



# Membrane Swelling and Proton Transport in Nafion<sup>®</sup>

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# Proton-Exchange Membranes: Design Targets (DOE)

- High conductivity ( $\sigma \geq 0.1\text{S/cm}$ )
- Low RH ( $\leq 60\%$ )
- Suitable for high temperature ( $\geq 120\text{ }^\circ\text{C}$ ) and 1 – 3atm
- Low  $\text{H}_2/\text{O}_2$  permeability ( $\leq 1\%$  crossover)
- Durability (life = 40,000 h)
- High chemical stability ( $\leq 10\%$  reduction in  $\sigma$  over life)
- Good mechanical strength
- Good dimensional stability
- Inexpensive (MEA cost target  $\leq \$10/\text{kW}$  at 500,000 stacks/y)

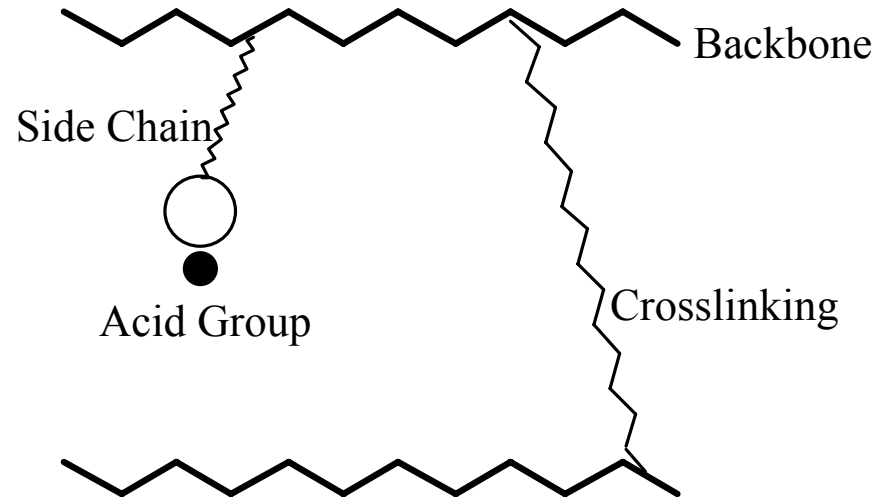
# Proton-Exchange Membranes: Design Parameters

## Polymer:

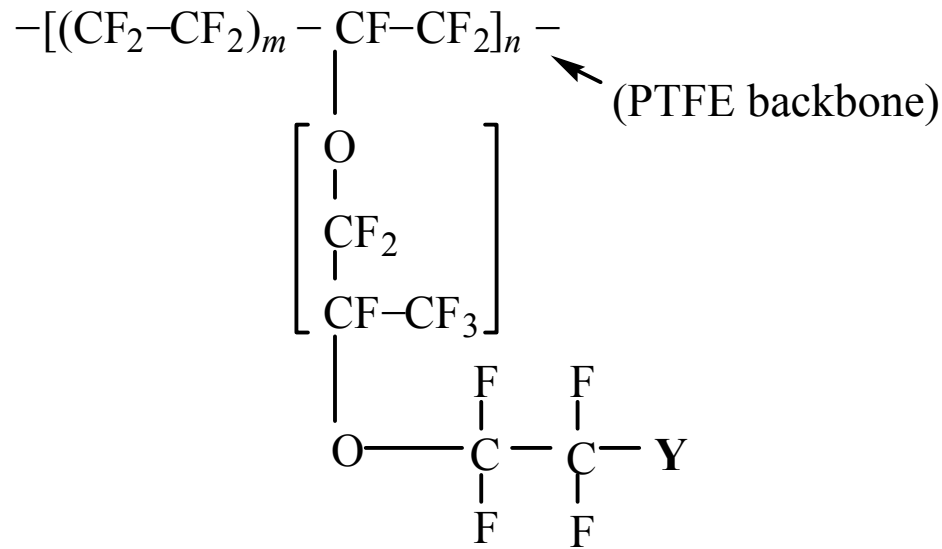
- Polymer backbone
- Side chain
- Equivalent weight
- Acid group/acid strength
- Degree of crosslinking
- Degree of swelling

## Other:

- Support matrix
- Inorganic Nanoparticles



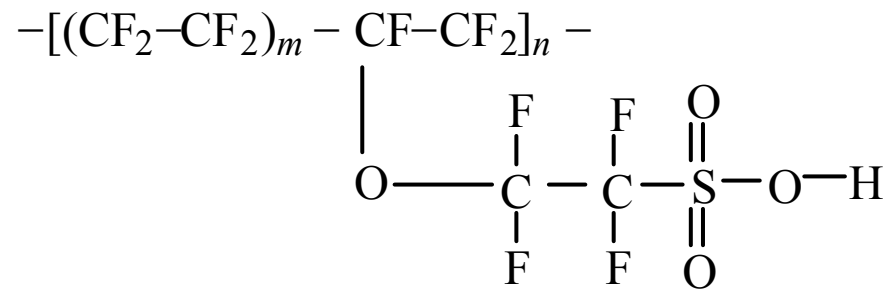
# Perfluorinated Membranes



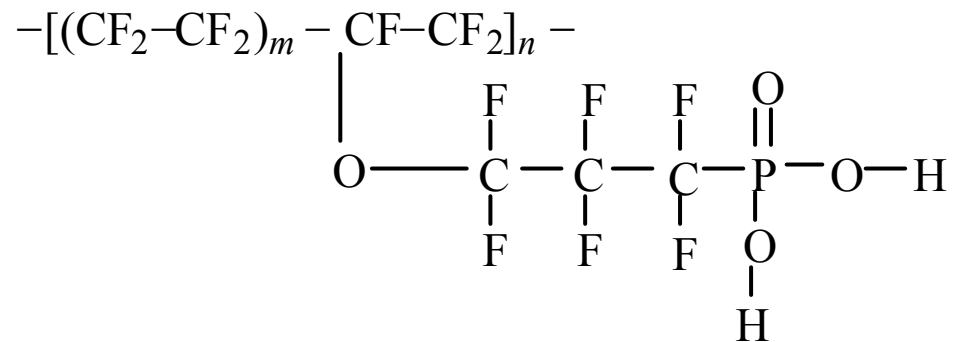
- |   |   |
|---|---|
| $\text{Y} = -\text{SO}_3\text{H}$                 | Sulfonic Acid DuPont (Nafion)<br>( $n = 1$ ; $m = 5-11$ ) |
| $\text{Y} = -\text{COOH}$                         | Carboxylic Acid (Asahi Chemical)                          |
| $\text{Y} = -\text{SO}_3\text{NHSO}_2\text{CF}_3$ | Sulfonylimide (DesMarteau)                                |

# Other Perfluorinated Membranes

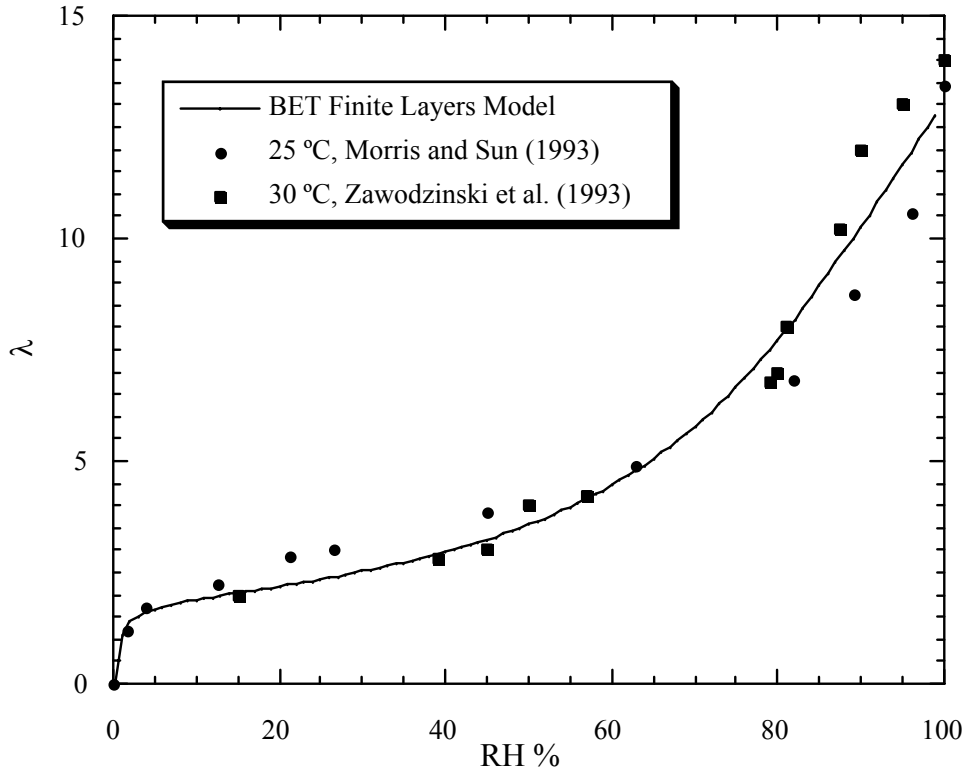
Dow Chemical:



Phosphonic Acid (Burton):



# Nafion<sup>®</sup> Hydration



$$\left. \begin{aligned} \lambda_L^{sat} &= 22 - 24 \\ \lambda_V^{sat} &= 13 - 14 \end{aligned} \right\}$$

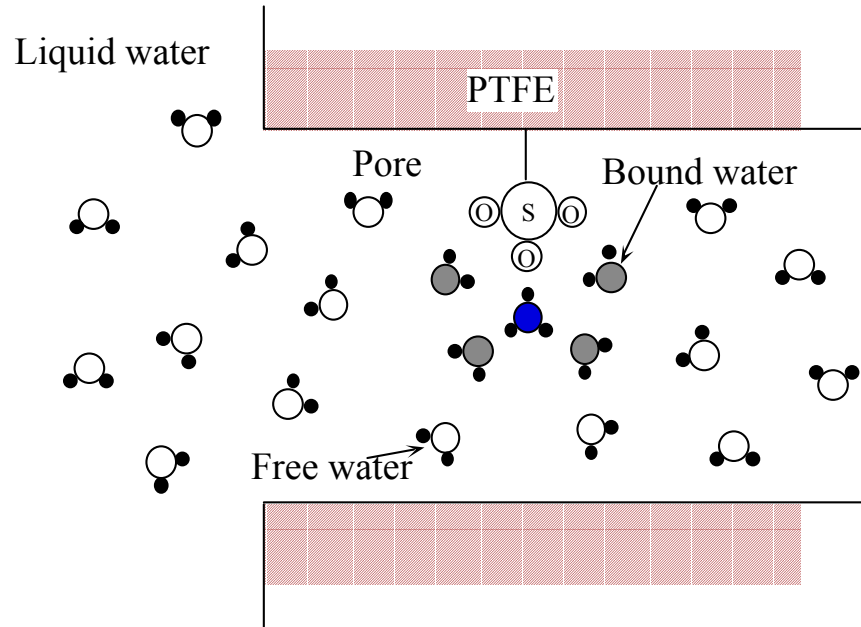
Schroeder's Paradox

Isotherm of water in Nafion<sup>®</sup> 117  
as a function of water vapor activity.

# Physicochemical Sorption Model

- Sorbed solvent molecules are of two types:
  - Chemically bound to acid sites,  $\lambda_i^C$
  - Free to equilibrate with external fluid,  $\lambda_i^F$
- As polymer chains stretch, they exert swelling pressure on imbibed liquid inhibiting further ingress
- The vapor-liquid interface exerts additional Kelvin pressure
- Polymer properties are time/temperature dependent

# Solvent Uptake



**Total Solvent Uptake:**  $\lambda_i = \lambda_i^C + \lambda_i^F$

$\lambda_i^C$  is from chemical equilibrium:  $\sum_{i=1}^n \nu_{\rho i} \mu_i = 0 \Rightarrow K_{\rho} = \prod_{i=1}^n a_i^{\nu_{\rho i}}$

$\lambda_i^F$  is from physical equilibrium:  $\mu_{i,M} = \mu_{i,f}$

# Physisorption Thermodynamics

Gibbs free energy of mixing:

$$\Delta G_m = G_{\text{mixture}} - (G_i + G_M)_{\text{pure}}$$

$$\Delta G_m = \underbrace{\Delta H_m}_{\Delta G_{\text{Residual}}} - \underbrace{T\Delta S_m}_{\Delta G_{\text{Config}}}$$

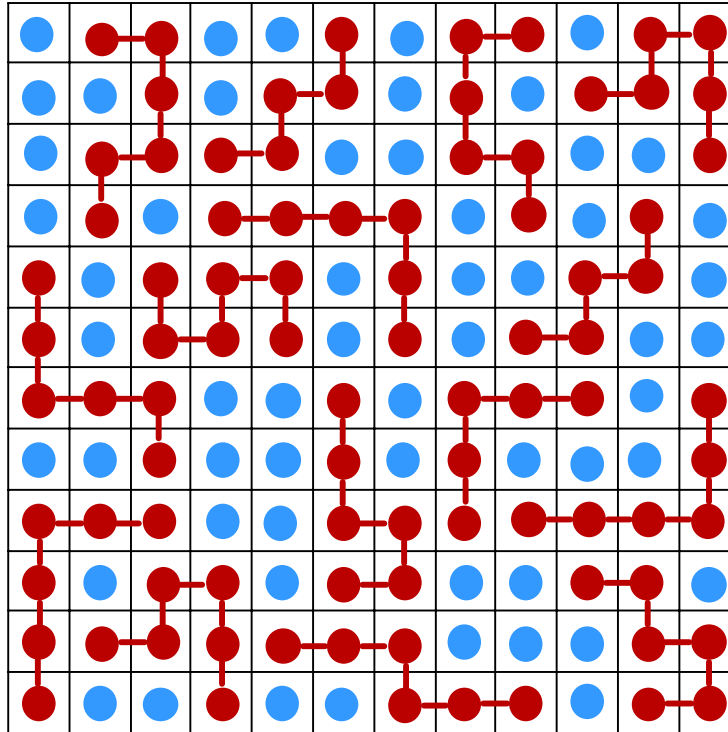
Flory-Huggins model:

$$S_{\text{Config}} = k_B \ln \Omega$$

$$\Delta H_m = \text{polymer-solvent interaction energy}$$

Chemical potential of imbibed solvent  $\mu_{i,M}$  depends upon  $T$ , swelling pressure, mixing configuration, and polymer-solvent interaction energy

# Flory-Huggins Model



$N_i$  = No. of Solvent Molecules

$N_M$  = No. of Polymer Molecules

$r = \bar{V}_M / \bar{V}_i$  = Ratio of Partial Molar Volumes

$M = N_i + rN_M$  = Total no. of Sites

$\varepsilon_i$  = Solvent Volume Fraction =  $N_i / (N_i + rN_M)$

$$\Delta G_m = \underbrace{k_B T \{ N_i \ln \varepsilon_i + N_M \ln(1 - \varepsilon_i) \}}_{-T\Delta S_m} + \underbrace{k_B T \{ \chi (N_i + rN_M) \varepsilon_i (1 - \varepsilon_i) \}}_{\Delta H_m}$$

# Solvent Chemical Potential

Chemical Potential of  $i$ :

$$\begin{aligned} \mu_{i,\alpha} &\equiv \left( \frac{\partial G_\alpha}{\partial n_i} \right)_{T,P,n_{j \neq i},\Phi,\dots} = \mu_{i,\alpha}(T; P; x_1, x_2, \dots, x_n; \Phi; \dots) \\ &= \Delta\mu_{i,\alpha}(T) + \Delta\mu_{i,\alpha}(P) + \underbrace{\Delta\mu_{i,\alpha}(x_1, x_2, \dots, x_n)}_{\text{Configurational}} + \\ &\quad \underbrace{\Delta\mu_{i,\alpha}(\Delta H_m)}_{\text{Interaction Energy}} + \Delta\mu_{i,\alpha}(\Phi) + \dots \end{aligned}$$

Standard form: 
$$\mu_{i,\alpha} = \mu_i^\circ(T, P^\circ) + \int_{P^\circ}^P \bar{V}_{i,\alpha} dP + \Delta\mu_{i,m} + z_i F\Phi + \dots$$

For mixing (Flory-Huggins)

$$\Delta\mu_{i,m} = \left\{ \frac{\partial(\Delta G_m)}{\partial(N_i/N_{Av})} \right\}_{T,P,N_{j \neq i},\Phi,\dots} \equiv RT \ln a_{i,\alpha}$$

# Solvent Chemical Potential

Solvent Chemical Potential:

$$\mu_{i,M} = \mu_i^o(T, P^o) + \bar{V}_{i,M} \Pi + RT \ln a_{i,M}$$

Flory-Huggins Model:

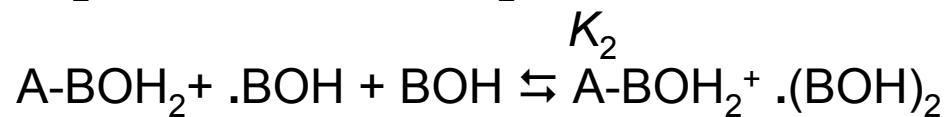
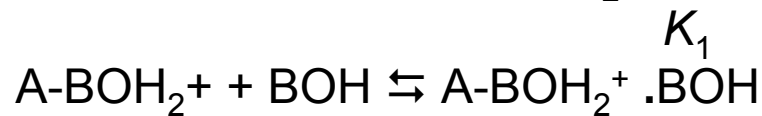
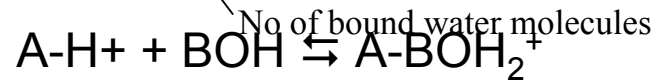
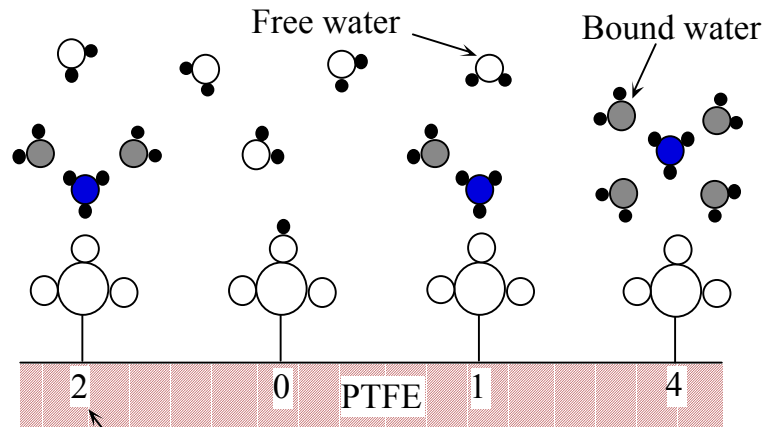
$$\ln a_{i,M} = \ln \varepsilon_i + \left(1 - \frac{1}{r}\right)(1 - \varepsilon_i) + \chi(1 - \varepsilon_i)^2$$

$\chi$  is a fitted parameter (Huggins):

$$\chi = \chi_1^0 + \chi_2^0 \phi_M + \chi_3^0 \phi_M^2 +$$

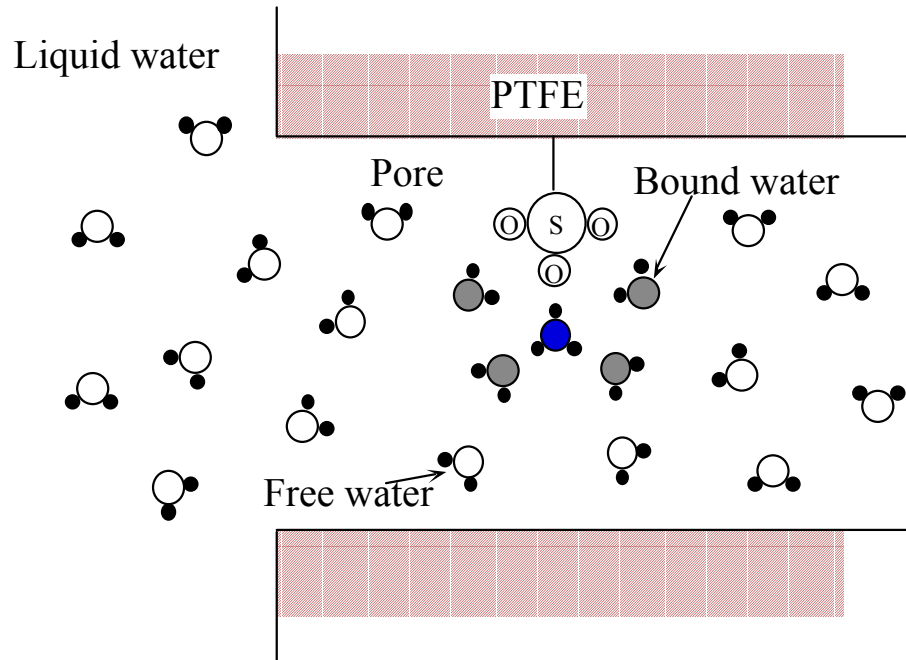
$$\text{and } \varepsilon_i = \frac{\lambda_i}{r + \lambda_i}$$

# Bound Solvent: Proton-Solvation



$$\lambda_i^C = \lambda_{i,m} \frac{K_1 a_i}{(1 - a_i)} \left\{ \frac{1 - (v + 1)a_i^v + v a_i^{v+1}}{1 + (K_1 - 1)a_i - K_1 a_i^{v+1}} \right\}$$

# Sorption from Liquid



- 1) Bound water is immobilized
- 2) Free water is free to exchange with external liquid:

$$\mu_{i,M}^F = \mu_{i,L}$$
$$\ln \frac{a_{i,M}^F}{a_{i,L}} = - \left( \frac{\bar{V}_i}{RT} \right) \Pi_M$$

# Swelling of Polymer Networks

Statistical theory of polymer elasticity (Flory):

$$\Delta G_{\text{Elastic}} = \frac{N_M k_B T}{2} \left\{ 2(\delta_x^2 + \delta_y^2 + \delta_z^2)^{\frac{1}{3}} - 3 - \ln(\delta_x \delta_y \delta_z) \right\}$$

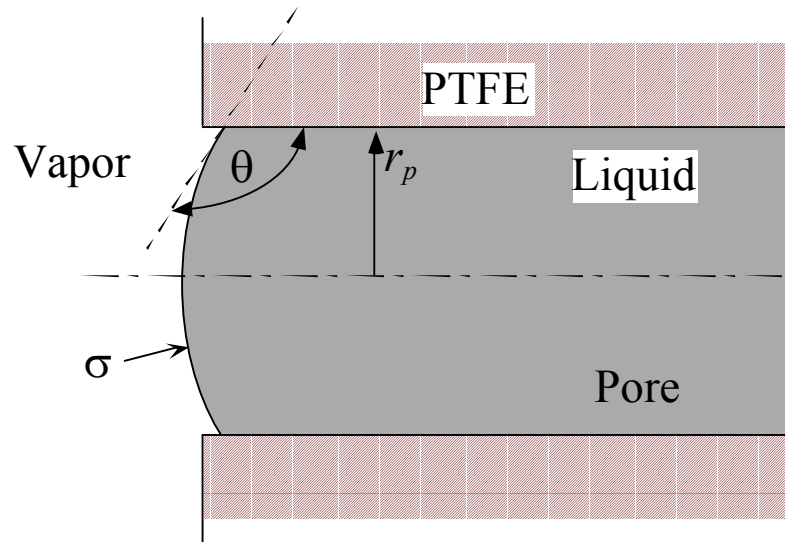
For  $G \equiv N_M k_B T / V_0$  and isotropic swelling

$$\Pi_M = G \left( \delta - \frac{1}{\delta^2} \right) \quad \delta = 1/\phi_M^{1/3}$$

with relation between shear modulus ( $G$ )  
and Young's modulus ( $E$ ):  $E = 2(1+\nu)G$

$$\Pi_M = \left( \frac{E}{3} \right) \frac{\varepsilon_i}{(1 - \varepsilon_i)^{1/3}}$$

# Sorption from Vapor



$$\mu_{i,M}^F = \mu_{i,V}$$

$$\ln \frac{a_{i,M}^F}{a_{i,V}} = - \left( \frac{\bar{V}_i}{RT} \right) (\Pi_M + \Pi_\sigma)$$

Young's equation:  $\Pi_\sigma = -\frac{2\sigma \cos\theta}{r_p}$ ;  $r_p = \frac{2\varepsilon_i}{S}$

# Summary of Results

$$\ln a_{i,M}^F = \ln a_{i,f} - \left( \frac{\bar{V}_i}{RT} \right) \Pi$$

$$\ln a_{i,M}^F = \ln \varepsilon_i^F + \left( 1 - \frac{1}{r} \right) (1 - \varepsilon_i^F) + \chi (1 - \varepsilon_i^F)^2 \quad \varepsilon_i^F = \frac{(\lambda_i - \lambda_i^C)}{r + (\lambda_i - \lambda_i^C)}$$

$$\lambda_i^C = \lambda_{i,m} \frac{K_1 a_i}{(1 - a_i)} \left\{ \frac{1 - (v + 1) a_i^v + v a_i^{v+1}}{1 + (K_1 - 1) a_i - K_1 a_i^{v+1}} \right\}$$

Liquid sorption:  $\Pi = \Pi_M$

Vapor sorption:  $\Pi = \Pi_M + \Pi_\sigma$

$$\Pi_M = \left( \frac{E}{3} \right) \frac{\varepsilon_i}{(1 - \varepsilon_i)^{1/3}} \quad \Pi_\sigma = - \frac{2\sigma \cos\theta}{r_p}$$

# Schroeder's Paradox: A Simple Explanation

For sorption from saturated vapor or liquid

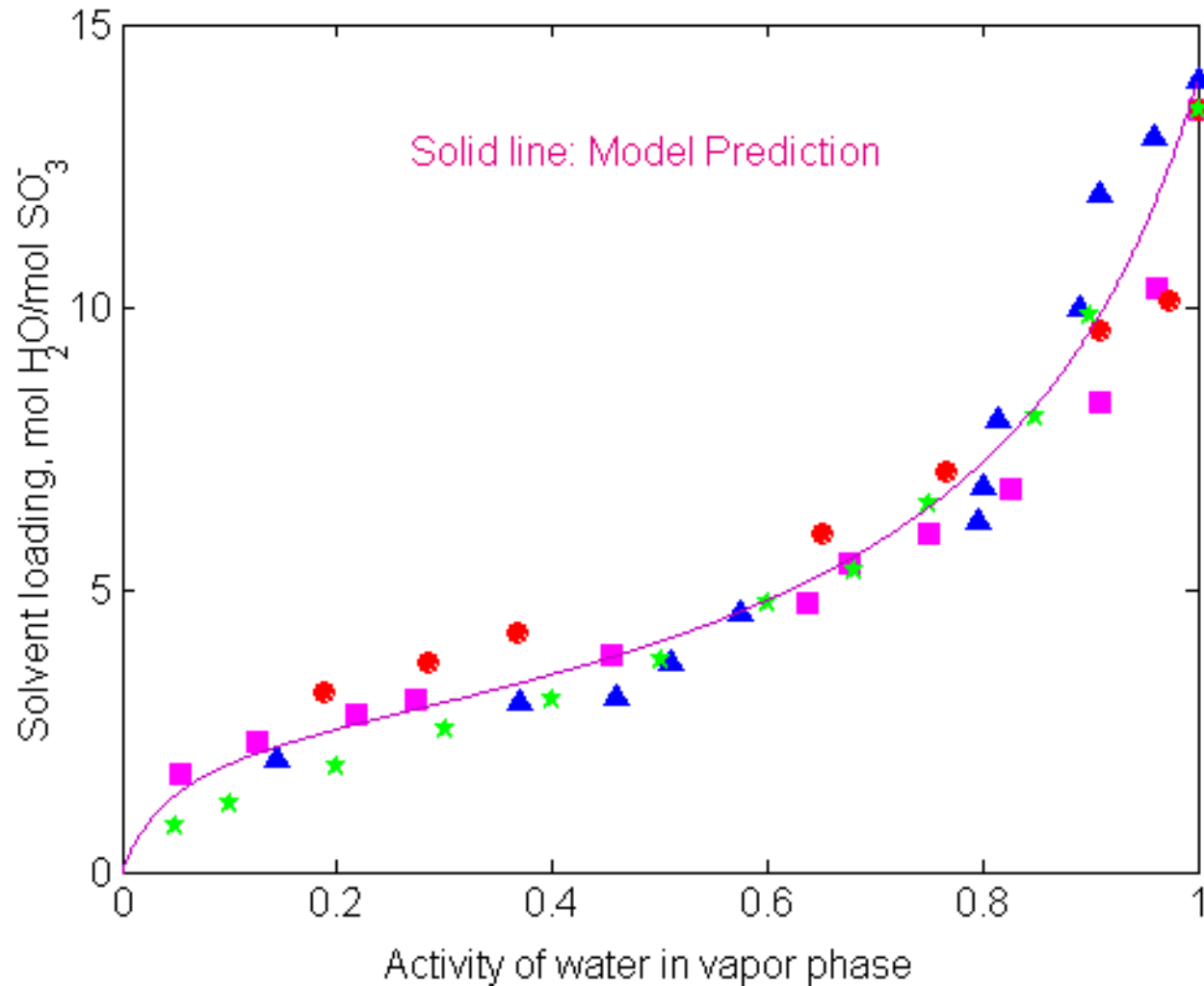
$$\frac{a_{i,M,\text{Liquid}}^F}{a_{i,M,\text{Sat Vapor}}^F} = \exp\left\{\left(\frac{\bar{V}_i}{RT}\right)\Pi_\sigma\right\}$$

$$\Pi_\sigma = -\frac{2\sigma \cos\theta}{r_p}$$

## Parameters used in the model

Symbol	Value	Unit	Comments
$\bar{V}_M$	537	cm <sup>3</sup> /mol	partial molar volume of Nafion <sup>®</sup>
$\bar{V}_i$	18	cm <sup>3</sup> /mol	partial molar volume of water
$K$	100	dimensionless	ionization constant of sulfuric acid
$\nu$	5	dimensionless	the number of equilibrium steps
$\lambda_{i,m}$	1.8	dimensionless	monolayer coverage being bound
$E$	296	MPa	Young's modulus
$\chi$	0.9 - 2.1	dimensionless	polymer-solvent interaction parameter

# Model Prediction of Water Sorption in PEM



# Dusty-Fluid Model

$$-\frac{c_i}{RT} \nabla_T \mu_i^e = \sum_{\substack{j=1 \\ j \neq i}}^n \frac{1}{c D_{ij}^e} (c_j N_i - c_i N_j) + \frac{N_i}{D_{iM}^e} + \frac{c_i B_0}{\eta D_{iM}^e} \left[ \nabla p + \left( \sum_{j=1}^n c_j z_j \right) F \nabla \Phi \right]$$

where  $D_{ij}^e = K_1 D_{ij} = (\varepsilon - \varepsilon_0)^q D_{ij}$        $D_{iM}^e = K_0 D_{iM}$

Summing this over all species

$$\left[ \nabla p + \left( \sum_{j=1}^n c_j z_j \right) F \nabla \Phi \right] = -\frac{RT}{W} \sum_{j=1}^n \frac{N_j}{D_{jM}^e}$$

where  $W \equiv 1 + \frac{B_0 c RT}{\eta} \sum_{h=1}^n \frac{x_h}{D_{hM}^e}$

Finally:  $-\frac{c_i}{RT} \nabla_T \mu_i^e = \sum_{j=1}^n H_{ij}^e N_j$

where

$$H_{ij}^e = (\delta_{ij} - 1) \left( \frac{x_i}{D_{ij}^e} + \frac{cRTB_0 x_i}{\eta W D_{iM}^e D_{jM}^e} \right) + \delta_{ij} \left( \frac{1}{D_{iM}^e} + \sum_{\substack{h=1 \\ h \neq i}}^n \frac{x_h}{D_{ih}^e} - \frac{cRTB_0 x_i}{\eta W (D_{iM}^e)^2} \right)$$

Inverting 
$$N_i = -\frac{1}{RT} \sum_{j=1}^n \kappa_{ij}^e c_j \nabla_T \mu_j^e$$

Alternate Fickian form: 
$$N_i = -\frac{c_i}{RT} D_i^e \nabla_T \mu_i^e$$

where effective diffusivity 
$$\frac{1}{D_i^e} = \sum_{\substack{j=1 \\ j \neq i}}^n \frac{1}{c D_{ij}^e} \left( c_j - c_i \frac{N_j}{N_i} \right) + \frac{1}{D_{iM}^e} - \frac{c_i B_0 RT}{\eta D_{iM}^e W} \sum_{j=1}^n \frac{1}{D_{jM}^e} \frac{N_j}{N_i}$$

Current density: 
$$i = F \sum_{i=1}^n z_i N_i$$

# Nafion<sup>®</sup> Conductivity for Water Immersed Membrane

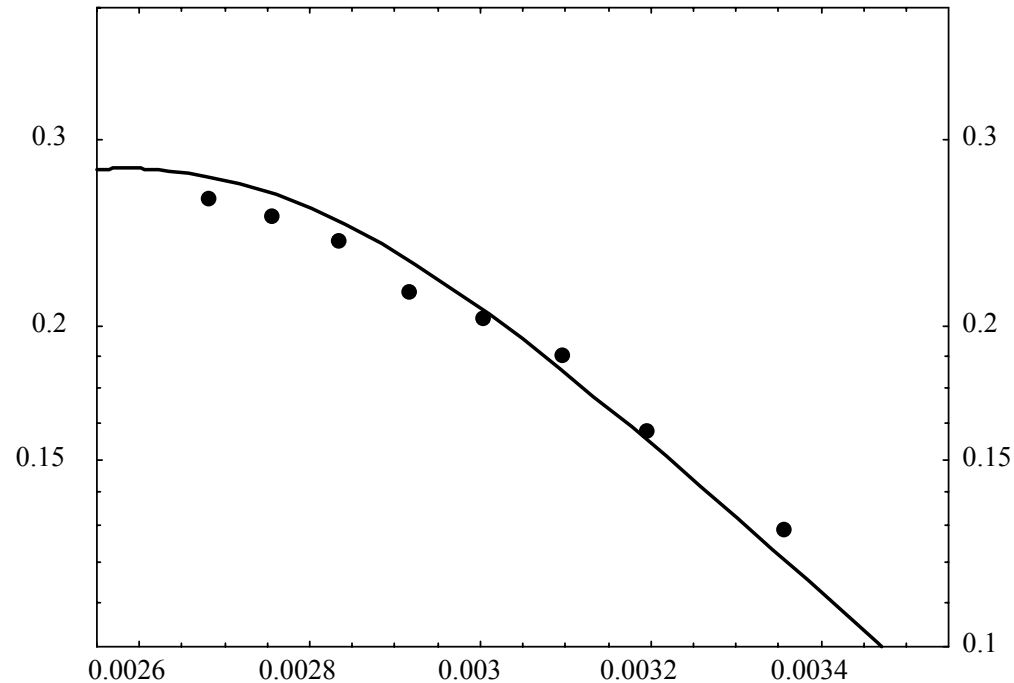


Figure: Nafion<sup>®</sup> 115 conductivity  $\sigma$  (S/cm) vs. reciprocal temperature for water immersed membrane.

# Nafion<sup>®</sup> Conductivity Versus Temperature for Constant Humidifier Temperature

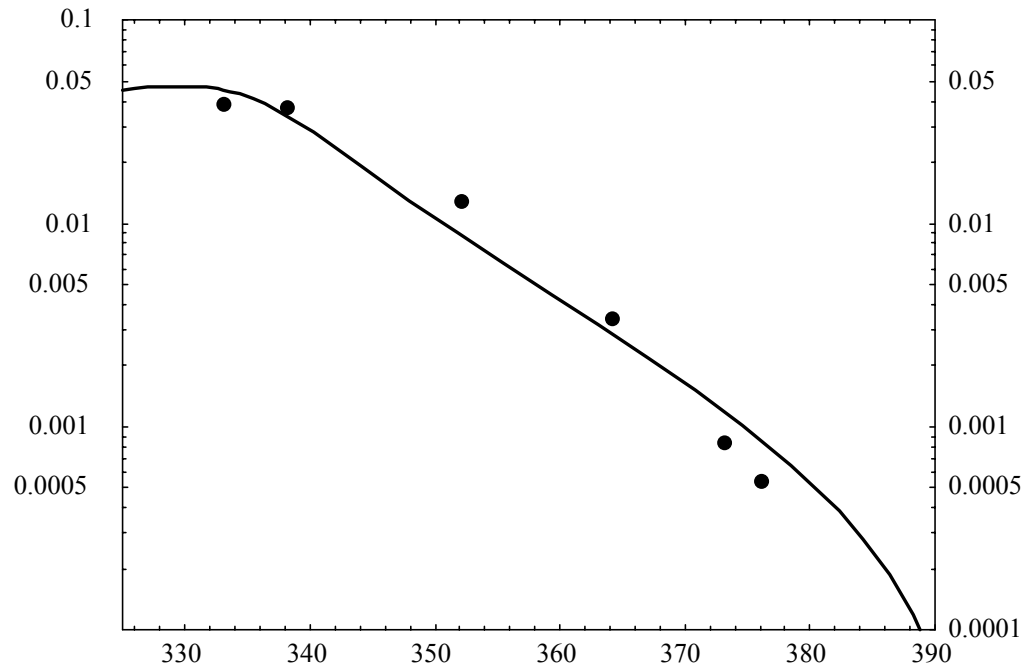


Figure: Nafion<sup>®</sup> 117 conductivity  $s$  (S/cm) vs. temperature (K) for a humidifier temperature of 60 °C (333 K).

# Nafion<sup>®</sup> Conductivity Versus Relative Humidity

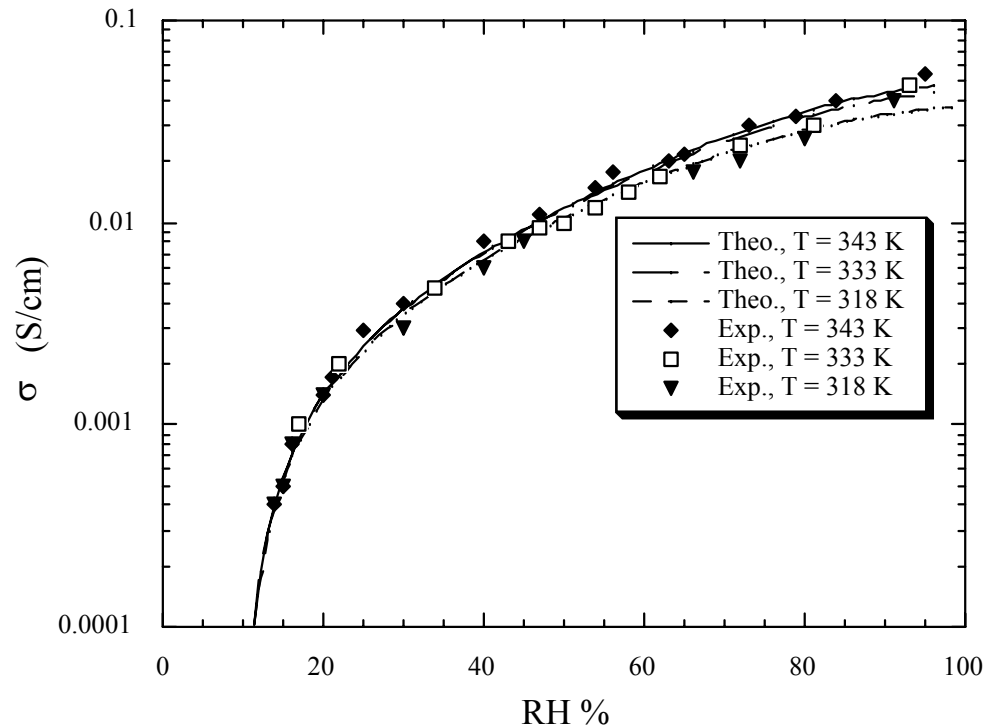


Figure: Nafion<sup>®</sup> 117 conductivity (S/cm) vs. RH (%) at different temperatures

# Conclusions

- A plausible model for sorption and transport in Nafion<sup>®</sup> is developed
- Provides good predictions with a minimum of fitted parameters
- A reasonable explanation for the Schroeder's paradox
- Could potentially explain hysteresis and phase inversion
- Could potentially be useful in rational evaluation and (perhaps) design of new PEM candidates