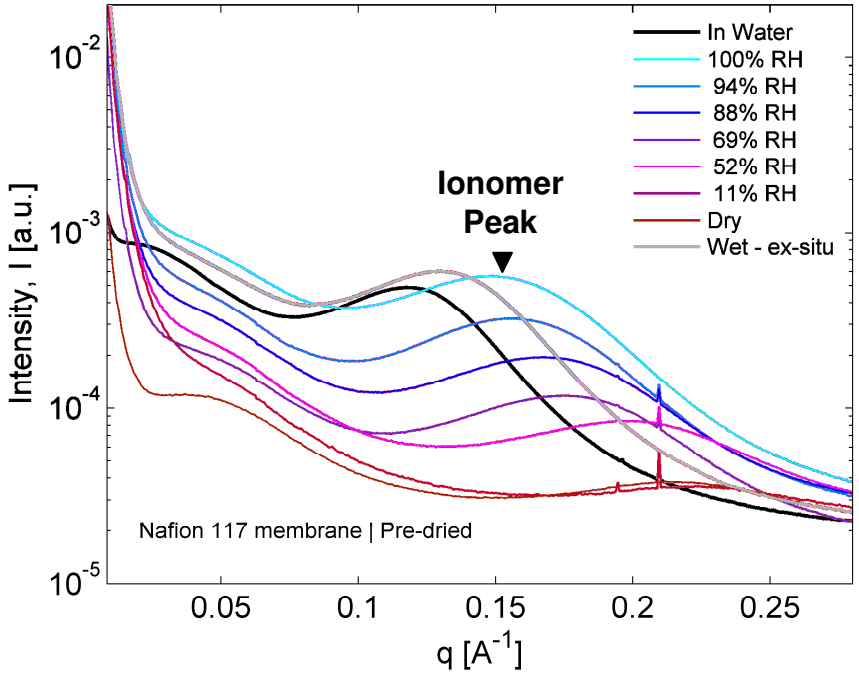
Beamline 7.3.3 at ALS

- **Both membrane have similar trends**
  - Ionomer peak grows with humidity
  - Nanoscopic swelling of ionic domains
- **Pre-boiled membrane has lower q**

Pre-boiled Membrane

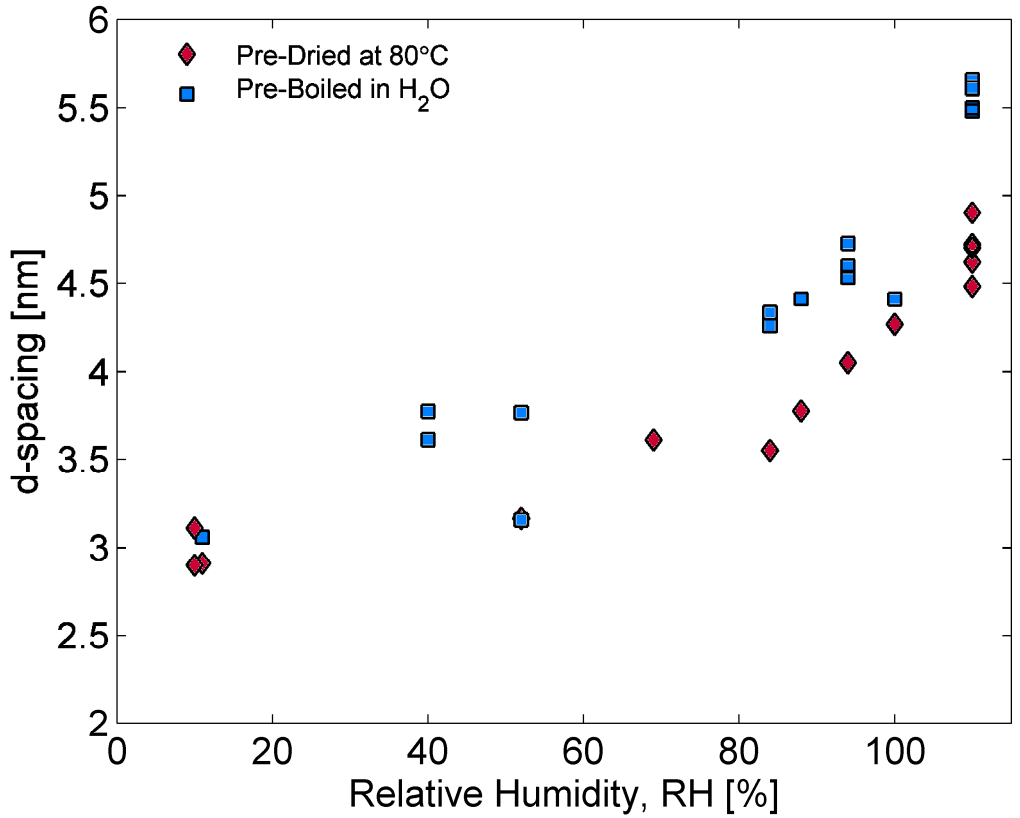


Pre-dried Membrane



Water Domain Spacing

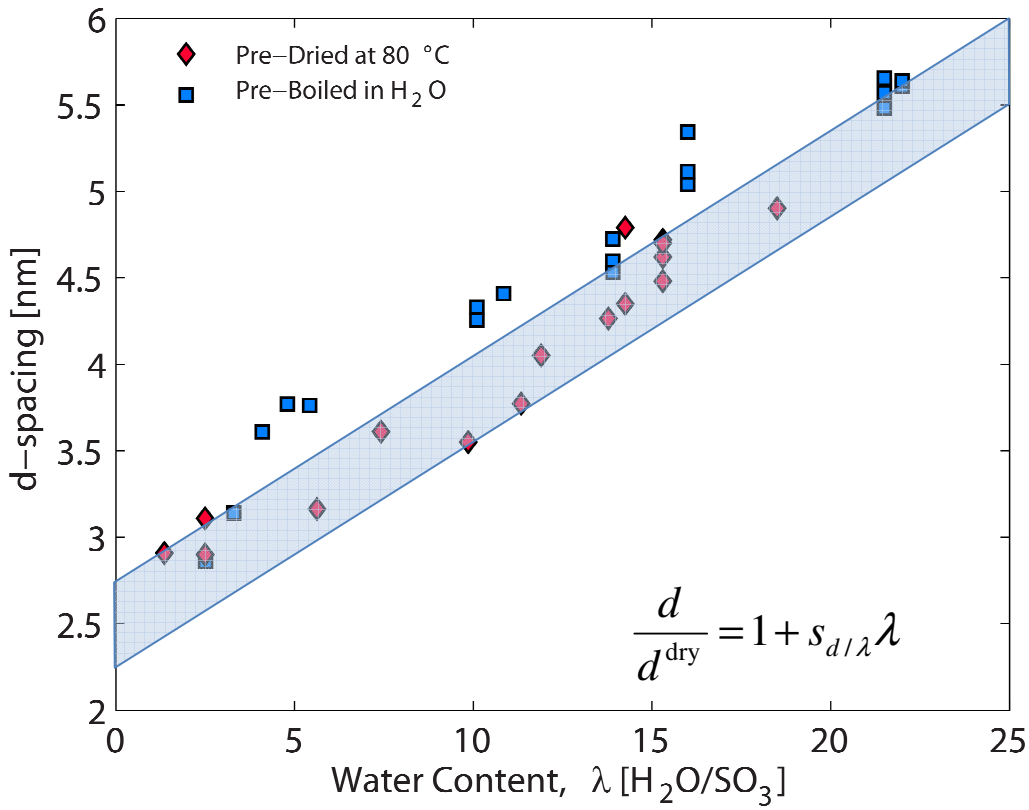
- **d-spacing correlates with water content**
  - Indication of nanoscale swelling of water domains



A. Kusoglu, S. Savagatrup, K.T. Clark, A.Z. Weber, Macromolecules, *in press.*

Domain Spacing and Structure of Nafion (SAXS)

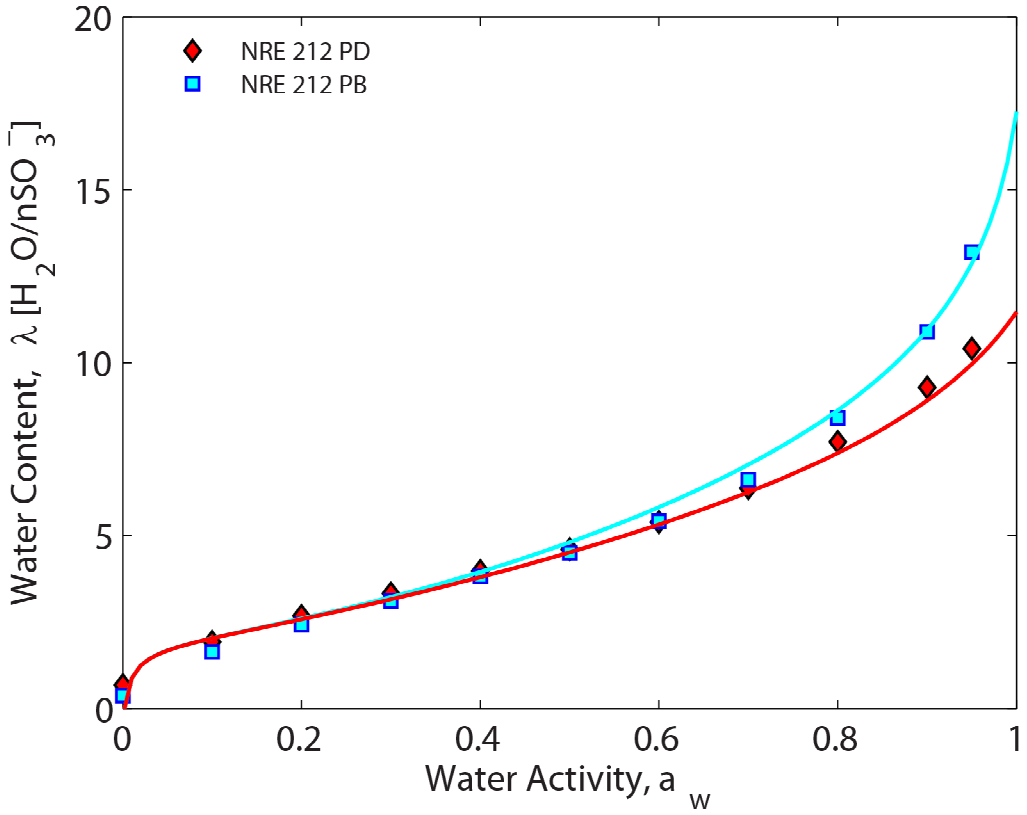
- **d-spacing correlates with water content**
  - Indication of nanoscale swelling of water domains
  - Provides insight to understand the structure-function relationship
    - Most transport properties depend on water content and d-spacing



A. Kusoglu, S. Savagatrup, K.T. Clark, A.Z. Weber, Macromolecules, *in press.*

Model Predictions: Thermal History

- **Difference in water uptake due to the pretreatment can be modeled with help of our findings on morphology**
  - Thermal History ➔ Different Modulus and d-spacing correlation



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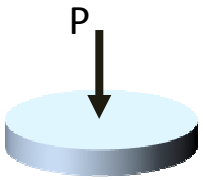
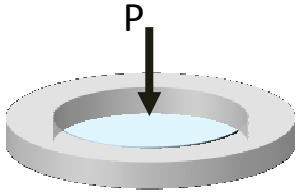
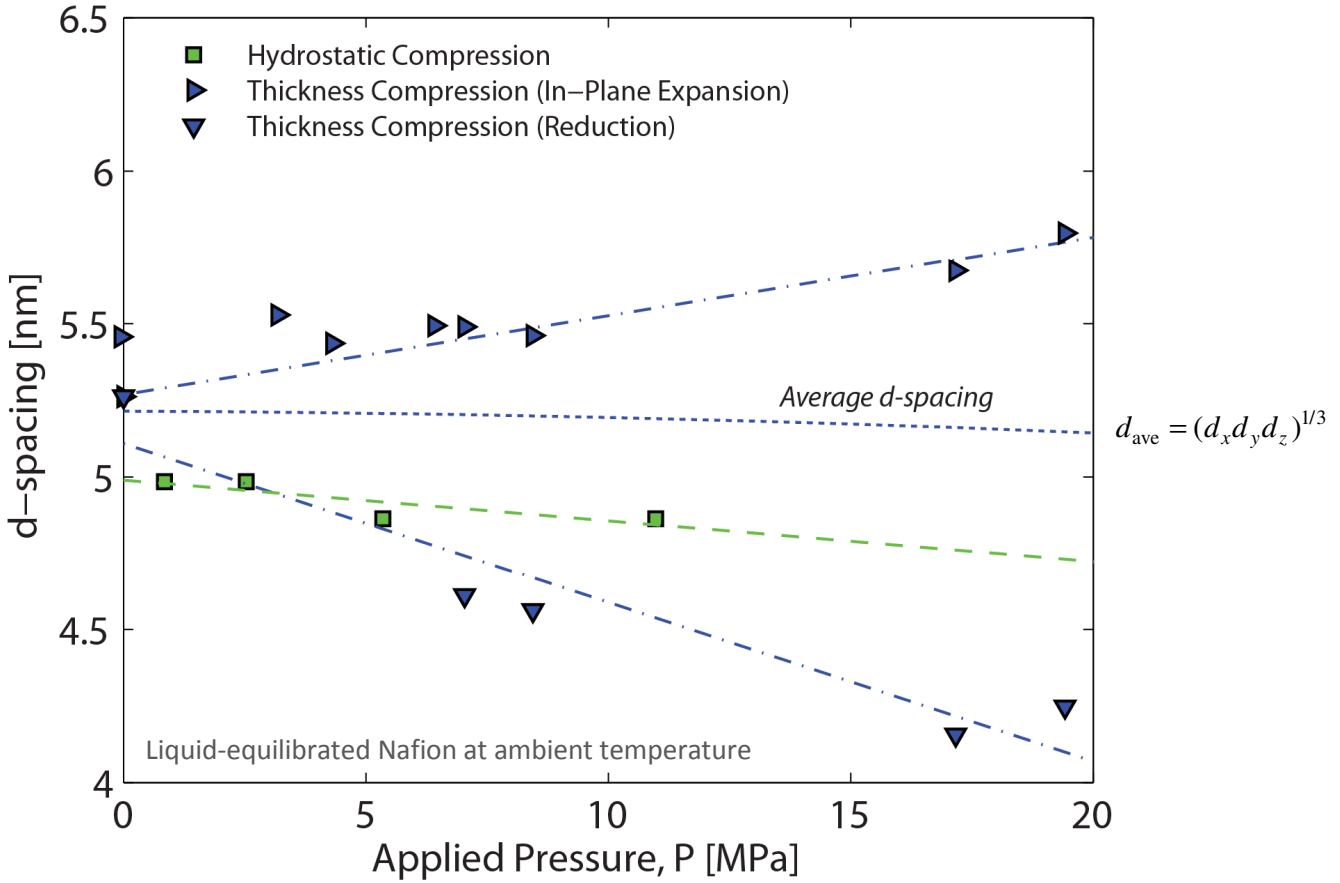
Effect of External Compression

Thickness Compression



Hydrostatic Compression





$$d_{ave} = (d_x d_y d_z)^{1/3}$$

- **Hydrostatic causes a slightly larger impact *on average domain spacing* compared to thickness compression**

A. Kusoglu, B. Kienitz, A.Z. Weber, *J Electrochem Soc*, **158** B1504 (2011).
A. Kusoglu, A. Hexemer, R. Jiang, C.S. Gittleman, A.Z. Weber, *J. Mem. Sci.*, **421-422**, 283 (2012).

See Poster 2-31

Effect of External Compression

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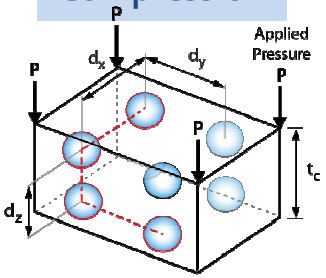
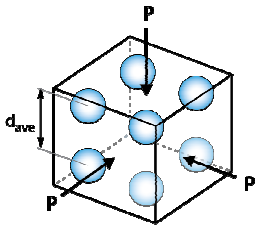
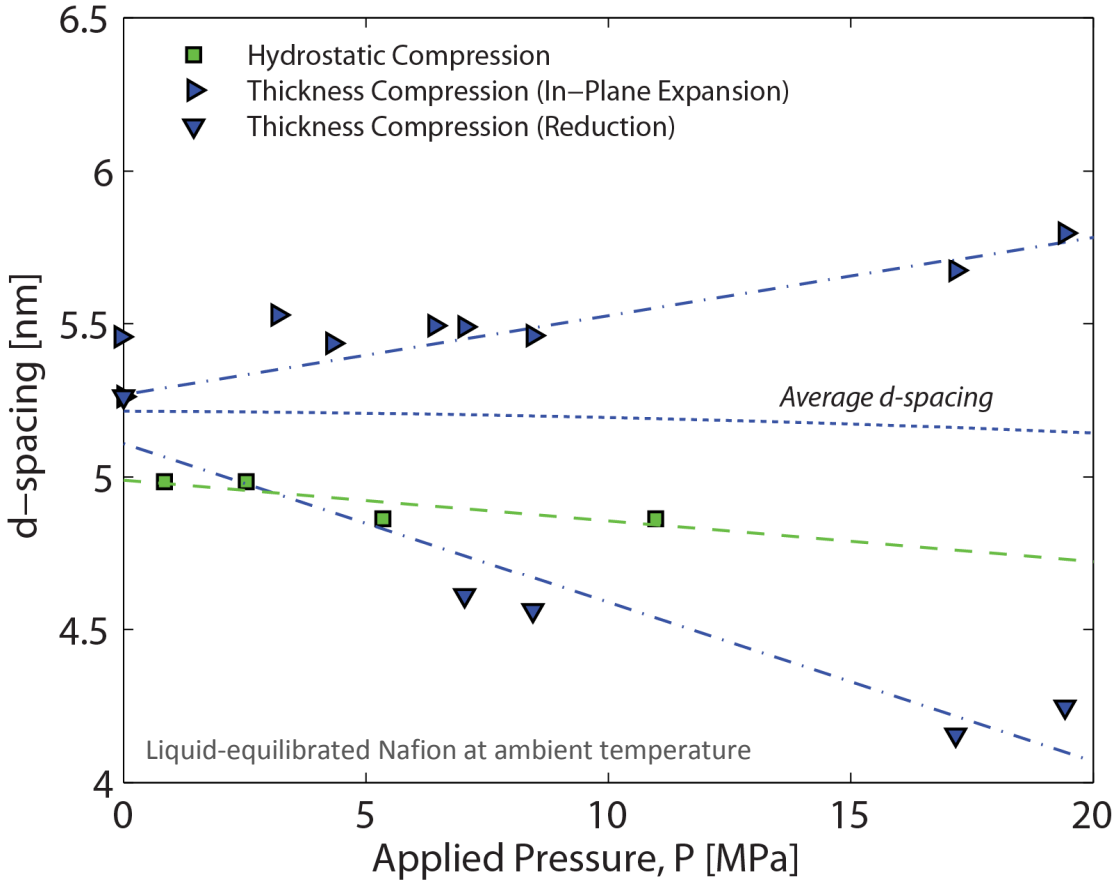


Hydrostatic Compression





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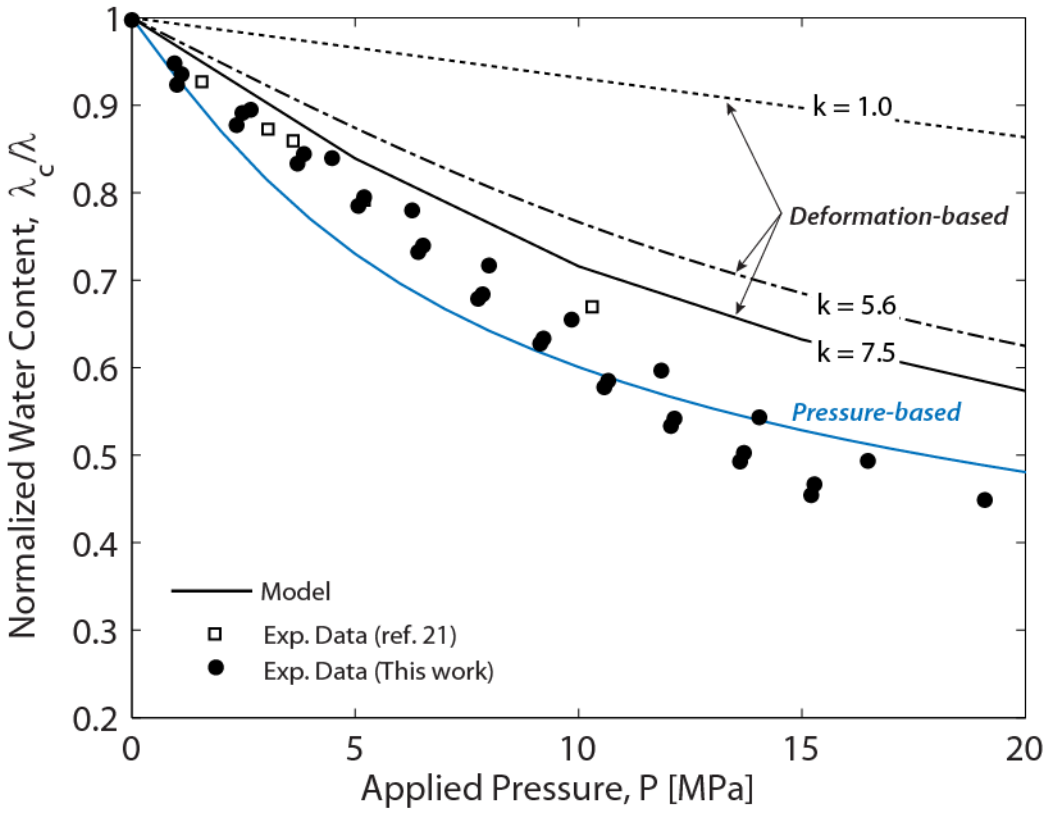
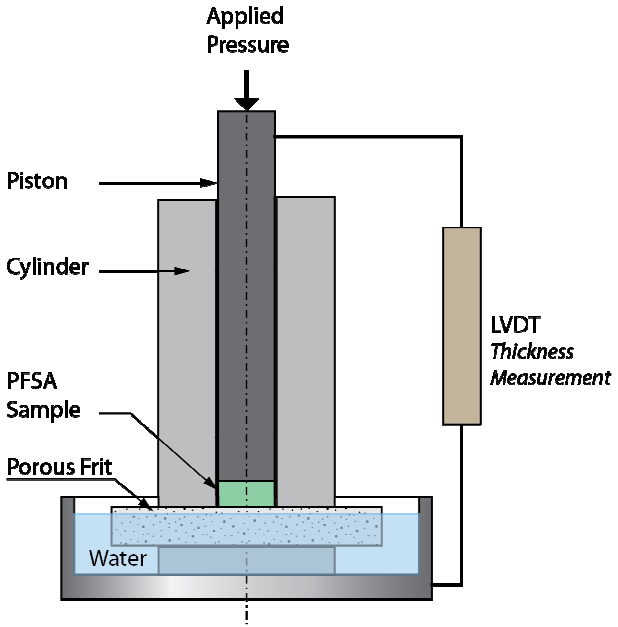
Model Validation: External Compression

- **Swelling pressure and water content under hydrostatic compression**
  - Good agreement with our data
  - Swelling under compression is governed by nanoscale domain deformation



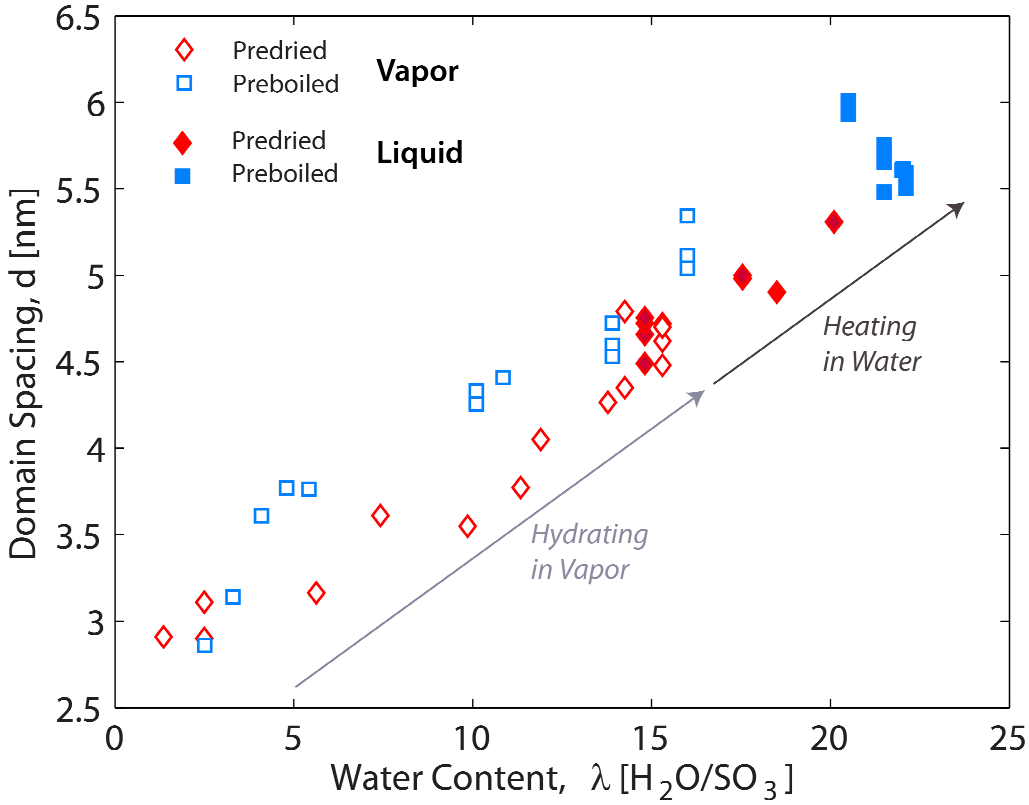


Designed by: M. K. Budinski, A. Cook Tsinghua Sci & Tech 15, 385 (2010)

A. Kusoglu, B. Kienitz, A.Z. Weber, *J Electrochem Soc*, **158** B1504 (2011) .

A Universal Correlation

- **Pretreatment, crystallinity and humidity effects are controlled by same chemical/mechanical balance**



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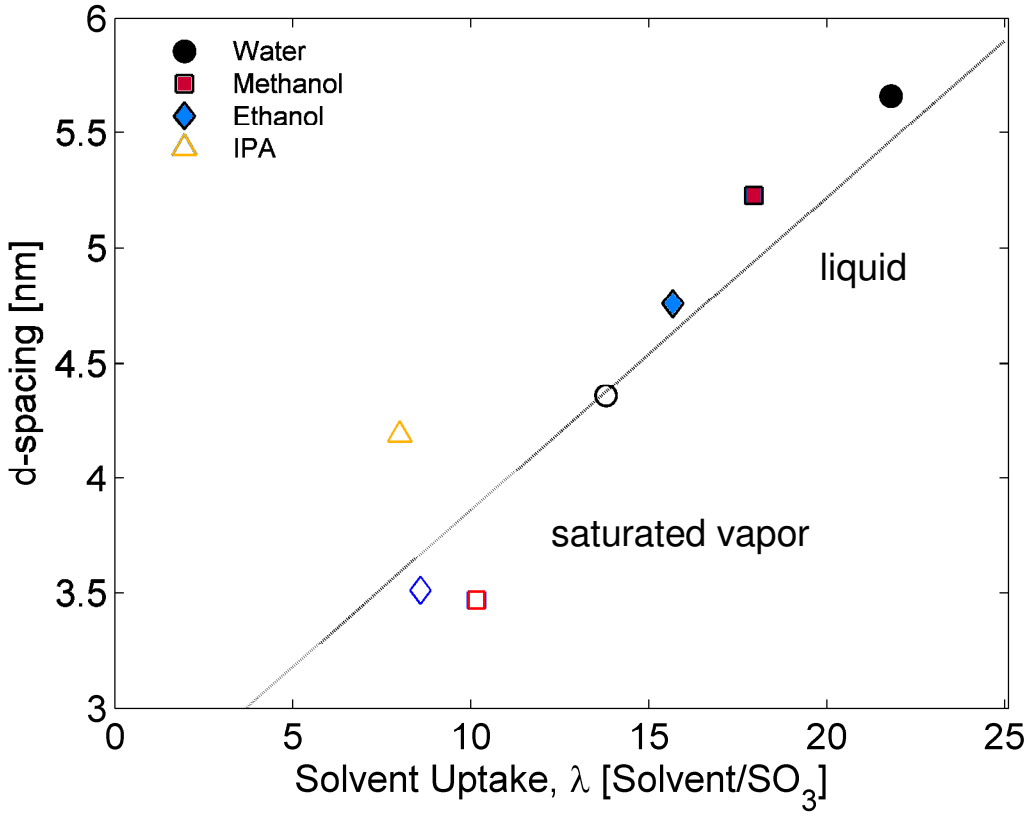
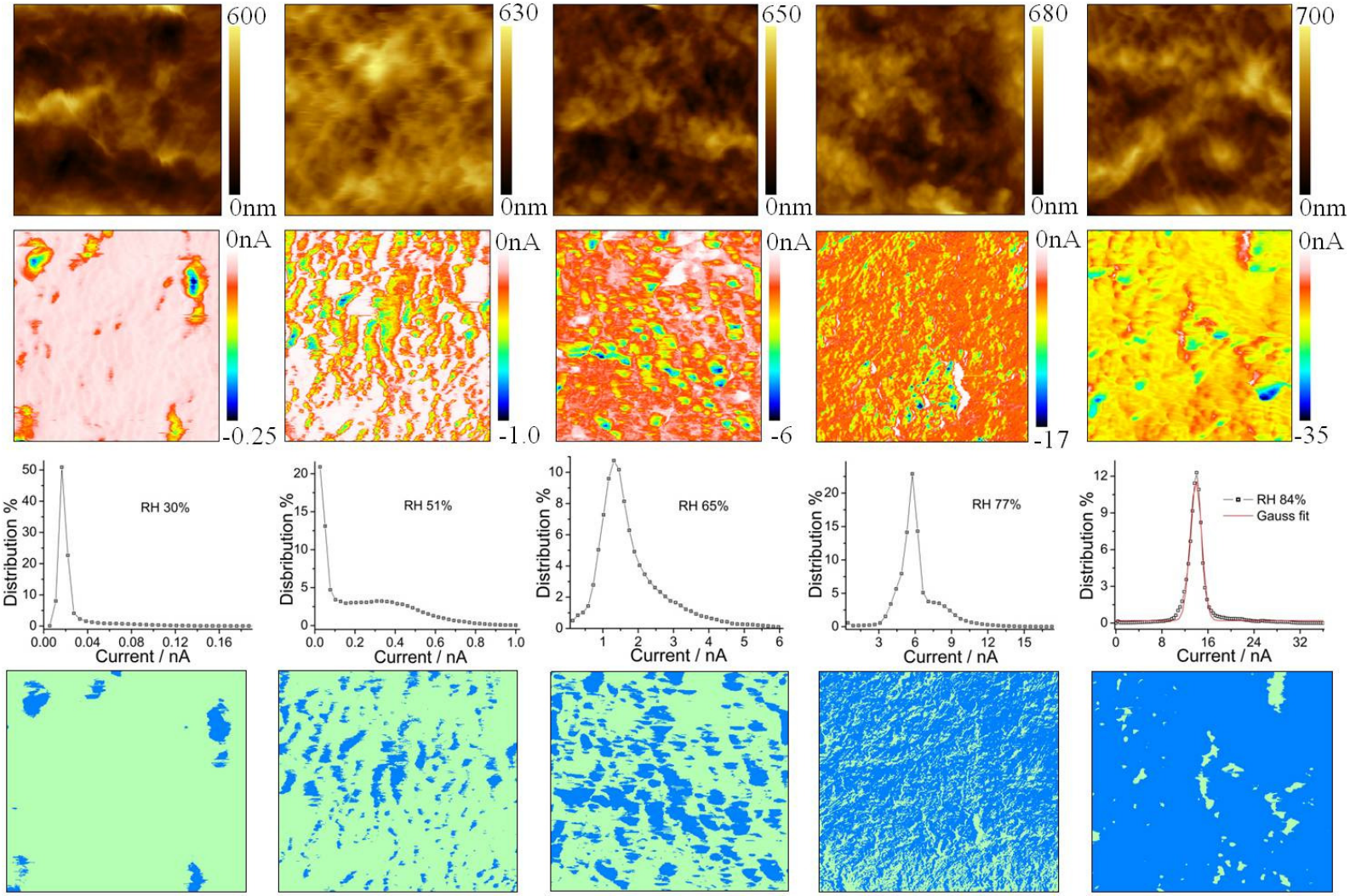
Nano-Swelling with Solvent Uptake

- **Solvent influences**
  - Total uptake (macro-swelling)
  - Hydrophilic domain-spacing (nano-swelling)
- **Difference in vapor- and liquid-equilibrated uptake (Schroeder's paradox)**



Conductive AFM of Membrane Surface

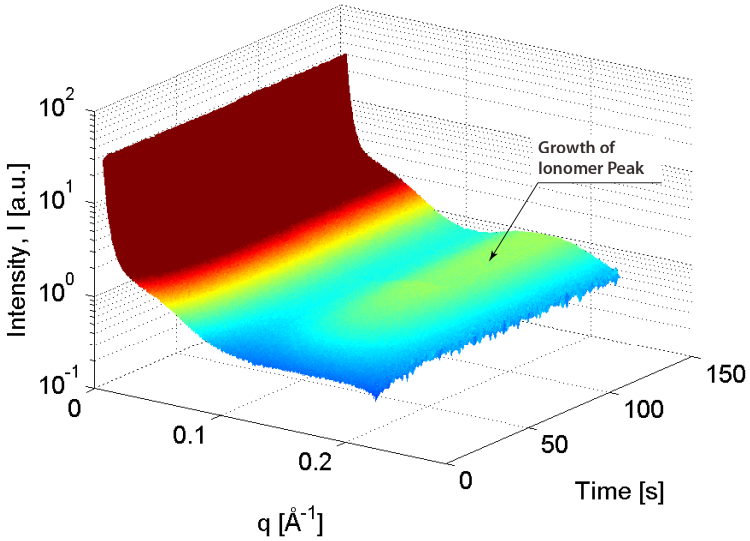
RH =	30%	51%	65%	77%	84%

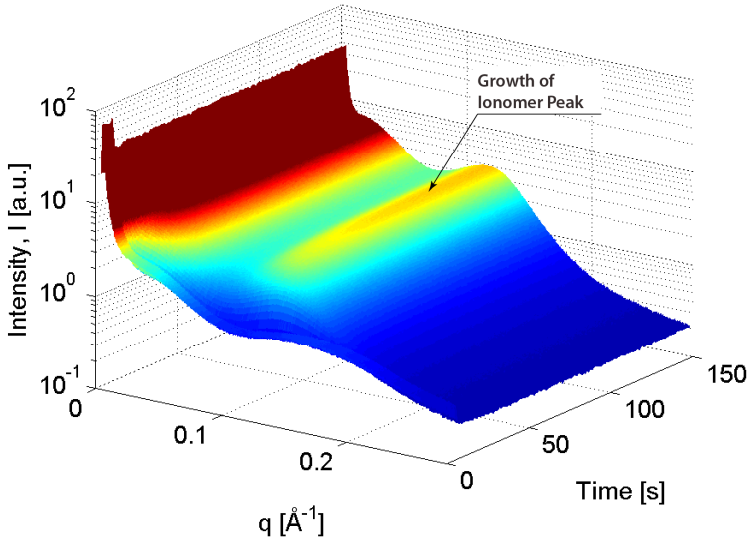


Q. He, I. T. Lucas, A. Kusoglu, A. Z. Weber, and R. Kostecki, *J. Phys. Chem. B*, **115**, 11650 (2011)

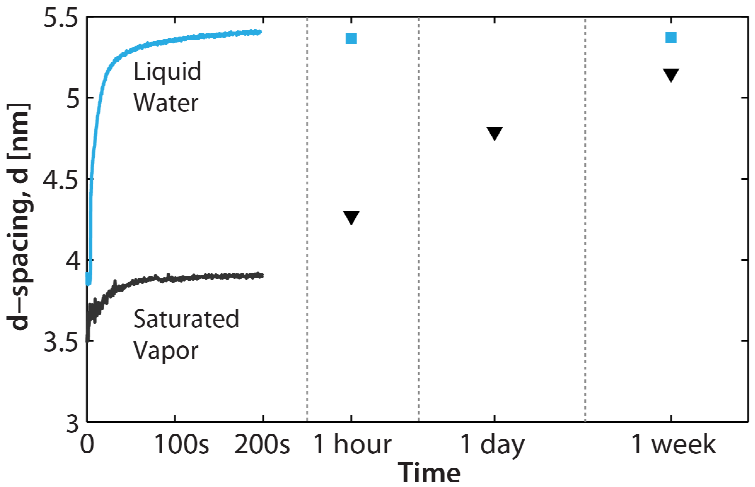
Dynamic SAXS of Water Uptake

Saturated Vapor SAXS images w/0.2 s time resolution **Liquid**





- **Interactions with liquid or vapor create different morphologies**
  - Interface seems to control kinetics
  - Liquid changes within seconds
  - Vapor takes much longer
    - On the order of days



A. Kusoglu, M. A. Modestino, A. Hexemer, R. A. Segalman, and A.Z. Weber, *ACS Macro Letters* **1**, 33 (2012).

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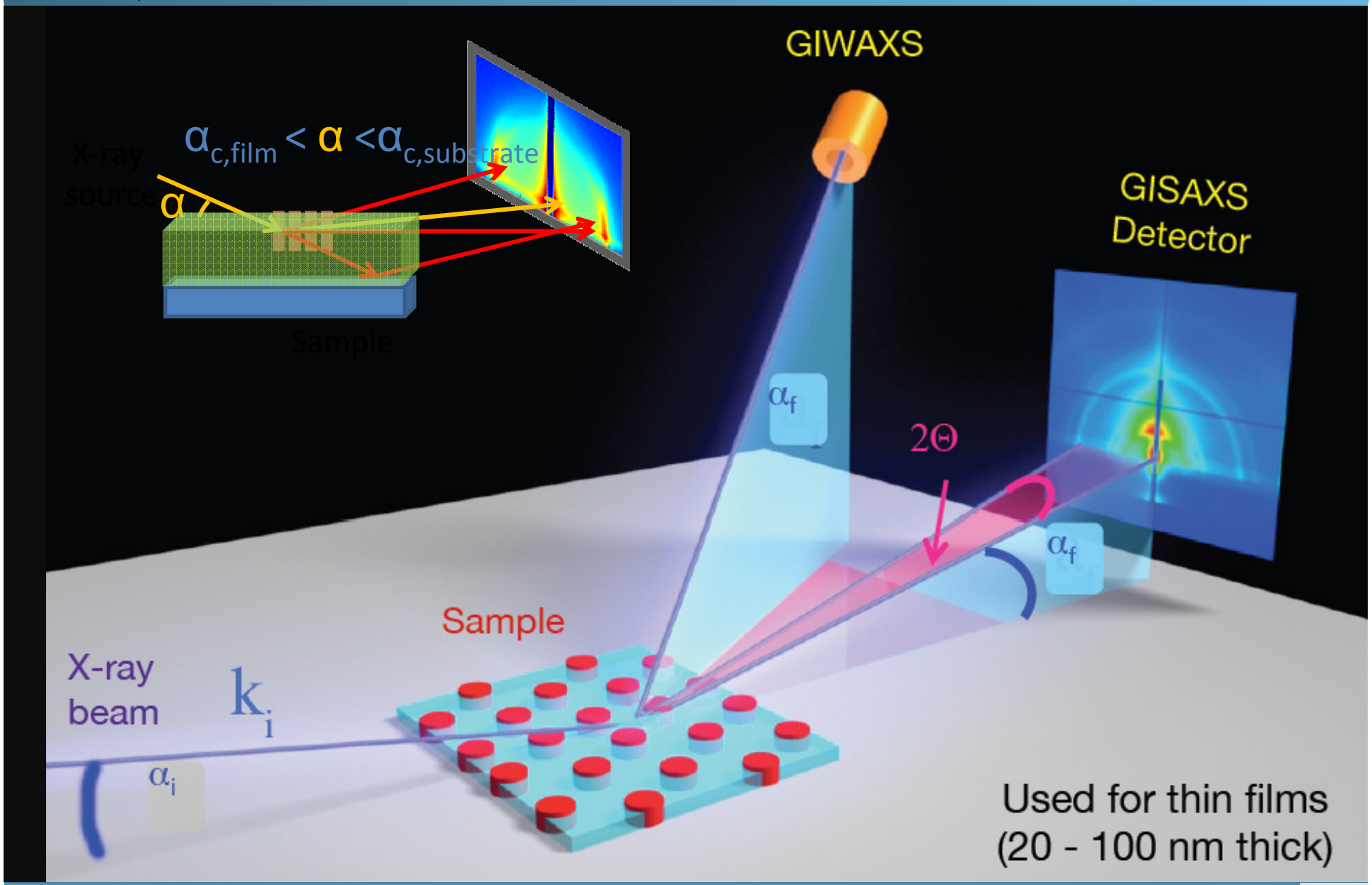
  - Interfacial aspects
    - Liquid vs. vapor

- **Thin films**
  - Grazing incidence (GI) SAXS
  - Water uptake
  - Thin(ner) films
    - Structure
    - Conductivity

- **Summary**

Probing internal structure: GISAXS



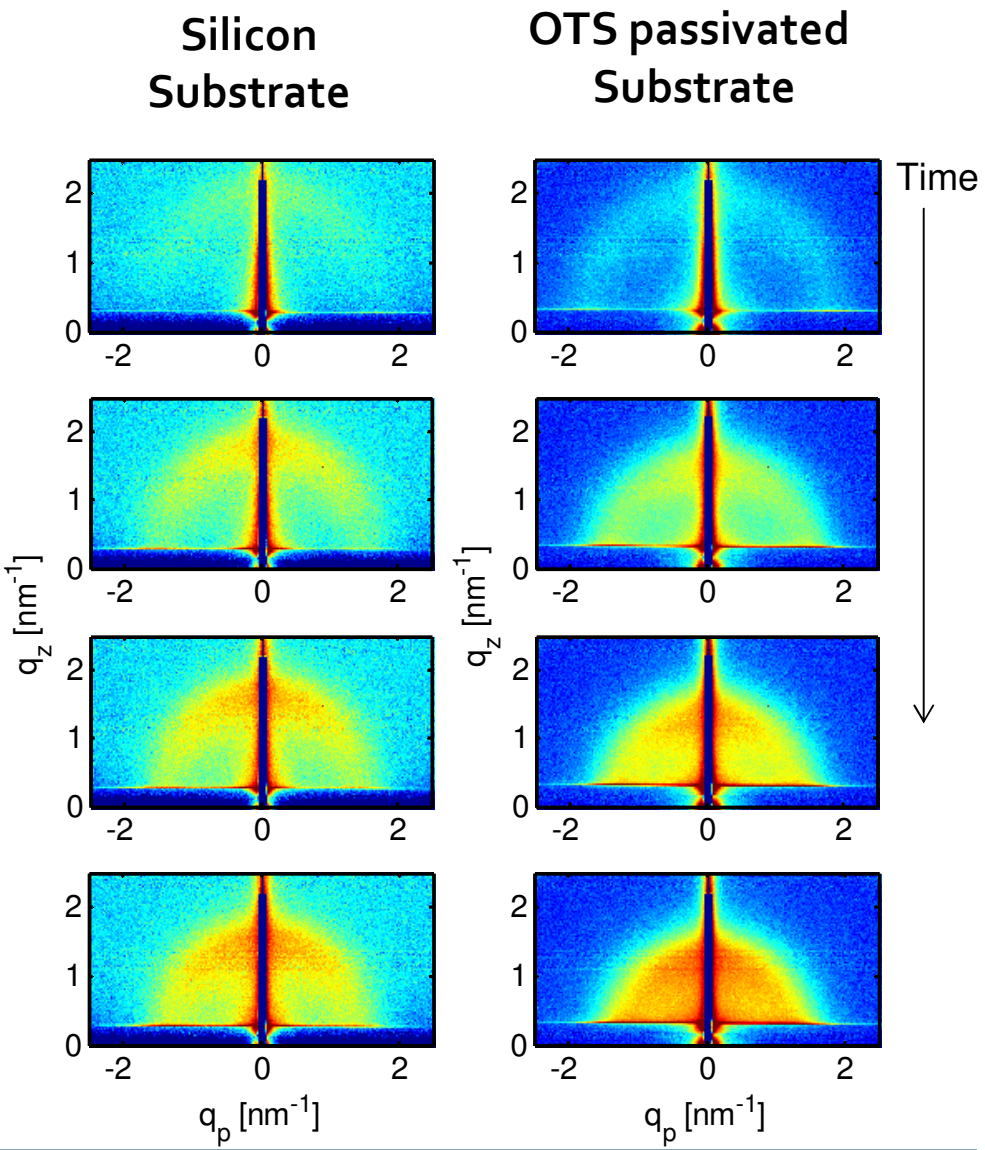
Nafion Thin Films

- **GISAXS of Nafion films during water uptake at 100% RH**
  - Hydrophobic OTS surface retards water uptake and shows parallel domains compared to hydrophilic Si surface

- Interfacial interaction with substrate affects domain orientation

- Solid interactions control water uptake like liquid/vapor ones

- Domain orientation controls kinetics of water uptake and film swelling



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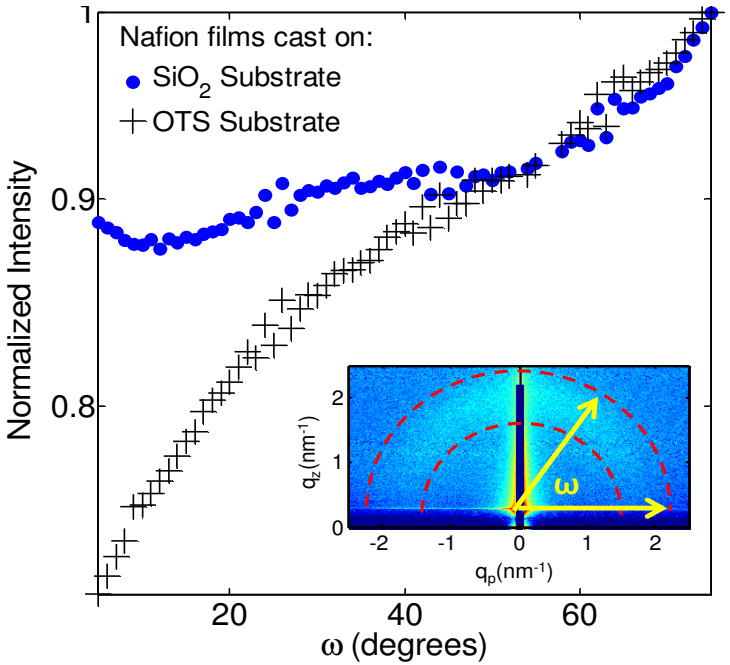
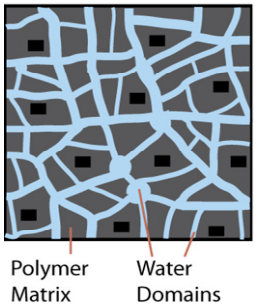
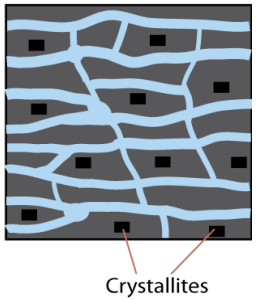
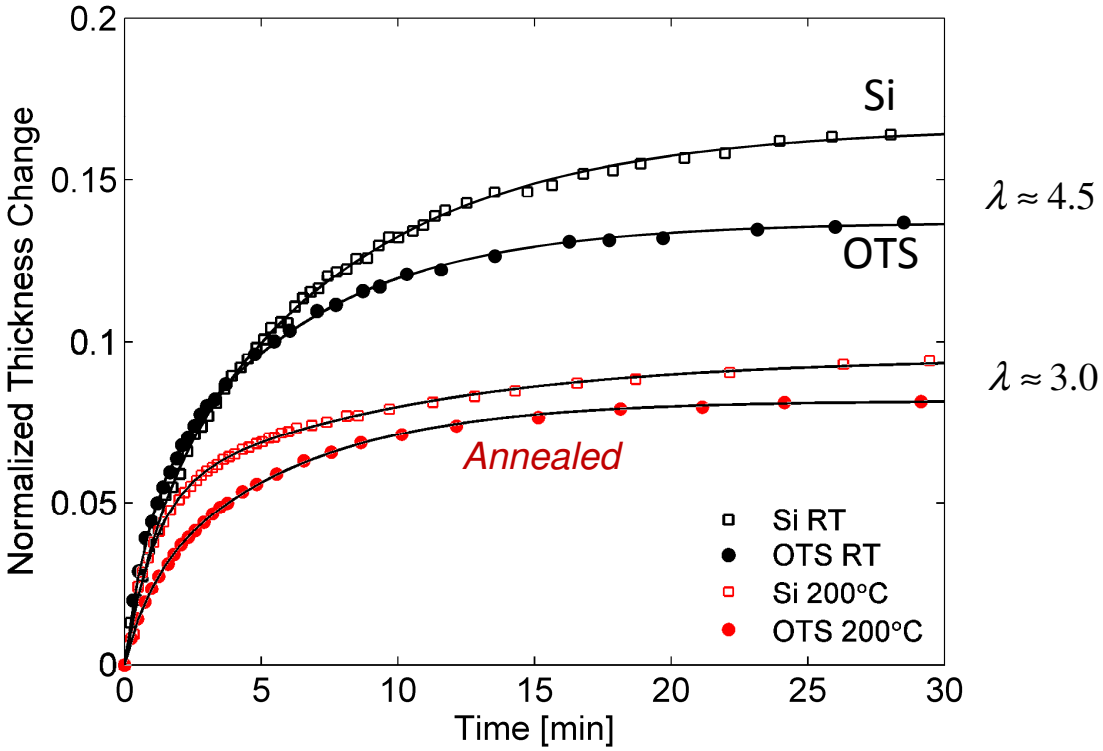






Nafion Thin Films

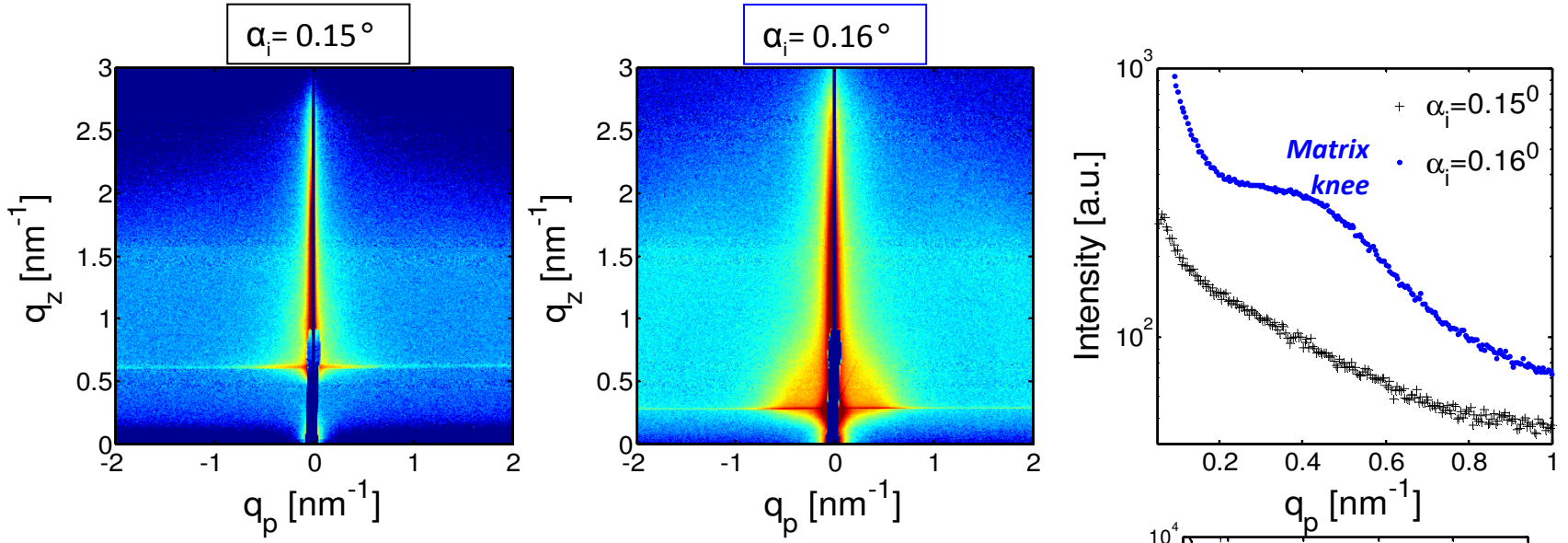
- **Nanoscale morphology impacts macroscopic water uptake**
  - 100 nm thin films swell even less than expected
  - Impact of OTS (hydrophobic) causes lower ultimate water uptake due to morphology differences
  - Annealing (crystallinity) reduces uptake



M.A. Modestino, A. Kusoglu, A. Hexemer, A.Z. Weber, R.A. Segalman, *Macromolecules* **45**, 4681 (2012).

Nafion Thin Films

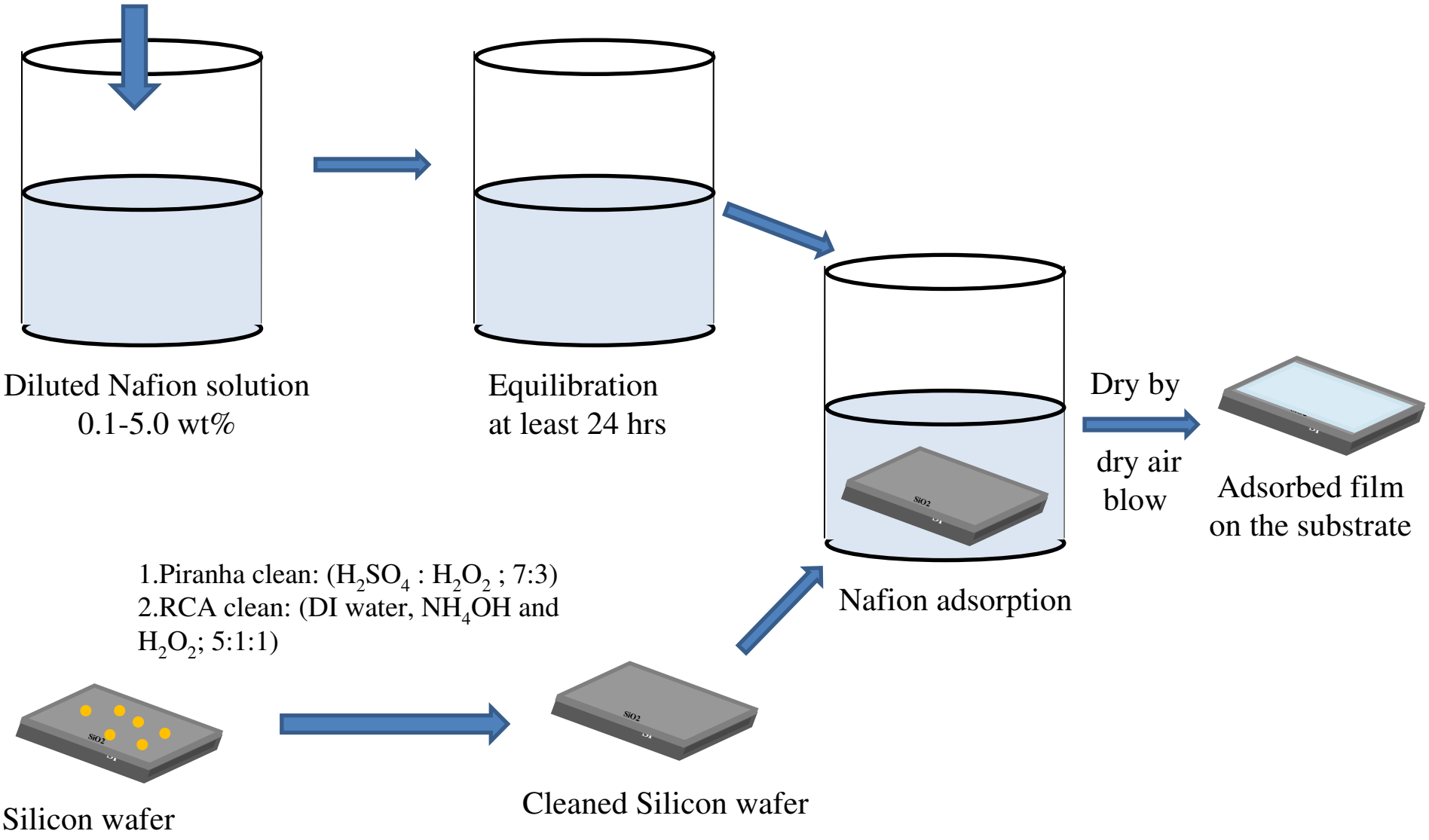
- **High density of crystallites near substrate interface**
  - No crystallites are present in the top surface of films



M.A. Modestino, A. Kusoglu, A. Hexemer, A.Z. Weber, R.A. Segalman, *Macromolecules* **45**, 4681 (2012).

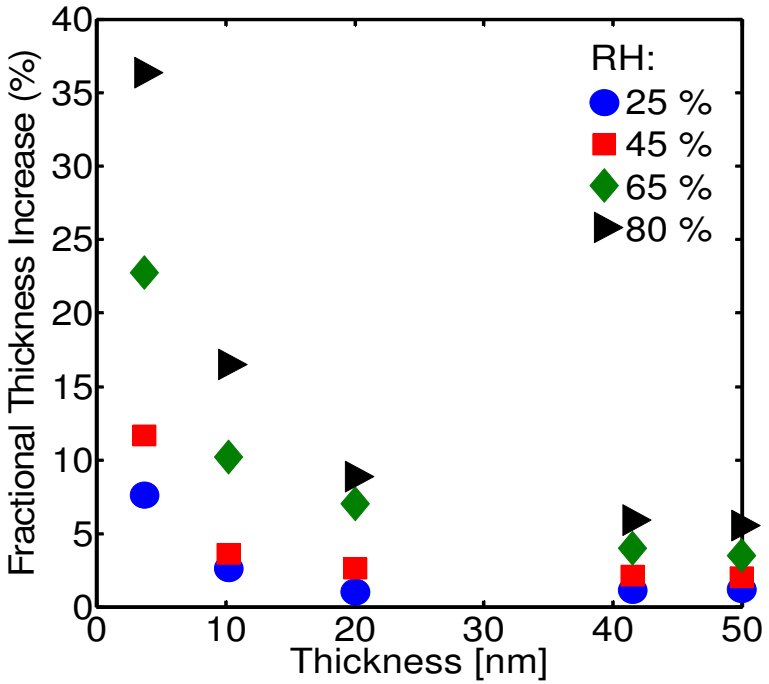
Nafion Thin(ner) Films

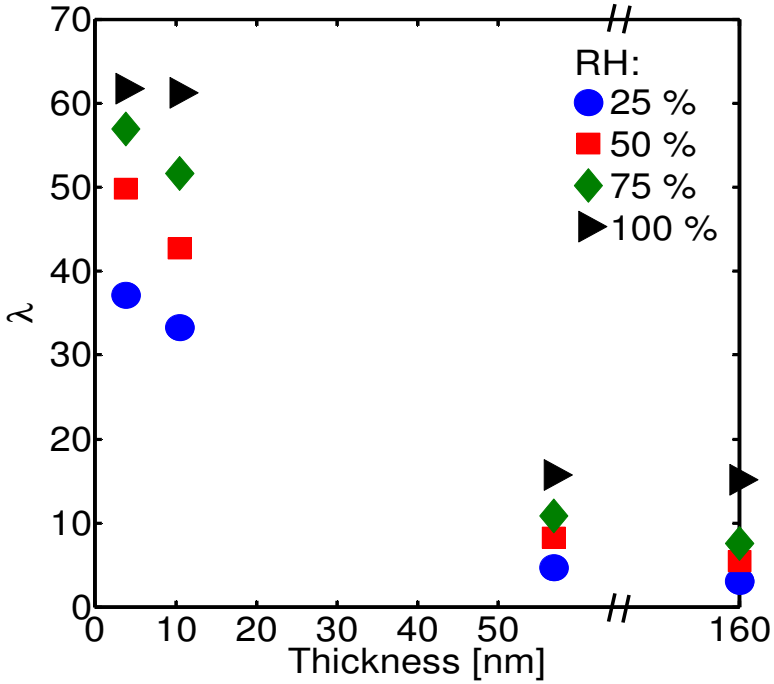
Iso-propyl alcohol



Nafion Thin(ner) Films: Water Uptake

- **From both ellipsometry and QCM, the thinner films have more swelling and higher water uptake**
  - Substantial substrate effect



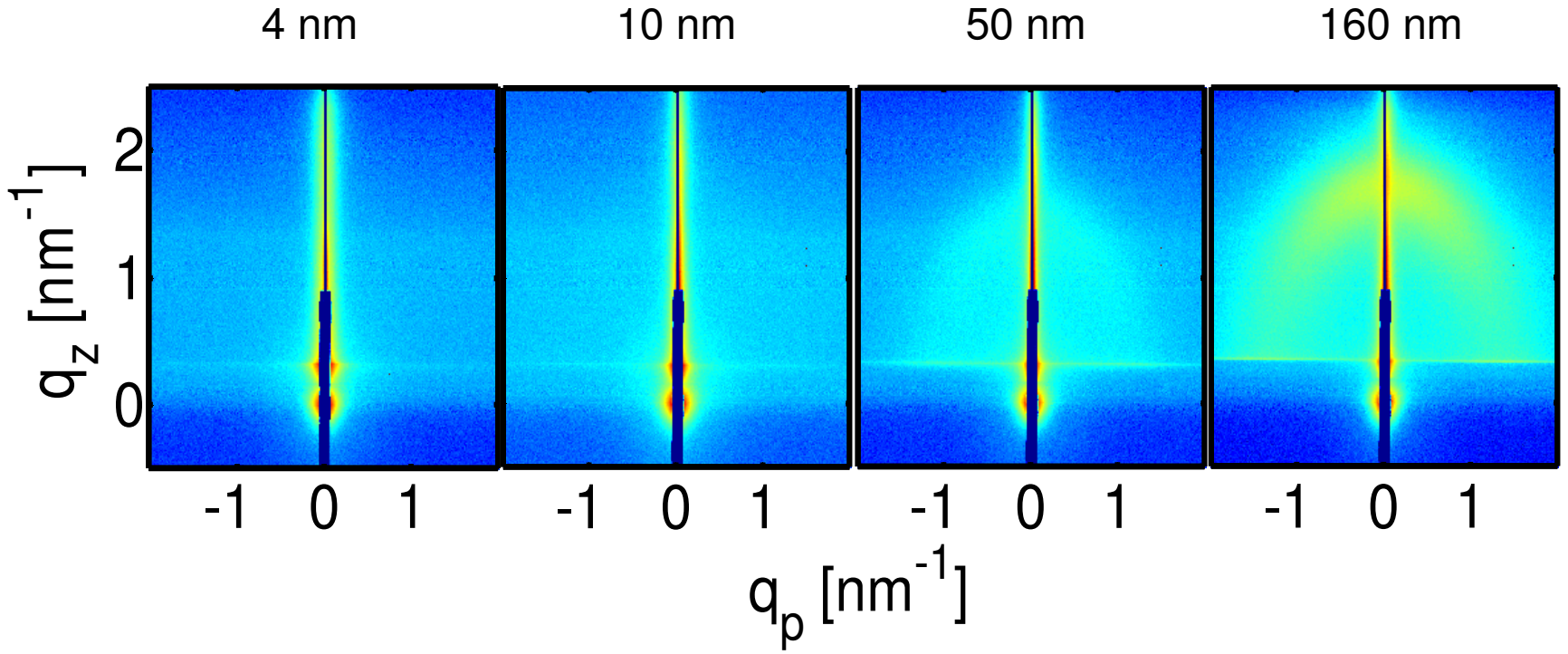


  - Opposite effect as seen with thinner films on gold*

*A. Kongkanand, *J. Phys. Chem. C,* **115,** 11318 (2011)

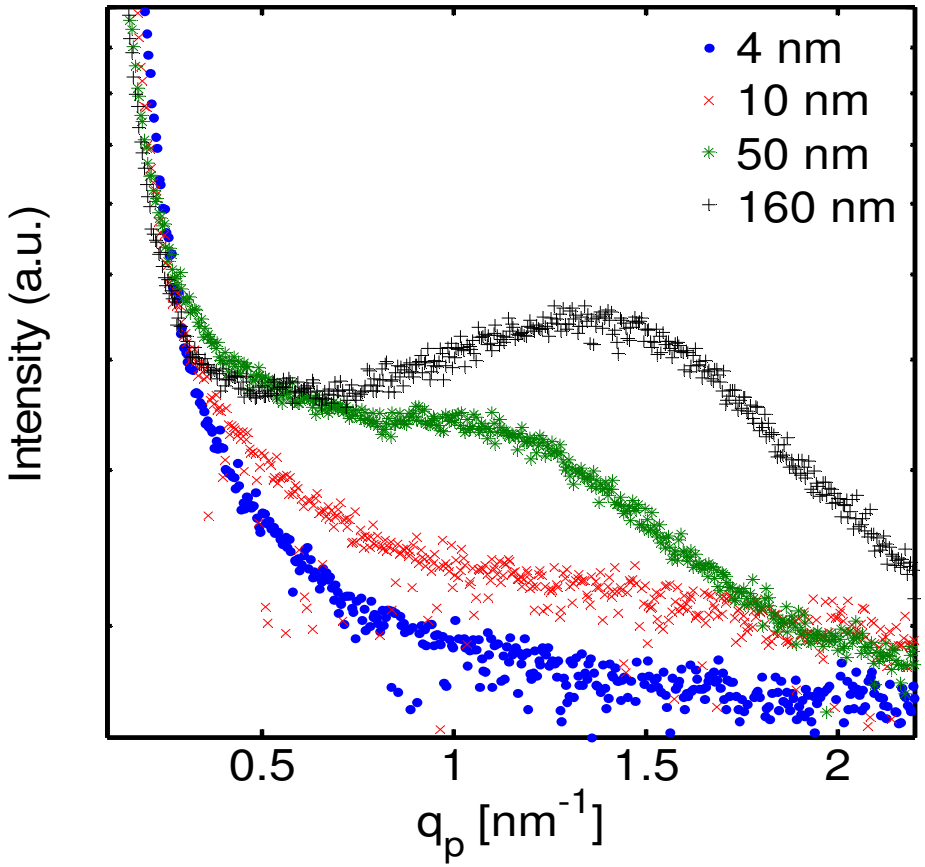
Nafion Thin(ner) Films: Structure

- **Thicker thin films have a structure similar to what we saw with the 100 nm films**
  - Thinner films seem not to have a strong or any structure



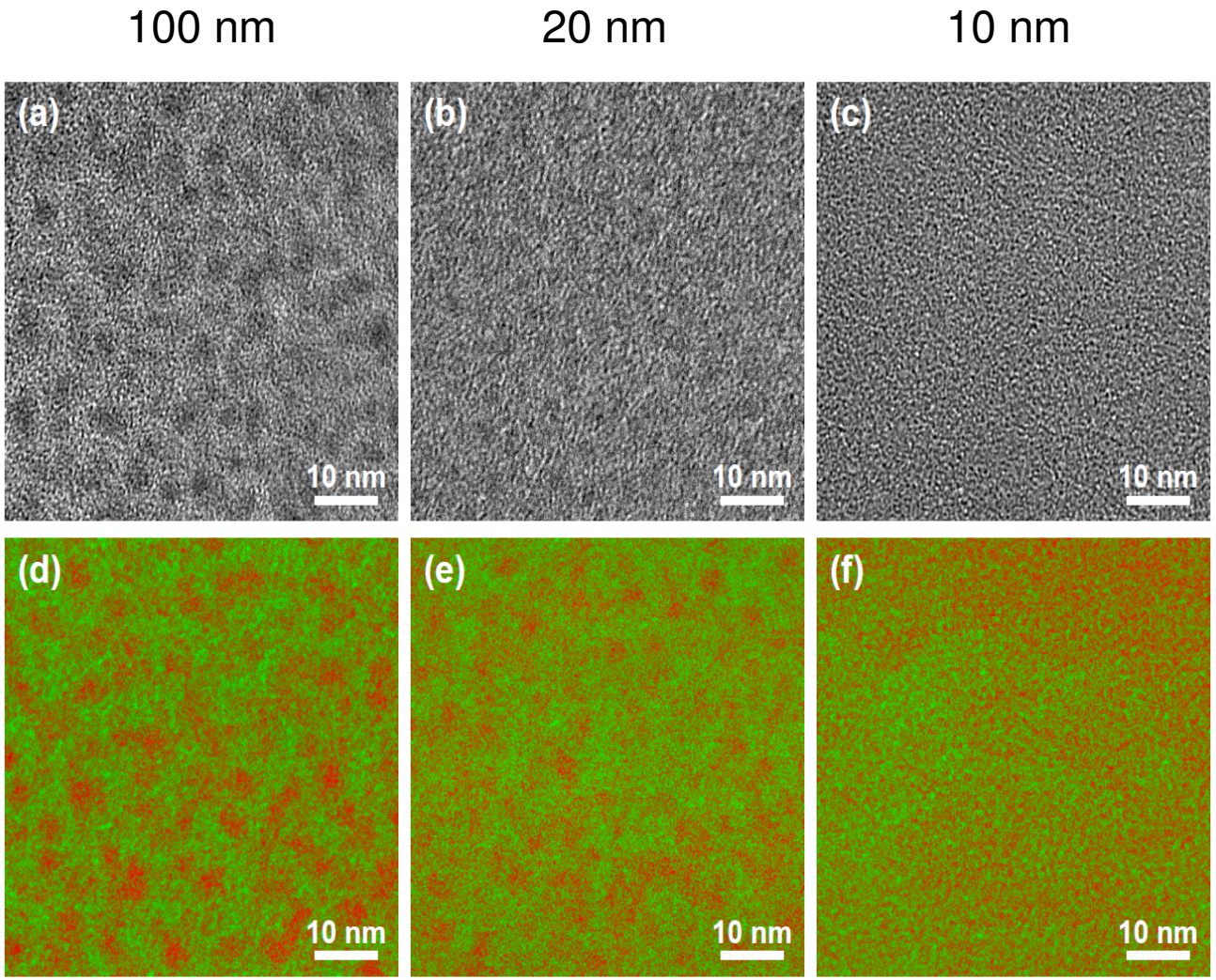
Nafion Thin(ner) Films: Structure

- **Ionomer peak and structure disappear with film thickness**
  - Probably due to loss of crystallinity and lower backbone mechanical energy that can resist chemical dissolution force
    - Uncorrelated structure with thinner films



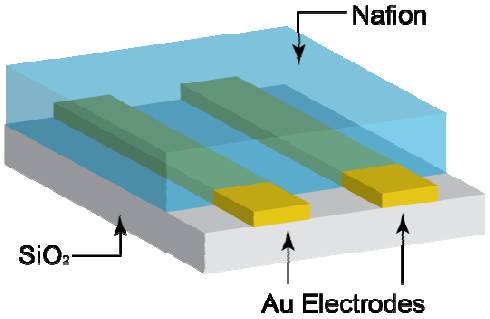
Nafion Thin(ner) Films: Structure

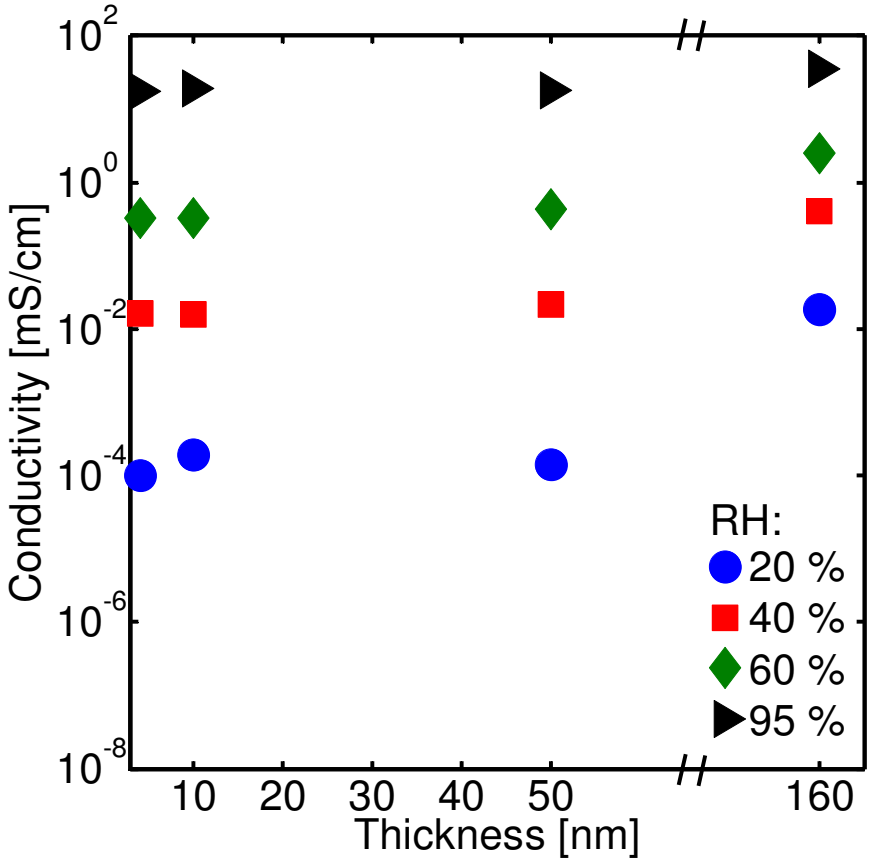
- **More mixing and smaller domains for the thinner samples by TEM**



Nafion Thin(ner) Films: Conductivity

- **For these films, conductivity decreases with relative humidity and only films > 50 nm are bulk-like**
  - Consistent with structural picture of domain isolation and substrate effect





Summary

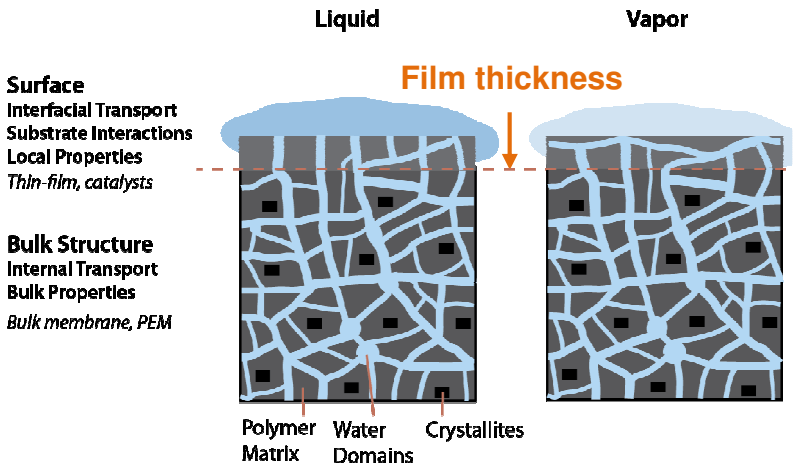
- **Multiscale membrane model**
  - Uptake is a balance between mechanical and chemical energies

Thermal history & substrate interactions → Mechanical properties & relaxation

Solvent polarity & interactions → Hydration & solvation

Sorption and final solvent uptake and morphology → λ

- **Interfacial phenomena**
  - Interface dominants uptake and transport
    - Free and substrate interfaces can behave similarly
- **Thinner films on SiO_2 substrates**
  - Loss of structure below 30 nm
  - Increase in water content and swelling
  - Lower conductivity



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Mechanical/Chemical Energy Balance in Perfluorinated Sulfonic Acid Membranes

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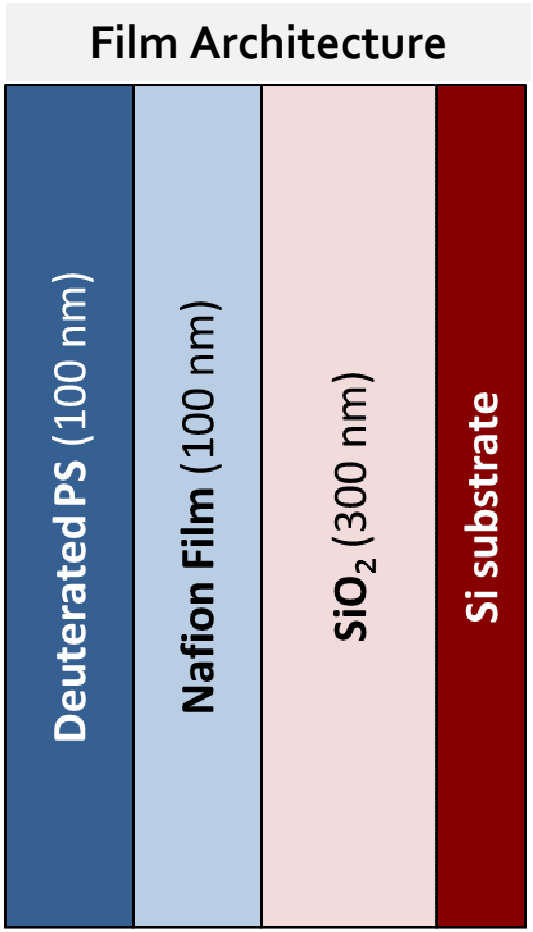
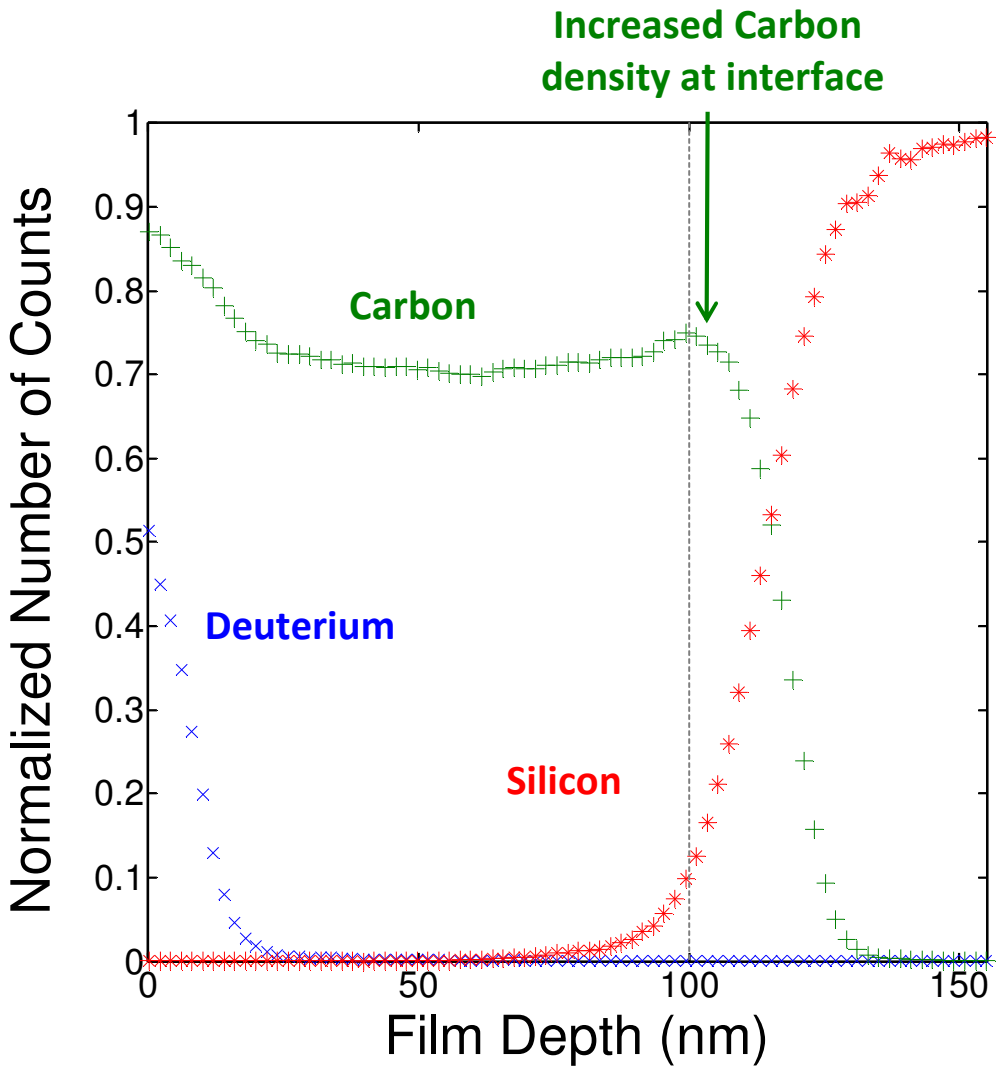
Element profiling: higher density near substrate

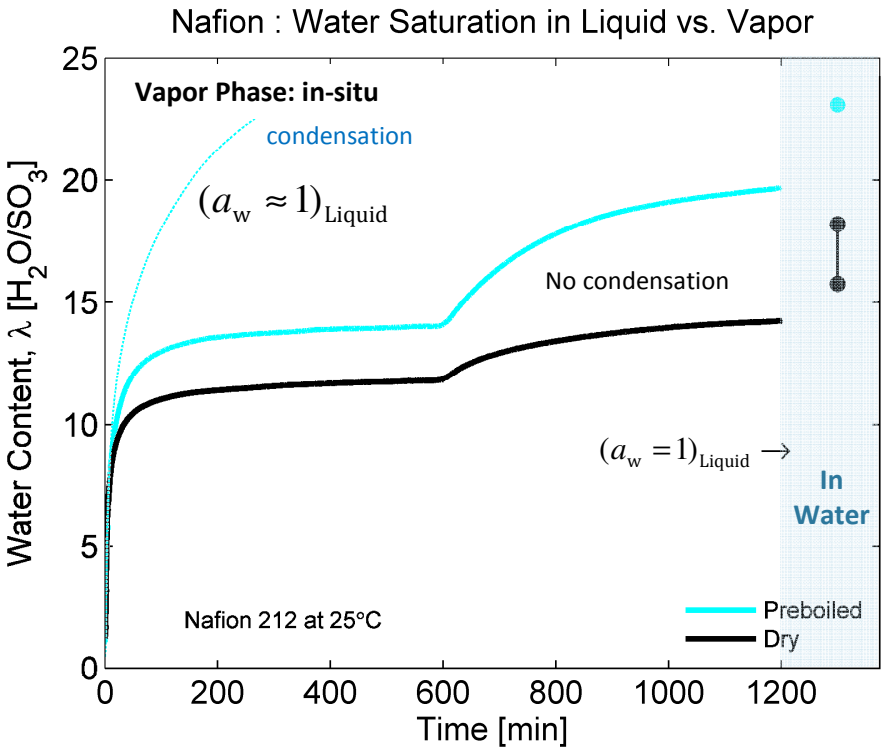




M.A. Modestino, A. Kusoglu, A. Hexemer, A.Z. Weber, R.A. Segalman, Macromolecules, (2012).

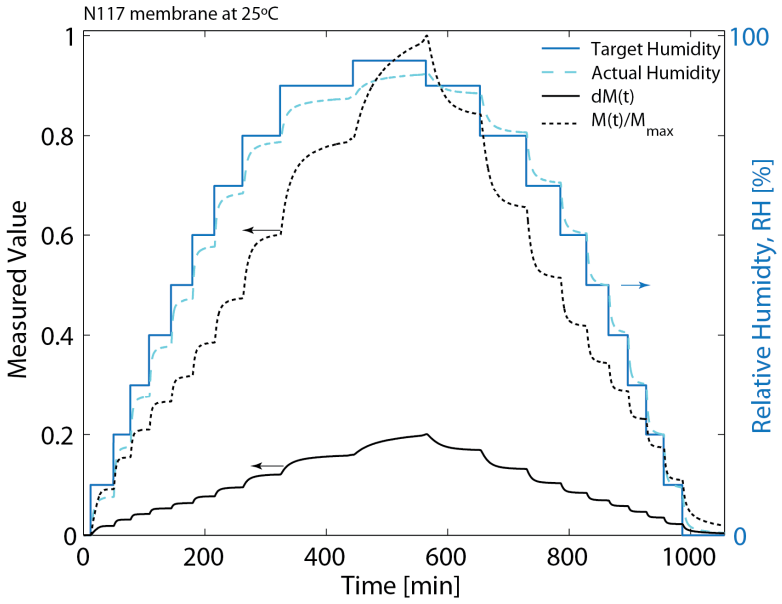
Challenges: Saturation in Vapor vs. Liquid

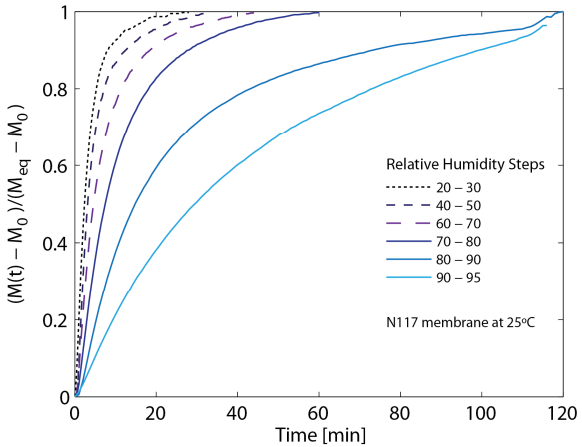
- **Dynamic Vapor Sorption**
  - In-situ vapor:
    - With condensation ➔ LIQUID
    - Without condensation ➔ VAPOR
  - Ex-situ Liquid:
    - Immersed in water ➔ LIQUID
- **Difficulty in controlling 100% RH**
  - A slight change in 100% RH in vapor environment can result in behavior similar in to that in liquid
  - Schroder's Paradox
    - Is this an error in weight measurement?
    - What about morphology?



Dynamic Vapor Sorption (DVS)

- **Dynamic Gravimetric Sorption (DVS)**
  - Sorption/desorption with Step RH, T loads

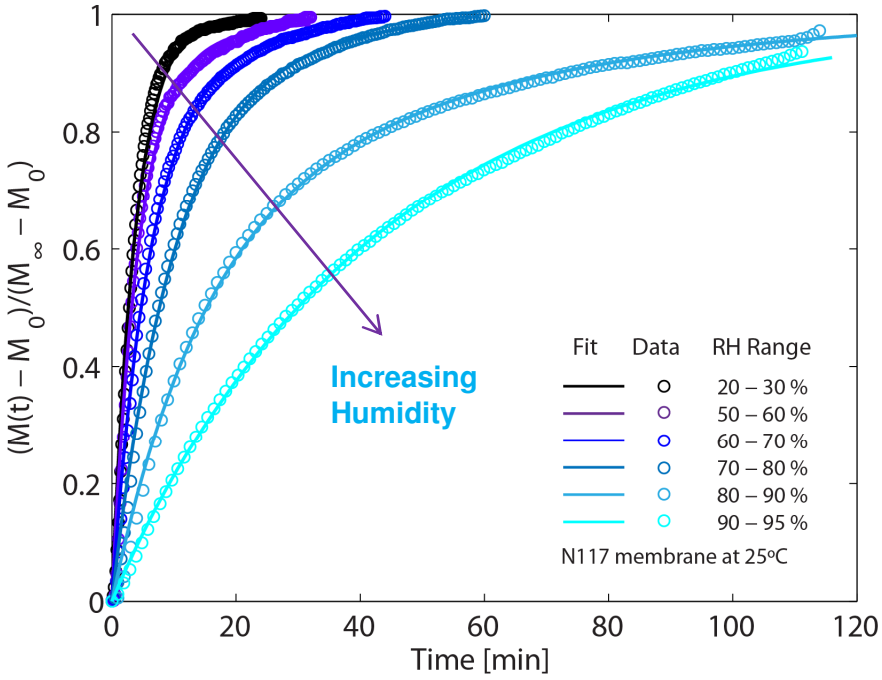




- **Water uptake during hydration**
  - Rate of absorption decreases at higher humidity intervals

$$\frac{M(t)-M_0}{M_\infty-M_0} \propto 1-\sum_n \exp(-k_n t)$$

  - Time constants ~ 30 to 100 min $k_{1,2} = \frac{1}{\tau_{1,2}}$

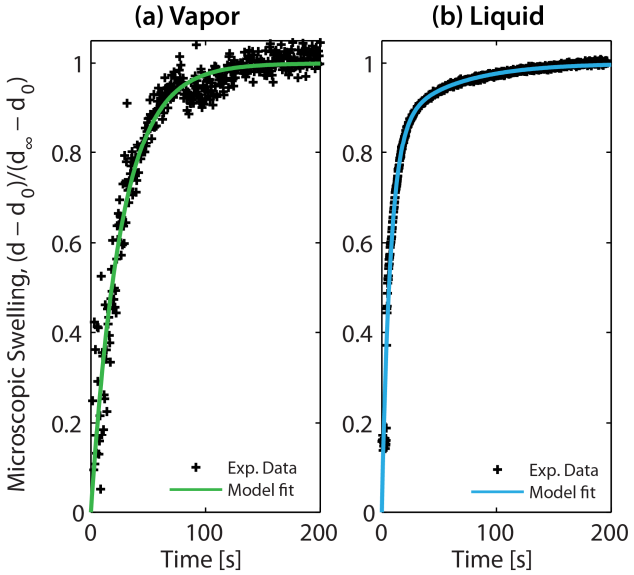


Probing Fast Sorption in Nafion

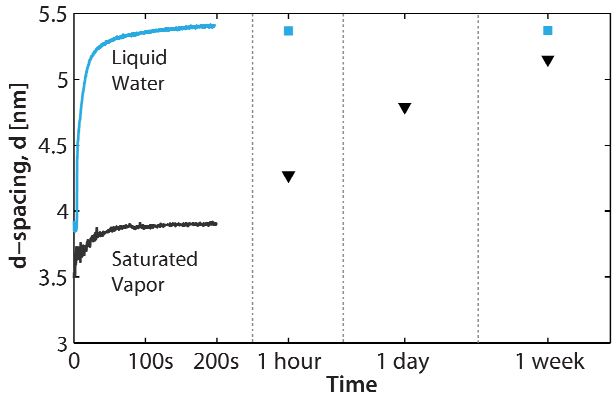
- **Swelling of water domains**
- **Time constants**
  - Short-term process
    - In water : 2 sec
    - Sat. vapor : 30 sec
  - Long-term process
    - In water : 2 sec
    - Sat. vapor : 10^4 sec ~ days
- **Schroeder's Paradox**
  - Different morphology between vapor-liquid
    Big difference in domain size during early stages of water uptake
  - Interactions with liquid or vapor seems to control sorption kinetics
    Instant equilibrium in liquid water
    Long-term processes dominate in vapor

A. Kusoglu et al. (2011) Macro-Letters

- **Short-term process**



- **Long-term process**



Membrane Model: Remarks

- **Water content vs. Fraction**
  - Bound Water + Free Water

$$\lambda = \lambda^B(a_w) + \lambda^F(a_w)$$

    - Bound water: solvation and primary adsorption of water molecules
    - Free water: sorption/swelling (FH theory)

  - Residual Water at 0% RH

$$\lambda_{res} = \lambda(a_w = 0) = 0$$

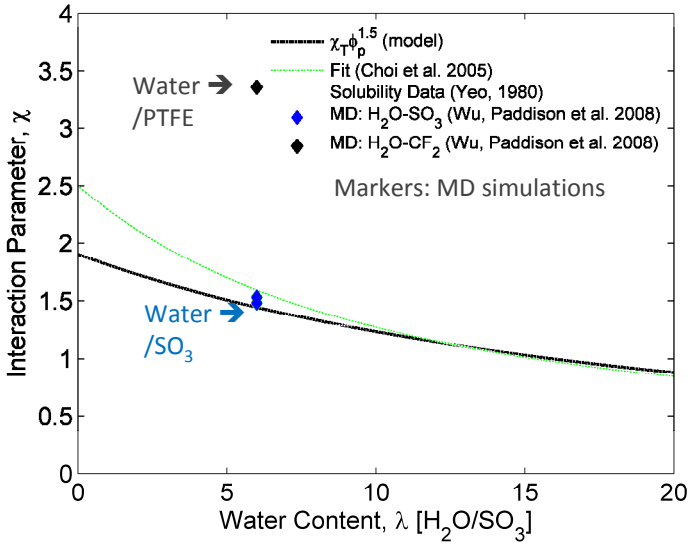
    - Can be determined upon heating

  - Volume Fraction

$$\phi_w = \frac{\lambda^F \overline{V}_w}{\lambda^F \overline{V}_w + \overline{V}_p(EW)}$$

- **Interaction parameter**
  - Common expressions for FH theory

$$\chi(T) = A + \frac{B}{T} \qquad \chi \propto \phi_w$$

  - Expression for PFSA-like ionomers
    - Based on experimental evidence

$$\chi(T,\phi_p) = \underbrace{\chi_S \phi_p^{1.5}}_{Swelling} + \underbrace{\chi_T\left(1 - \frac{298}{T}\right)}_{Thermal}$$