Continuum Modeling of Membrane Properties

Ahmet Kusoglu, Adam Z. Weber
Environmental Energy Technologies Division
Lawrence Berkeley National Laboratory

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Outline

- **Effect of Constraints on Water Uptake**
- **Modeling and Role of Temperature**
- **Validation: Experimental Data**
  - Neutron Imaging (in-situ and ex-situ)
  - Mechanical Testing

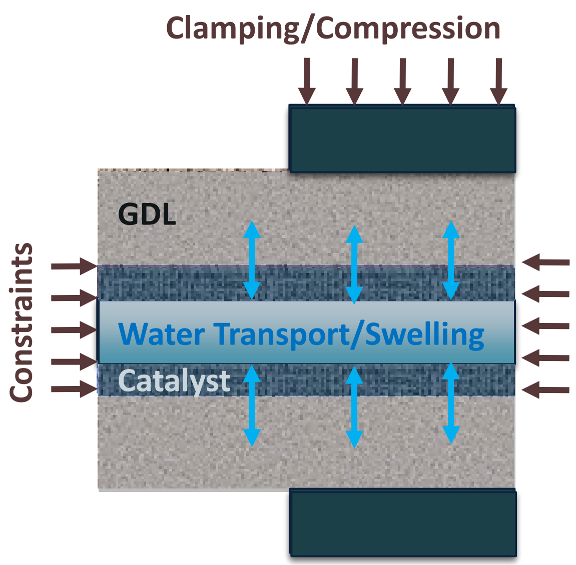
Motivation and Objective

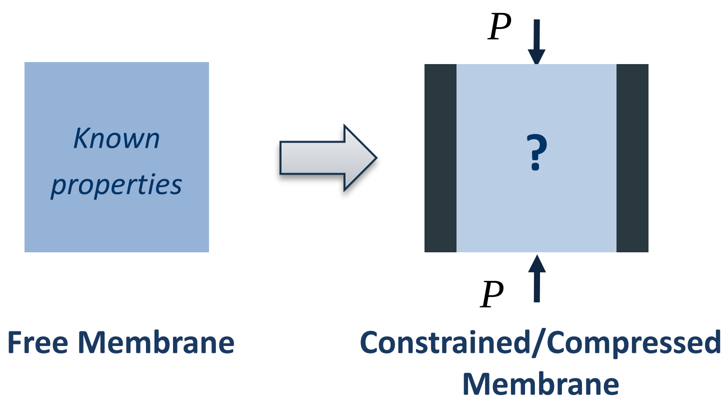
MOTIVATION

- **Electrochemical and mechanical loads co-exist.**
- **Does compression alter the Transport properties?**

OBJECTIVE

- **Water uptake of Compressed Membrane**
  - Modeling and Experimental Validation
- **Fundamentals of sorption of constrained membranes**
  - Interested in pressure higher than assembly pressure

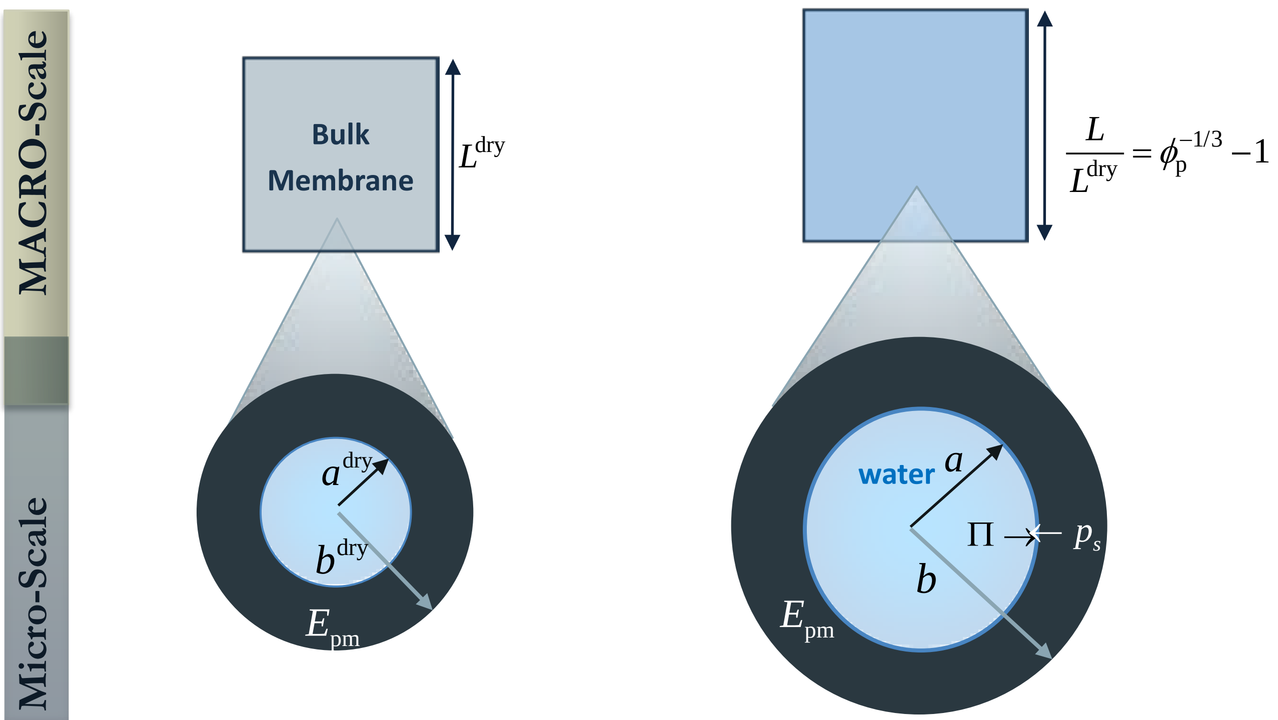




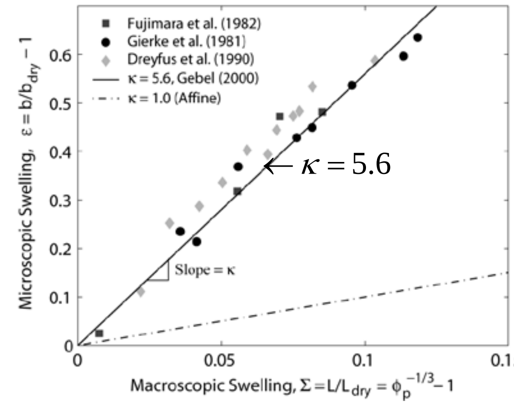
Swelling Pressure in Ionomer Membranes

Dry Membrane

Hydrated Membrane



Non-affine Deformation



$$\kappa \rightarrow \frac{\text{Micro-Deformation}}{\text{MACRO-Deformation}}$$

$$\frac{b}{b^{dry}} - 1 = \kappa\left(\frac{L}{L^{dry}} - 1\right)$$

Bridging Macro-scale (*L*) to micro-scale (*b*)

L = Sample length

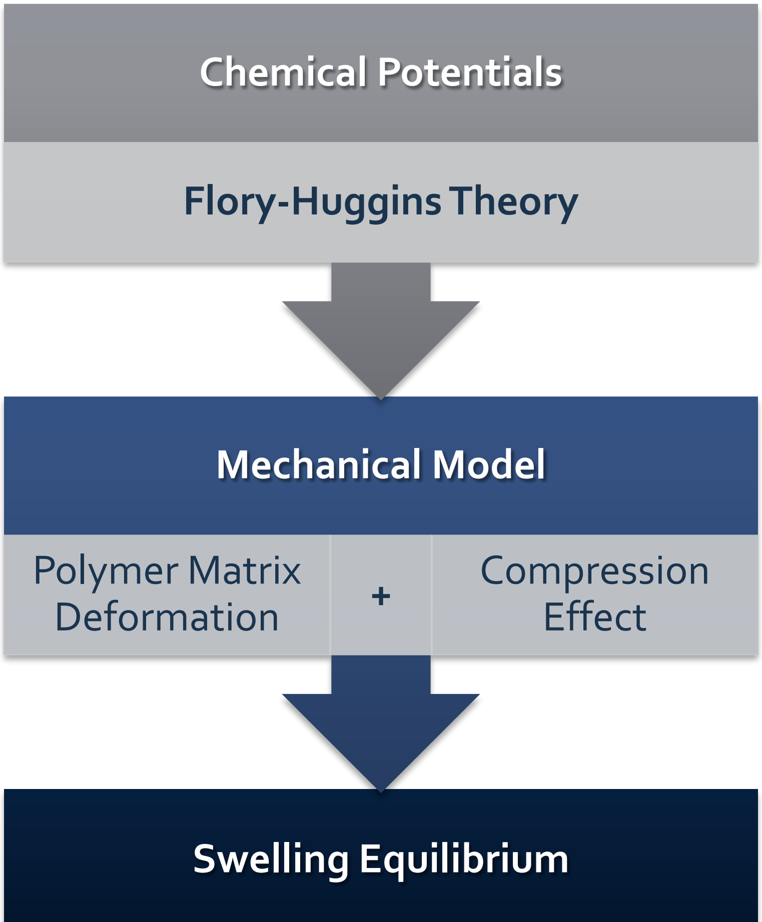
b = Domain spacing (e.g. Bragg distance)

Swelling Pressure:

$$\Pi = p_s = E_{pm} \times \frac{b - a}{b^{dry} - a^{dry}}$$

Kusoglu et al., Polymer, 50 (2009)

Equilibrium Swelling



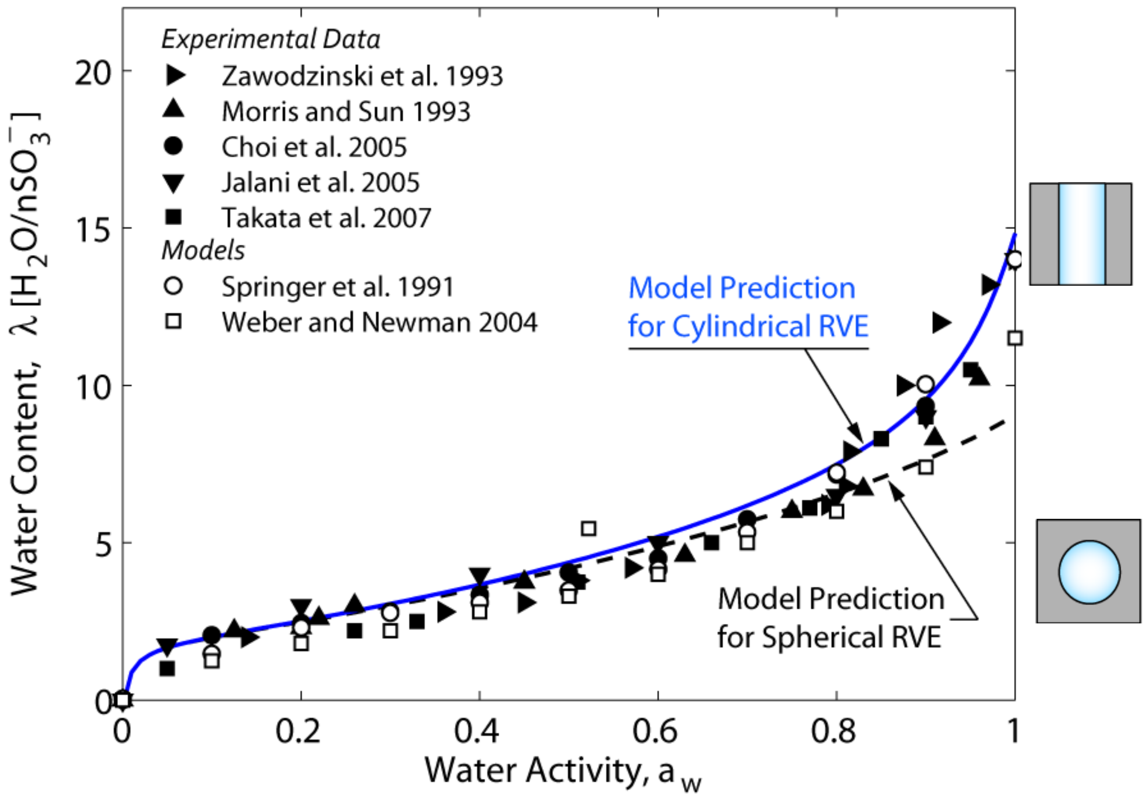
- **Multi-Scale Model:**
  - For PFSA Membranes
  - Morphology dependent
  - Bridges macroscopic and microscopic swelling behavior
  - Compression is introduced:
    - Pressure deforms the polymer backbone, and therefore limits sorption in hydrophilic domains
  - Extension of previous work

References:

1. A. Z. Weber and J. Newman, AIChE Journal, 50, 3215 (2004).
2. A. Kusoglu et al., Polymer, 50, 2481 (2009).

Model Predictions for Sorption Isotherms

- **Good agreement between data and model**
  - Model: Hydrophilic domains are cylindrical at higher humidities

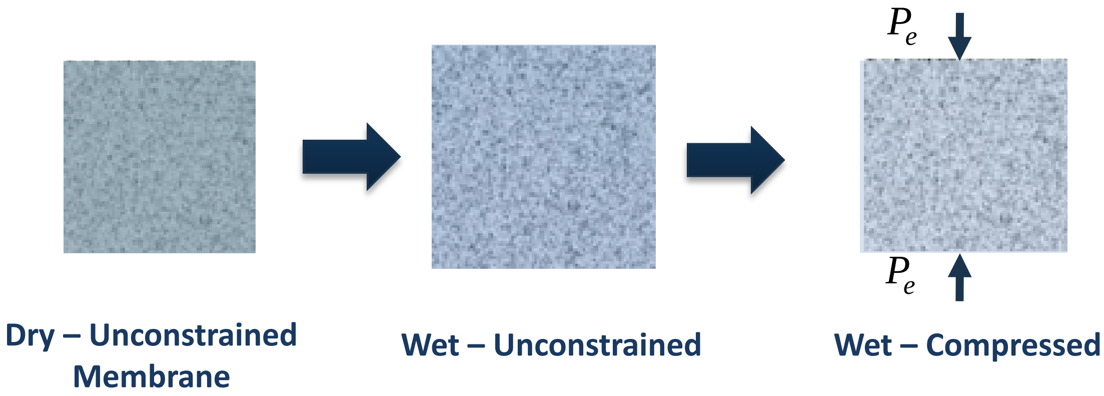


Kusoglu et al., Polymer, 50 (2009)

Origins of Constraints in Fuel Cells

- **Constraints due to Hydration loads**
  - Displacement-based constraints

- **Compression due to Mechanical Loads**
  - Force-based constraints



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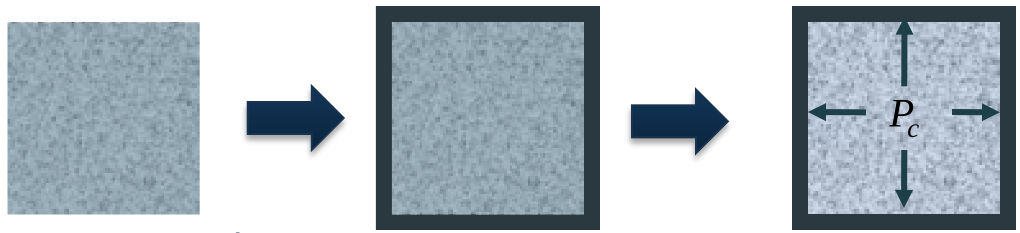
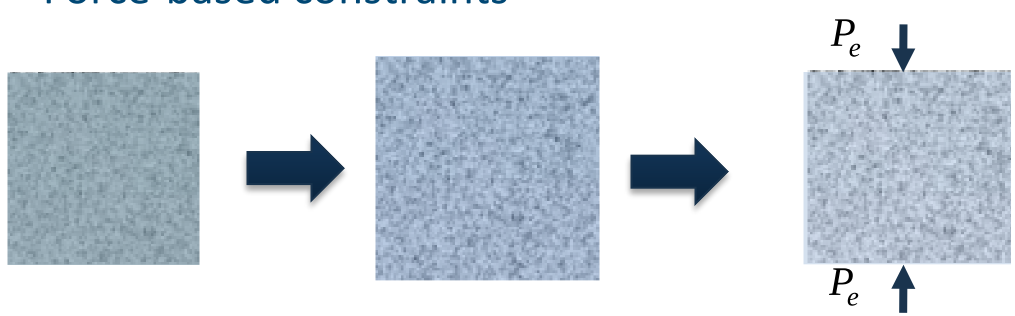


Dry – Unconstrained Membrane | **Dry – Constrained** | **Wet – Constrained**

- **Compression due to Mechanical Loads**
  - Force-based constraints



Dry – Unconstrained Membrane | **Wet – Unconstrained** | **Wet – Compressed**

Role of Temperature

Pressure : swelling induced

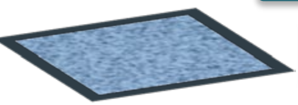
High Temperature → Membrane relaxes, Deforms less → Creates less pressure

Pressure : externally applied

High Temperature → Membrane relaxes, Easier to Deform → Creates more deformation

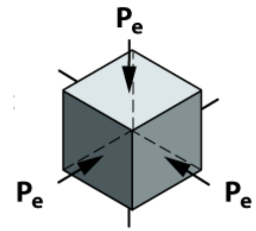
Role of Temperature on Water Uptake

Constrained Membrane

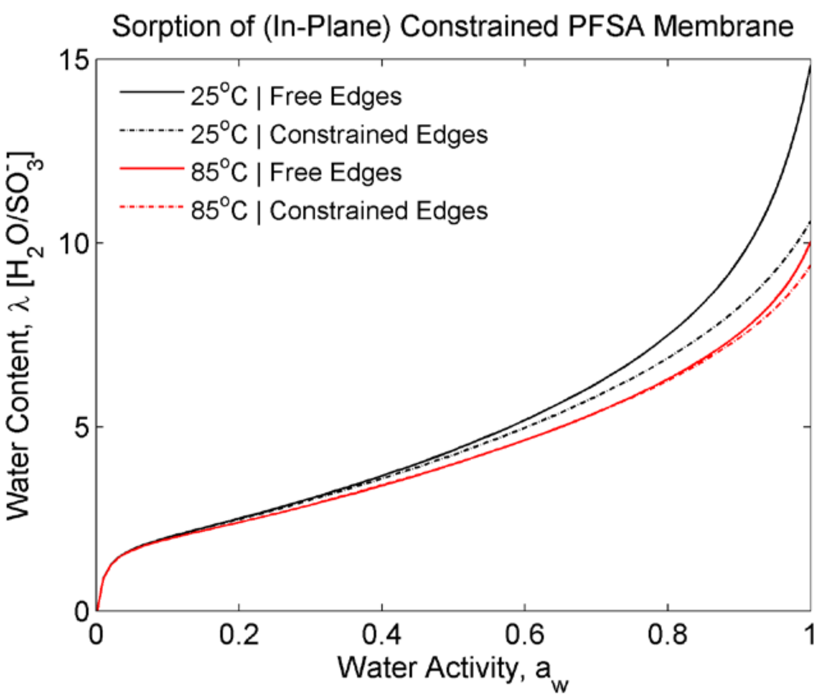


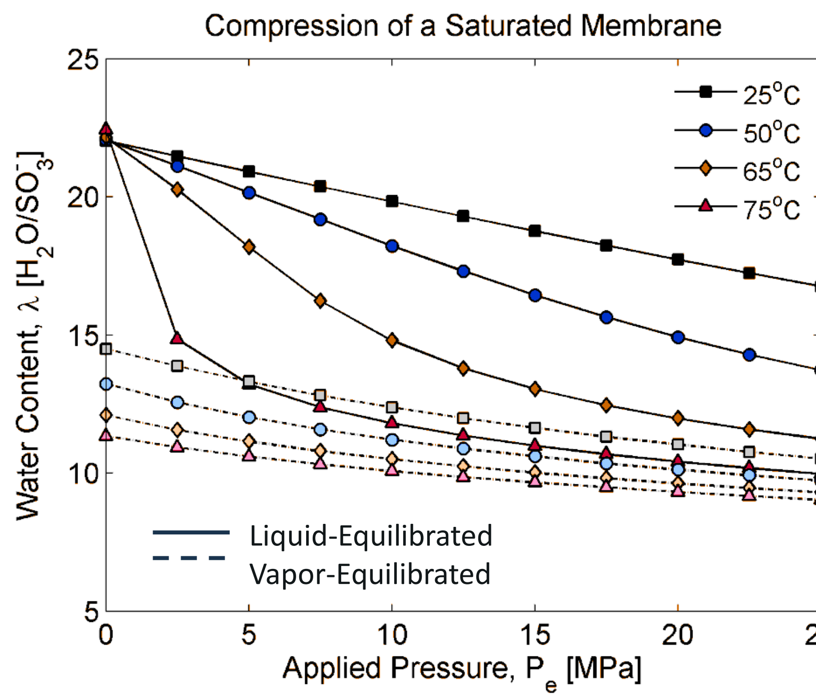
- High Temperature
- Membrane relaxes
- Swelling Pressure drops

Compressed Membrane



- High Temperature
- Membrane relaxes
- Internal Pressure increases





Validation

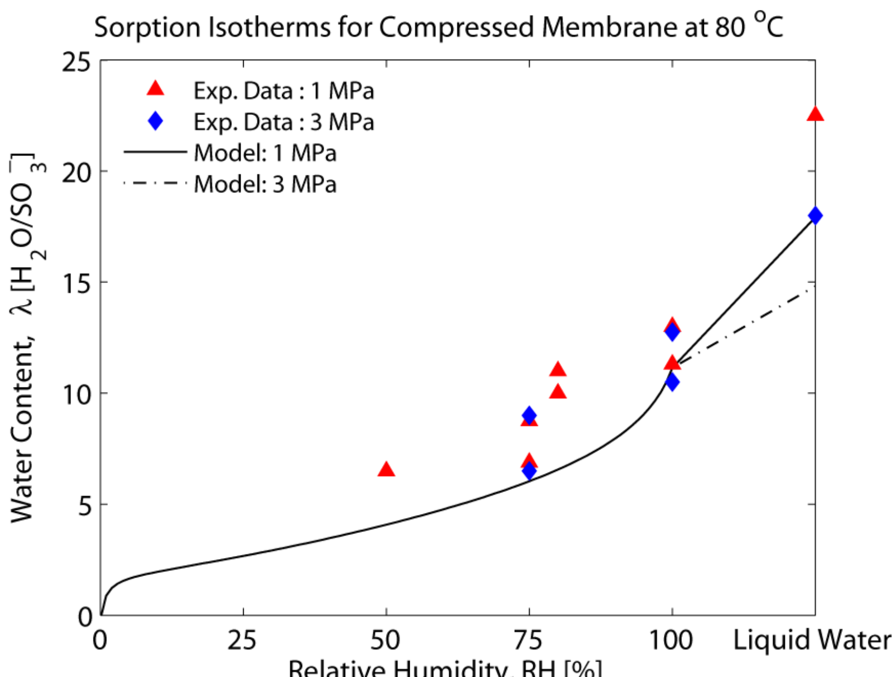
- **Experimental Data on Water uptake of Compressed Membrane**

1. Membrane in fuel cell	Neutron Imaging	LANL/NIST
2. Membrane (ex-situ)	Mechanical Testing	GM
3. Membrane (ex-situ)	Neutron Imaging	LBL/MNRC

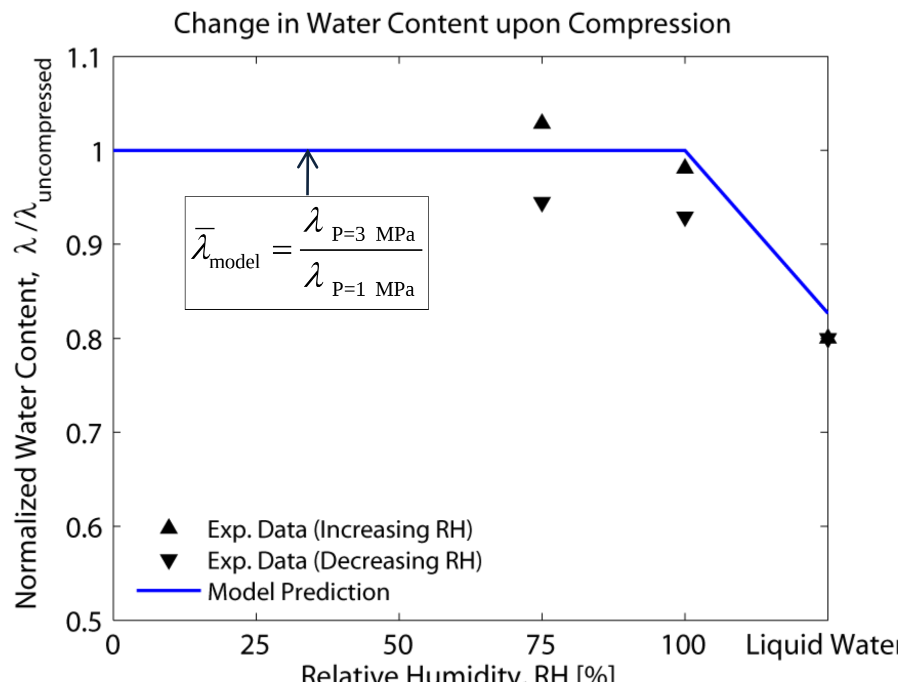
In-situ Water uptake of Membrane

Ref: **Spernjak et al.** *Measurement of Water Content in Polymer Electrolyte Membranes using High Resolution Neutron Imaging*

- **Sorption Isotherms at 80°C**
  - Restricted Membrane : 1 MPa
  - Compressed Membrane : 3 MPa
    - Data from Neutron Imaging (LANL)



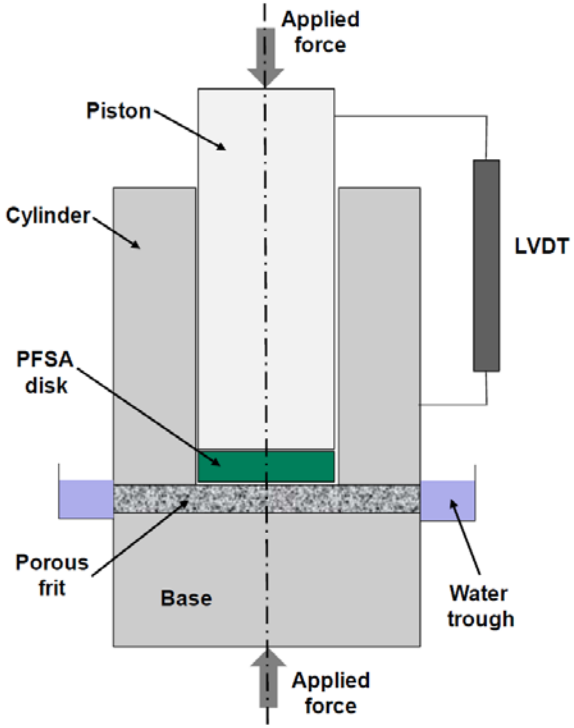
- **Normalized water content**
  - Determined as: $\bar{\lambda} = \frac{\lambda_{Compressed}}{\lambda_{Uncompressed}}$



Membrane in Fuel Cell: Compression in this range does not impact uptake unless under liquid equilibration

Swelling Pressure: Data vs. Model

- **GM's experimental setup**
  - Measures the internal pressure
    - Budinski and Cook



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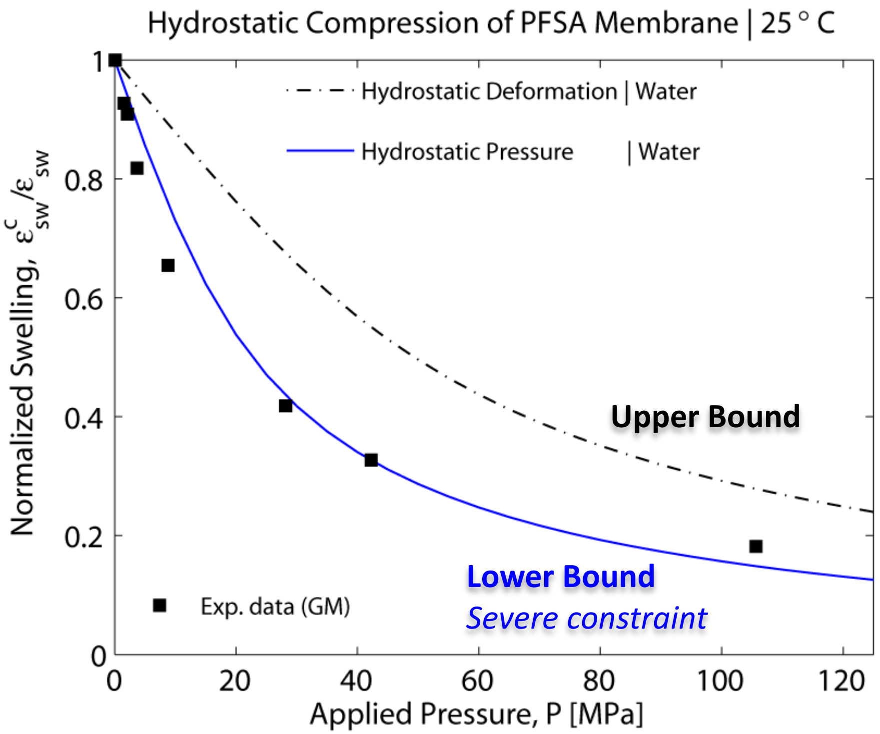
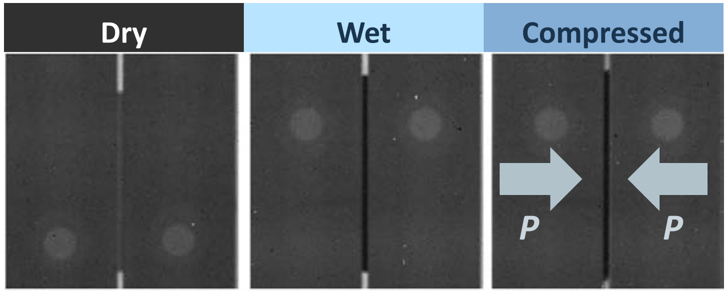
- **Swelling vs. Applied Pressure**
  - Good agreement between measured data and model

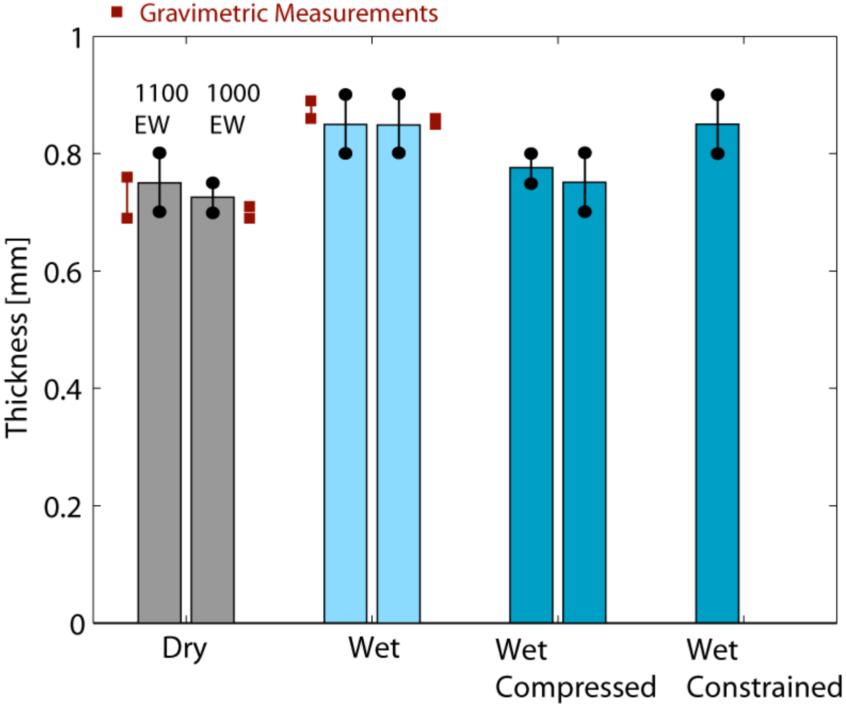


Neutron Imaging of Compressed Membrane

- **Neutron Imaging**
  - MNRC at UC Davis
  - Resolution: 0.1 mm
- **Samples: 30 mil thick membrane**
  - Custom-made by Ion Power
  - 1100 and 1000 EW
- **Procedure**
  - Dry and Wet membranes
  - Wet – Compressed (6-10 MPa)
    - Between aluminum plates
  - Wet – Pre-constrained
    - Membrane is constrained between polycarbonate plates and then equilibrated in water for 1 day

- **Edge-on images**





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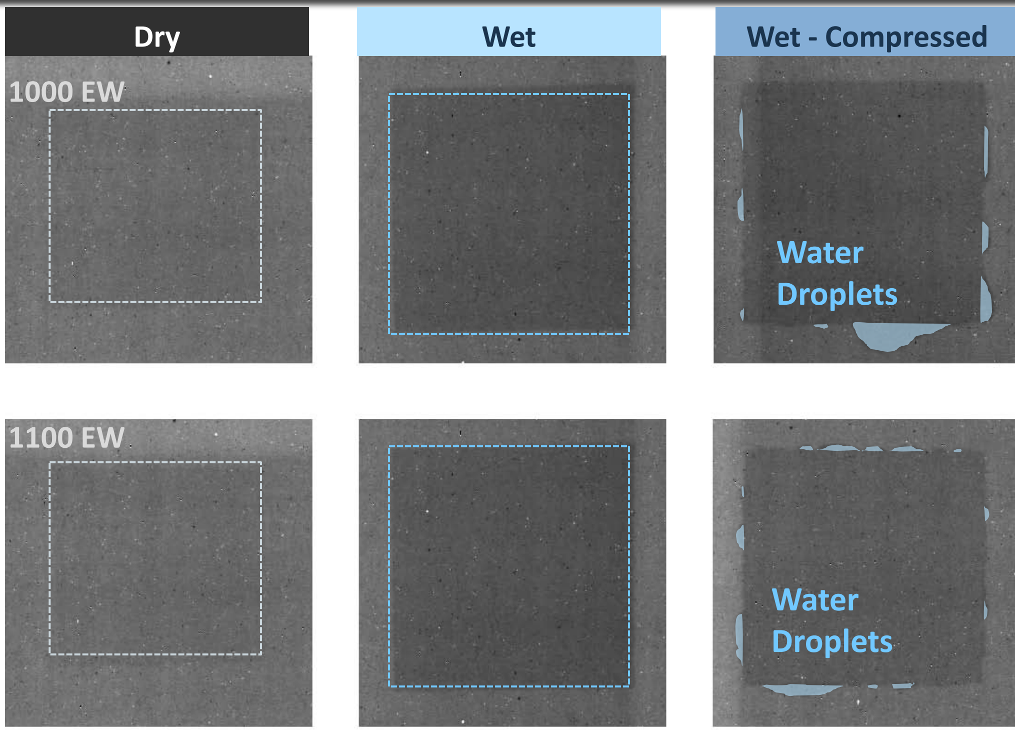
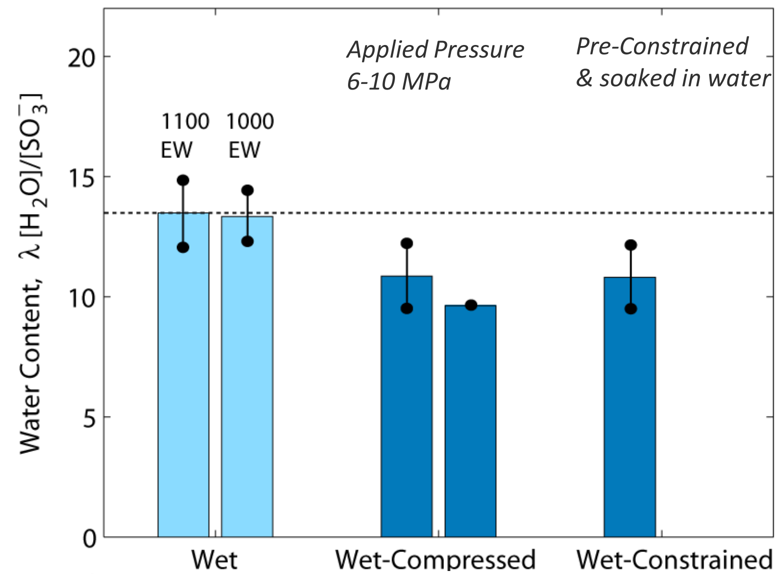
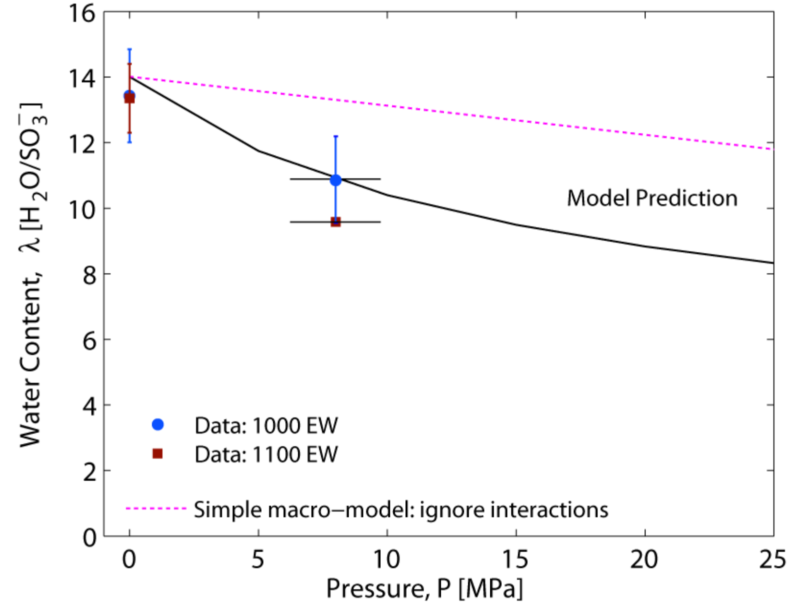
Water Content of Compressed Membrane





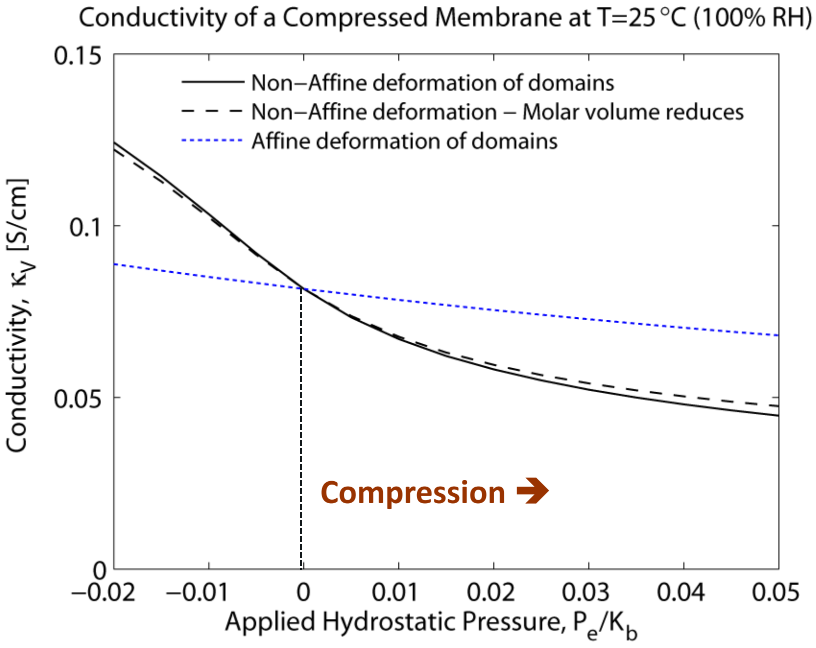


- Water uptake is limited by Compression
- 15 – 25% decrease in water content
- > 40% of this water loss is in droplet form

What happens to Transport Properties?

- **Compression is effective at high humidities, especially in water**
  - Theory and Validations

- **Current and Future Work**
  - Sorption, conductivity and morphology
    - Fundamentals of material behavior – *membrane level*
  - Transport properties and Fuel cell performance
    - Fuel cell model with compression effect – *cell level*



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