A Combi Approach to Characterizing Fuel Cell Membranes

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Outline

- Background and significance
- Library preparation
- Systems development
  - HT Conductivity
  - HT MECHanical
  - HT Sorption & Permeability
- PVDF/PE membrane screening experiments
- Statistical analysis

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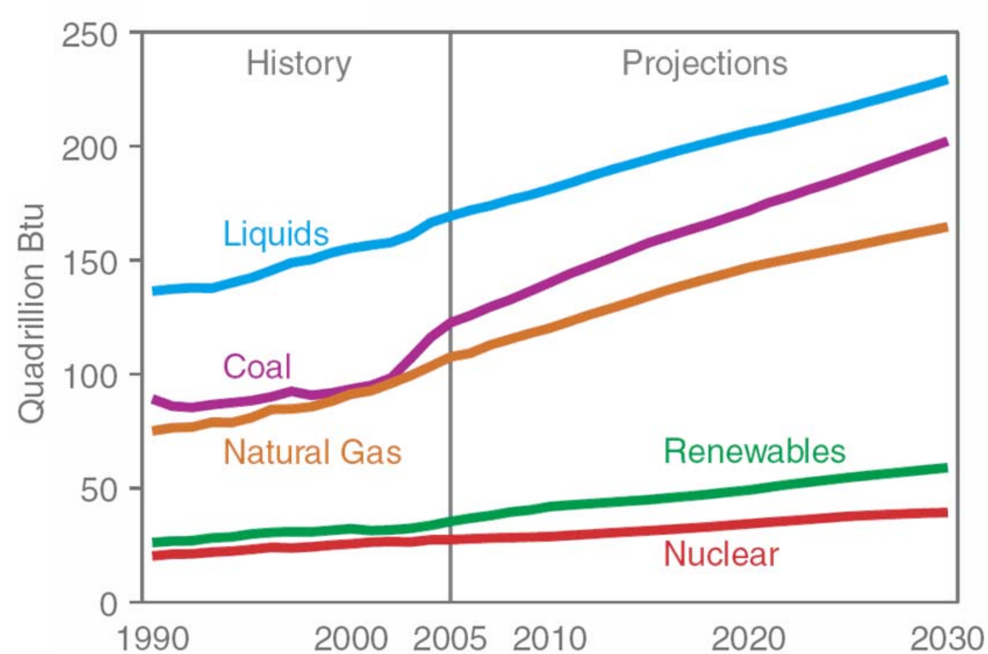
Global Energy

- Fast-paced ever increasing energy demand associated with higher living standards
  - World energy consumption expected to rise to 542 quadrillion BTUs by 2015 (60% more than in 1998)
- Social and environmental awareness

SOURCE	CONVERSION
Wind	Fuel cells
Geothermal	Photovoltaics
Biomass	Turbines
Hydrogen	Pelamis
Solar	
Wave and tidal	

World Marketed Energy Use by Fuel Type, 1990-2030



Source: Energy Information Administration, 2008

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PEMFCs: 2010 DOE targets

Characteristic	Actual	2010 Target
Operating temperature	≤80°C	≤120°C
Inlet water vapor partial pressure	50 kPa_{abs}	≤1.5 kPa_{abs}
Membrane conductivity at: ▪ Inlet water vapor partial pressure and operating temperature ▪ Room temperature (~25°C) ▪ -20°C	 100 mS/cm 70 mS/cm 10 mS/cm	 100 mS/cm 70 mS/cm 10 mS/cm
Oxygen cross-over[(a)]	5 mA/cm^2	2 mA/cm^2
Hydrogen cross-over[(a)]	5 mA/cm^2	2 mA/cm^2
Area specific resistance	0.03 Ω-cm^2	0.02 Ω-cm^2
Cost[(b)]	65 \$/m^2 [(c)]	40 \$/m^2
Durability with cycling at: ▪ Operating temp ≤80°C ▪ Operating temp >80°C	 ~2000 hr[(d)] Not available[(f)]	 5000 hr[(e)]
Unassisted start from (temperature)	-20°C	-40°C

(a) Tested in MEA at 1 atm O_2 or H_2 at nominal stack operating temperature.
(b) Based on 2002 dollars and costs projected to high volume production (500,000 stacks per year).
(c) Based on 2004 TIAX Study
(d) Steady-state durability is 9,000 hours.
(e) Includes typical drive cycles.
(f) High-temperature membranes are still in a development stage and durability data are not available.

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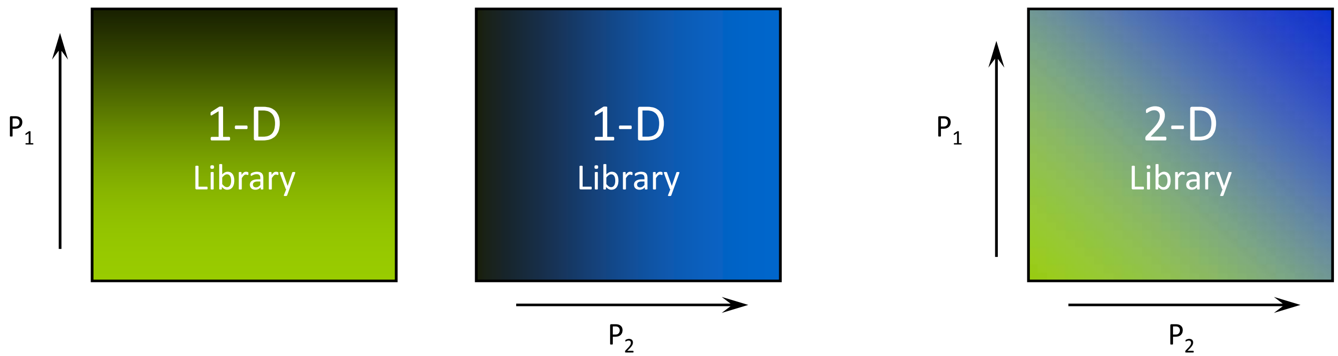
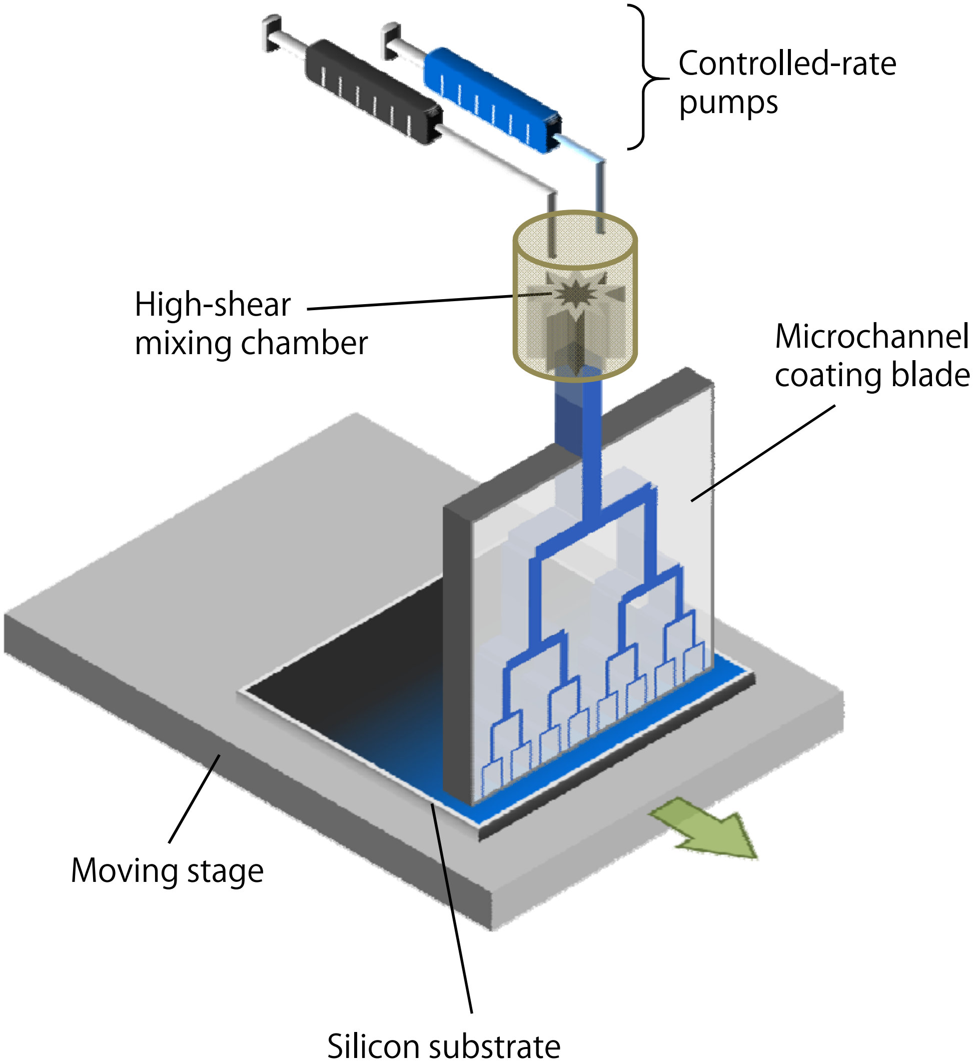
Develop combinatorial libraries based on blending inert and polyelectrolyte components

Combinatorial Libraries

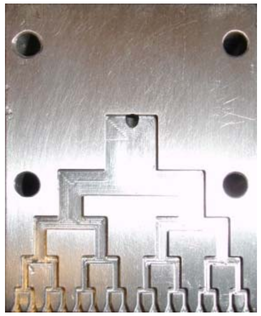
- Combinatorial approach
  - *Libraries* with 1-D and 2-D orthogonal property gradients (i.e., composition, anneal temperature)
  - Simultaneous evaluation of numerous dissimilar properties



Combinatorial Libraries

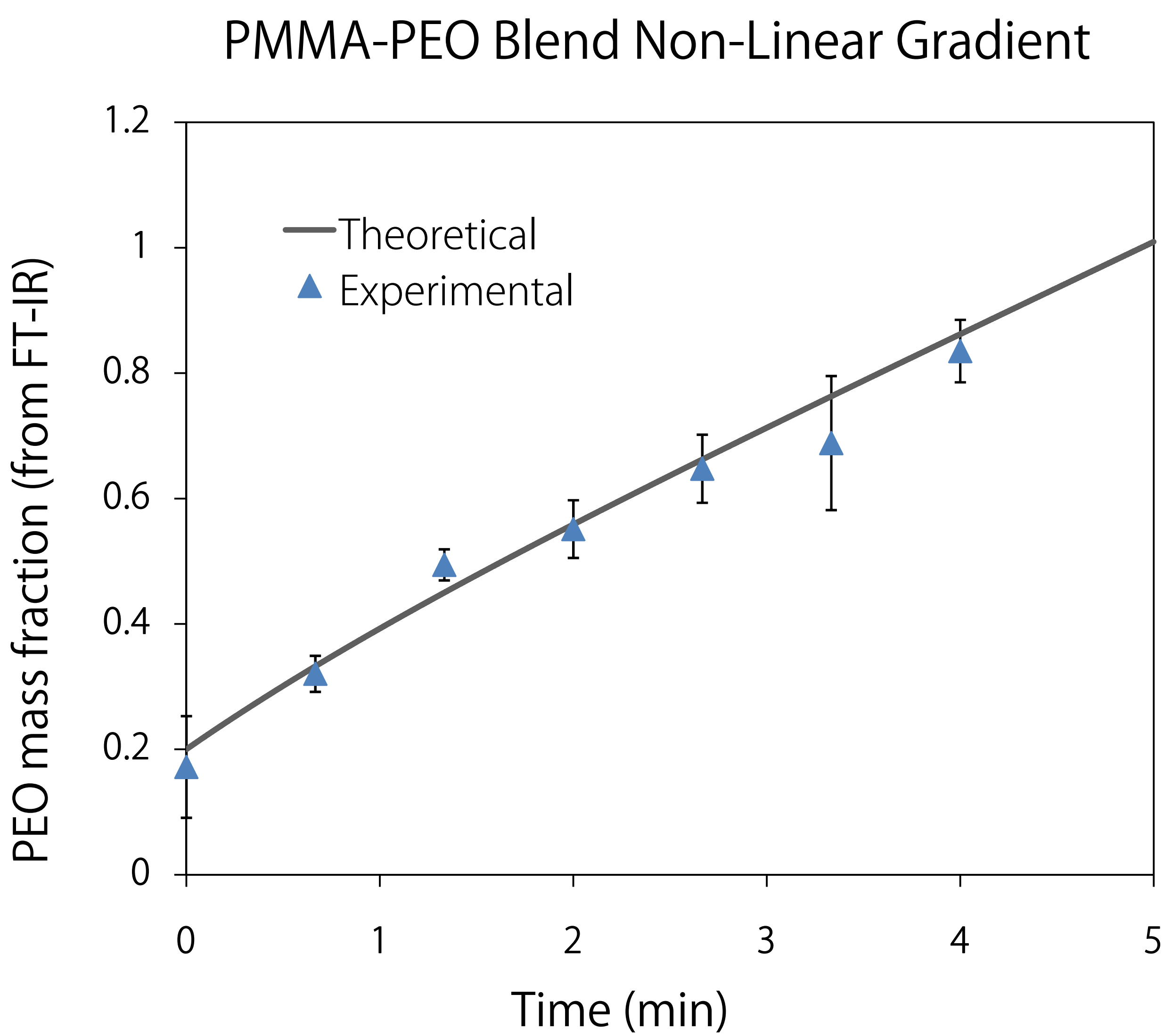


- New methodology: Microchannel direct gradient infusion
- Advantages:
  - High shear CSTR-like mixing chamber (overcome high viscosity effects)
  - Direct film deposition over substrate (minimize flow instability)



- Microfluidic manifold based on a generalized Murray's law
- Tangential shear stress at the wall remains constant throughout the whole network

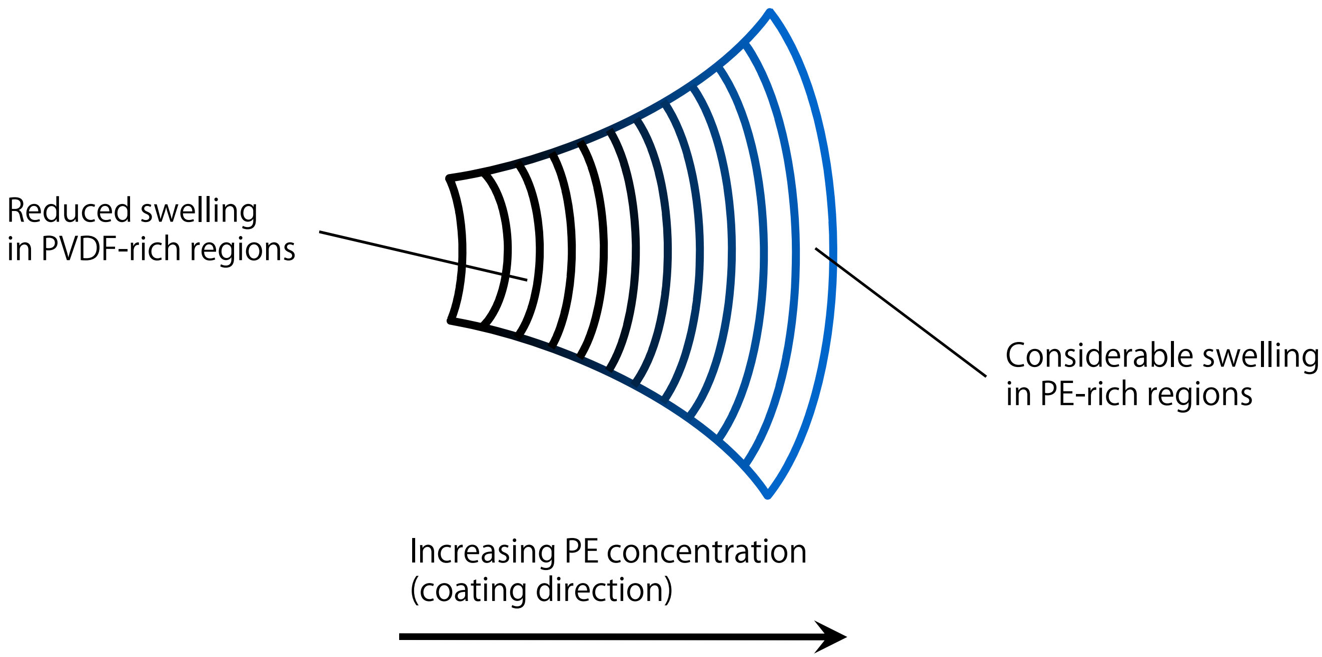
Combinatorial Libraries



- Microchannel direct gradient infusion: PMMA-PEO model system
  - Densities : 1.27 and 1.26 for 1wt% solution
  - r_{PEO} : 0.117 to 0.292 ml/min
  - r_{PMMA} : 0.14 to 0 ml/min

Combinatorial Libraries

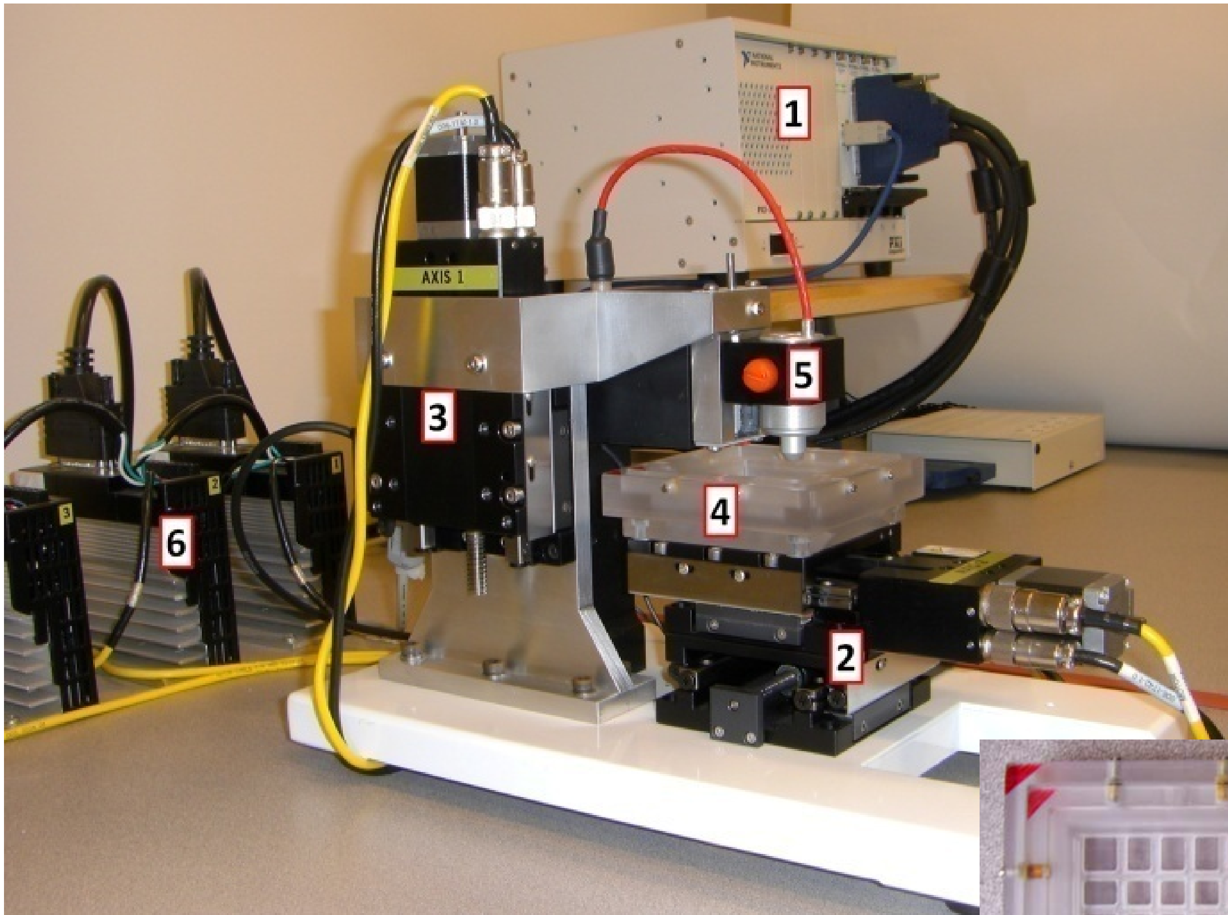
- Limitations of the "continuous gradient" combinatorial approach for PEMs:
  - Asymmetric swelling when membrane is hydrated:
    Bi-metallic strip effect (membrane warping)



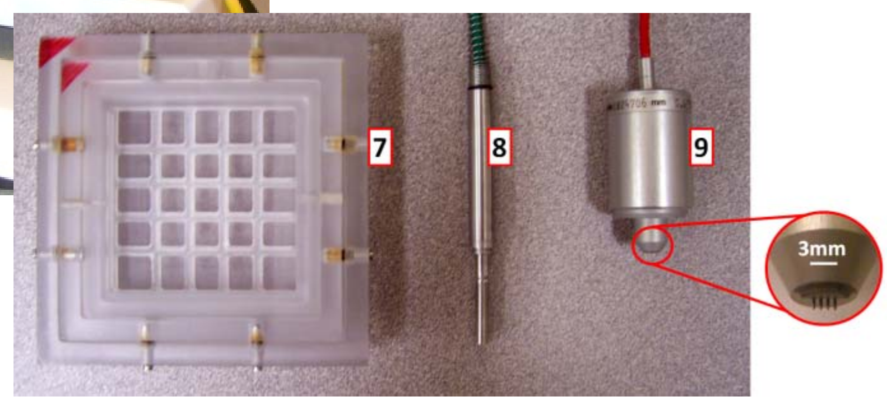
  - Correlation of properties and composition is problematical

Systems development

HTC: Design Overview

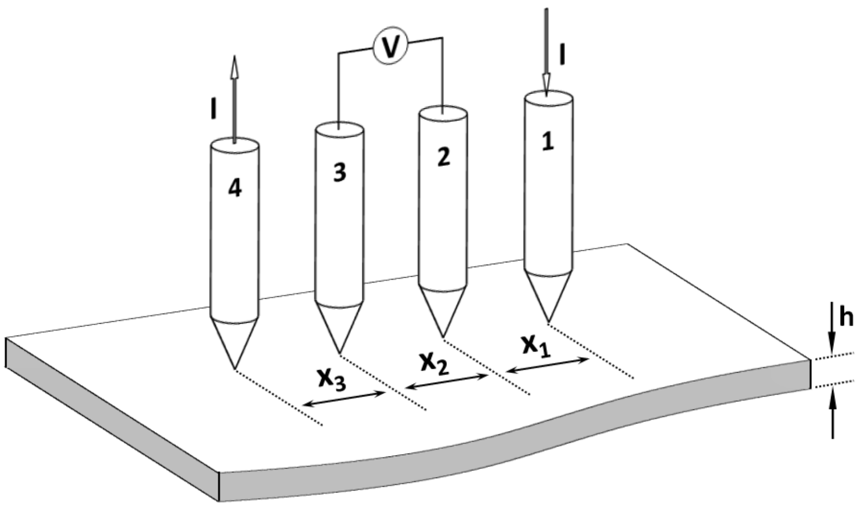


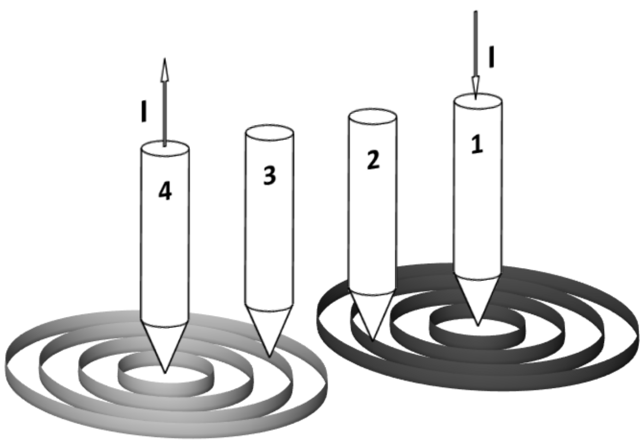
- (1) Programmable stepper motion controller and multifunction DAQ system
- (2) Motorized sample positioning X-Y stage
- (3) Motorized vertical axis and optical encoder
- (4) Sample holder (installed)
- (5) Four-point resistivity probe
- (6) Microstepping drives



- (7) Sample holder
- (8) Linear displacement digital gauging probe
- (9) Miniature four-point resistivity probe

HTC: 4-Point Probe Model for Thin Membranes





- General electric field model

$$-\nabla \Phi = \rho \frac{I}{A}$$

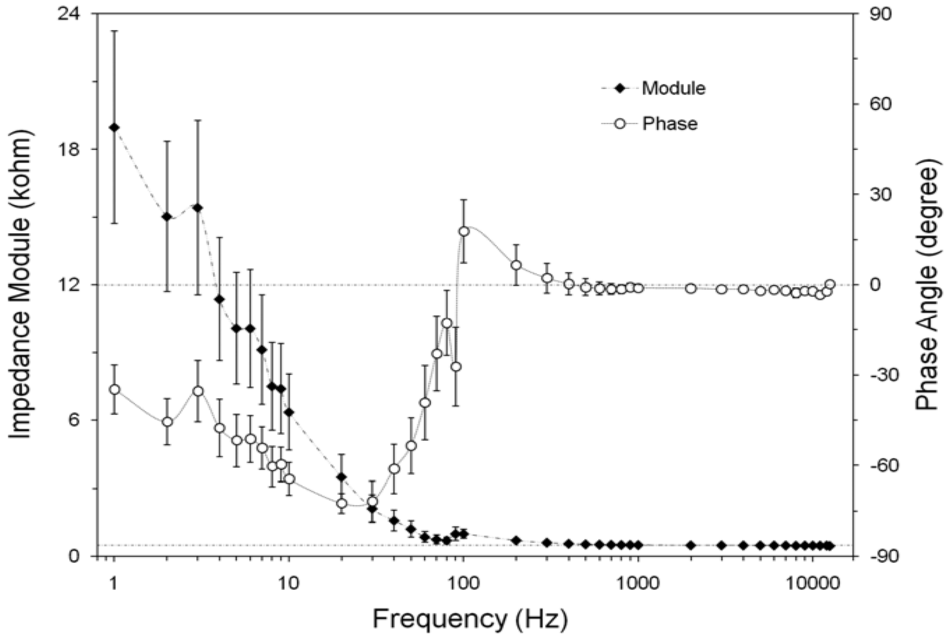
- Standard linear conductivity cell: Straightforward solution, simple geometrical dependence

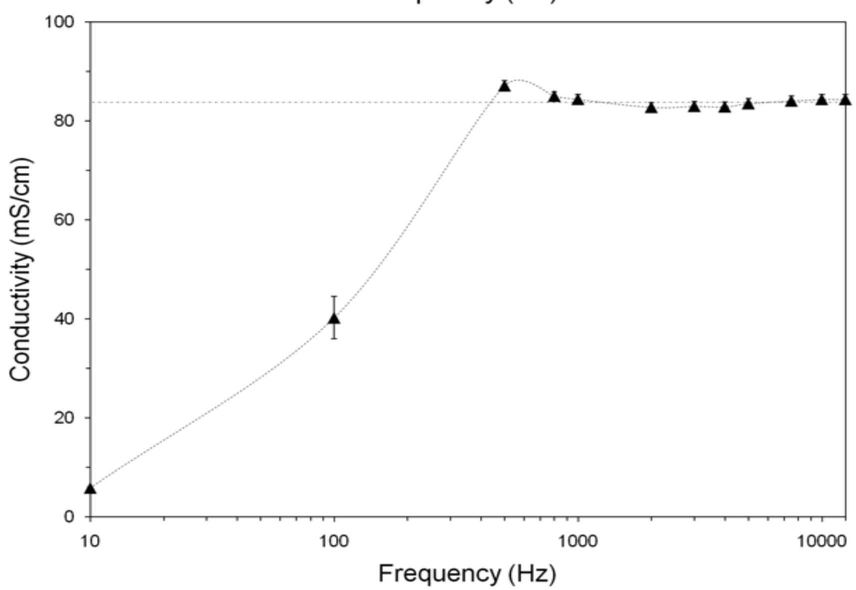
$$\rho = R_0 \frac{A}{d}$$

- 4-point probe: Complex geometrical implications, Fourier-Bessel solution
  - Model simplification: Non-conductive substrate, small membrane thickness ($h << X_i$) → Cylindrical iso-current surfaces

$$\left.\frac{1}{\rho}\right|_{Z'' \to 0} = -\frac{1}{Z_{(j\omega)} 2\pi h} \ln\left[\frac{x_1 x_3}{(x_2 + x_1)(x_2 + x_3)}\right]$$

HTC: Validation (Nafion® 112)





- I-V approach limitation at low frequencies (<~800Hz):
  - Unable to resolve the response signal fundamental frequency
  - Strong impedance phase and module variability
- Average Nafion® 112 conductivity (in 18.2 MΩ water at 25ºC @ 1000Hz):

  84.5 ± 0.54 mS/cm

Value within 1.8% of the value reported by the manufacturer at identical testing conditions (83 mS/cm)*

*[Nafion PFSA Product Information *NAE101*, DuPont, Feb., 2004]

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HTC: Signal Filtering (Sine Correlation)

$$Q(t) = n(t) + Q_{DC} + Q_0 \sin\left[\omega t + \phi(\omega)\right] + \sum_n Q_n \sin\left[n\omega t + \phi_n(\omega)\right]$$ Response signal

$$\mathrm{Re} = \lim_{T\to\infty} \frac{2}{T}\int_0^T Q(t)\sin\omega t\, dt = Q_0 \cos\phi(\omega)$$

$$\mathrm{Im} = \lim_{T\to\infty} \frac{2}{T}\int_0^T Q(t)\sin\left(\omega t + \frac{\pi}{2}\right) dt = Q_0 \sin\phi(\omega)$$

Sine correlation bandpass filter centered at the fundamental frequency of the excitation signal

Better performance and narrower bandpass than complex spectrum and Fourier based signal filtering

- Signal phase

$$\phi_k(\omega) = \arctan 2\left[\frac{\mathrm{Im}_k}{\mathrm{Re}_k}\right]$$

- Complex impedance

$$Z_{(j\omega)} = |Z| e^{j\varphi} = \frac{V_0\, e^{j(\omega t + \phi_V)}}{I_0\, e^{j(\omega t + \phi_I)}} \longrightarrow \begin{cases} |Z| = \dfrac{V_0}{I_0} & \text{Impedance module} \\ \varphi = \phi_V - \phi_I & \text{Impedance phase} \end{cases}$$

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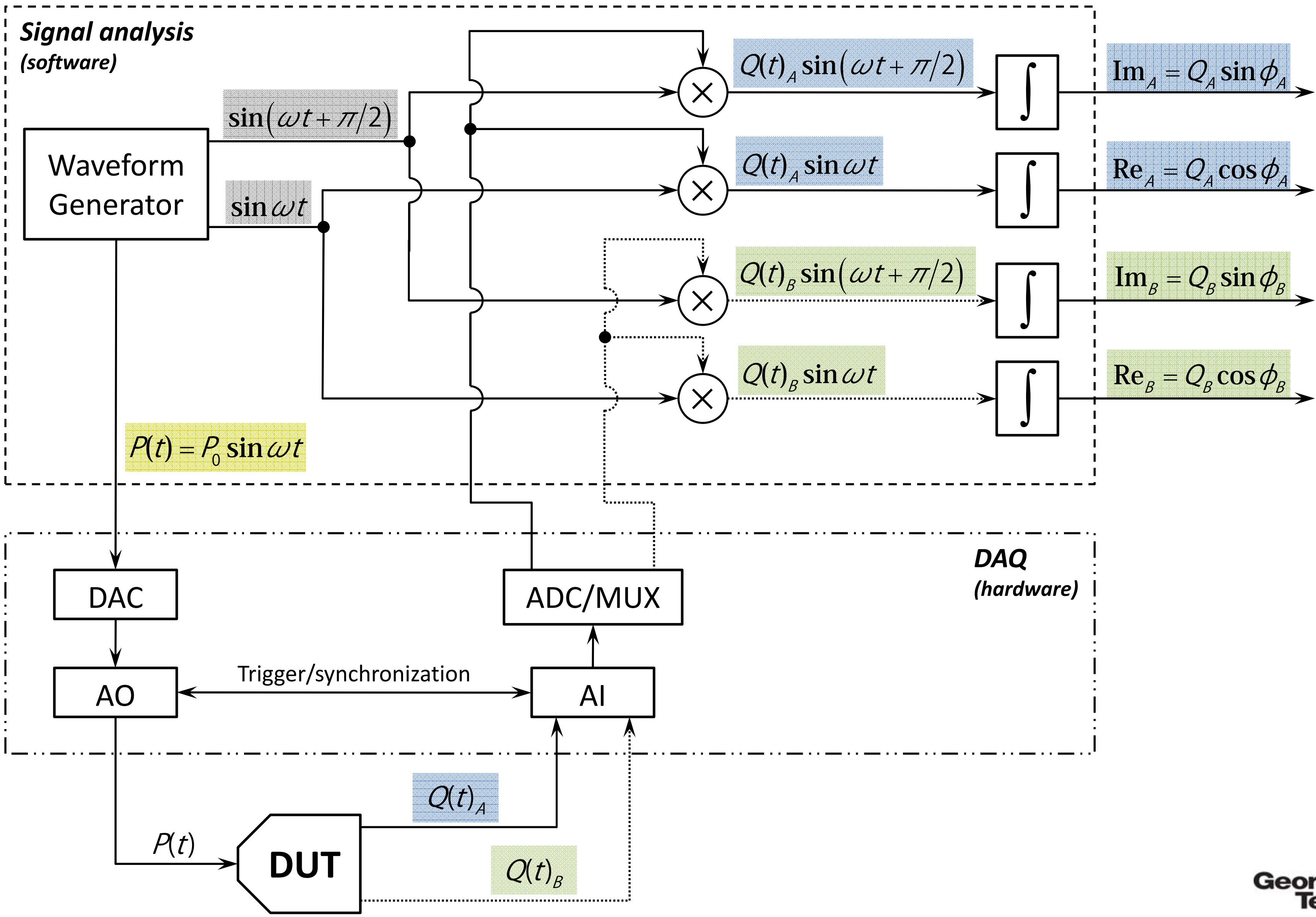
HTC: Signal Filtering Implementation



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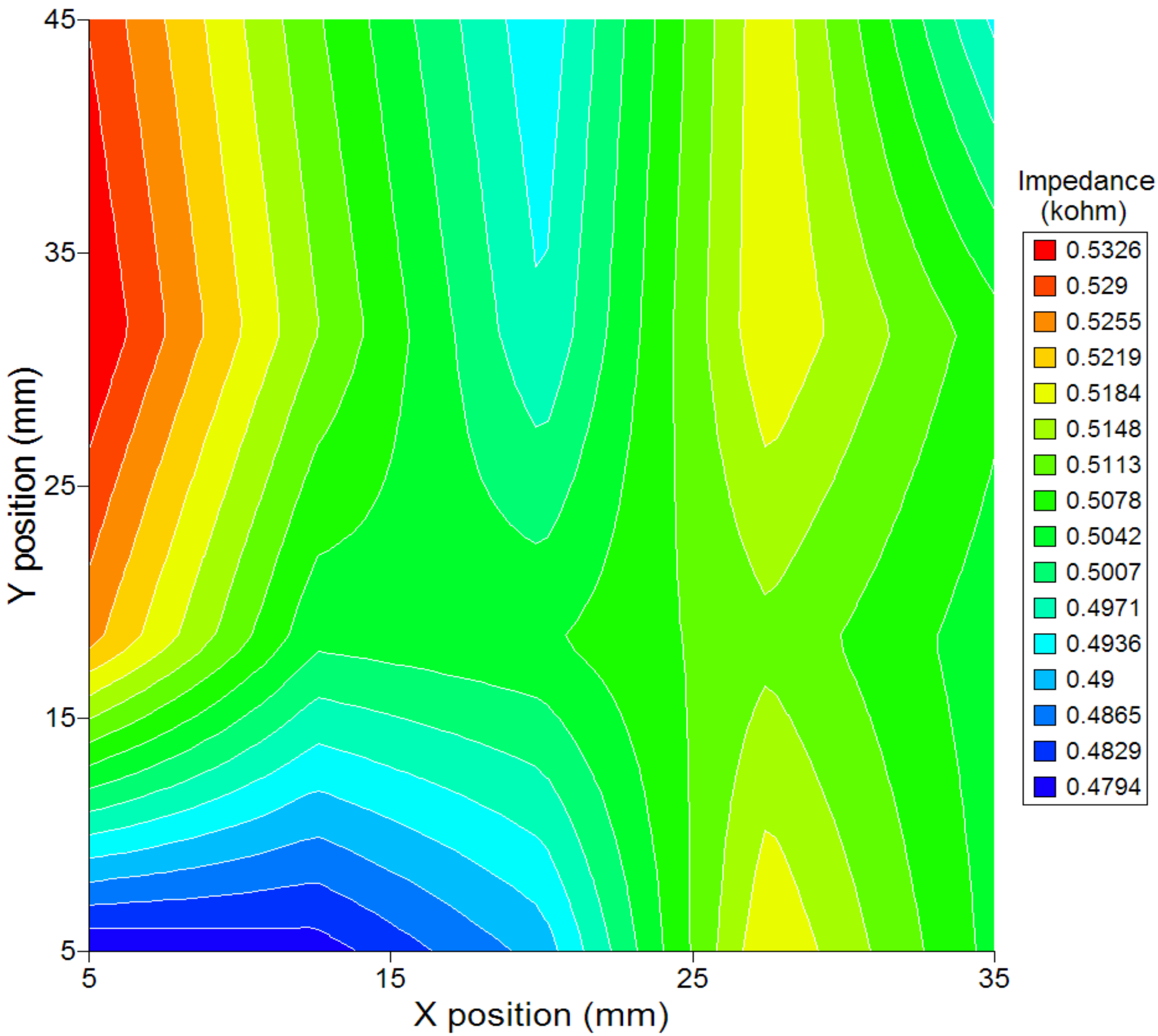
HTC: Property Maps (Nafion® 112)



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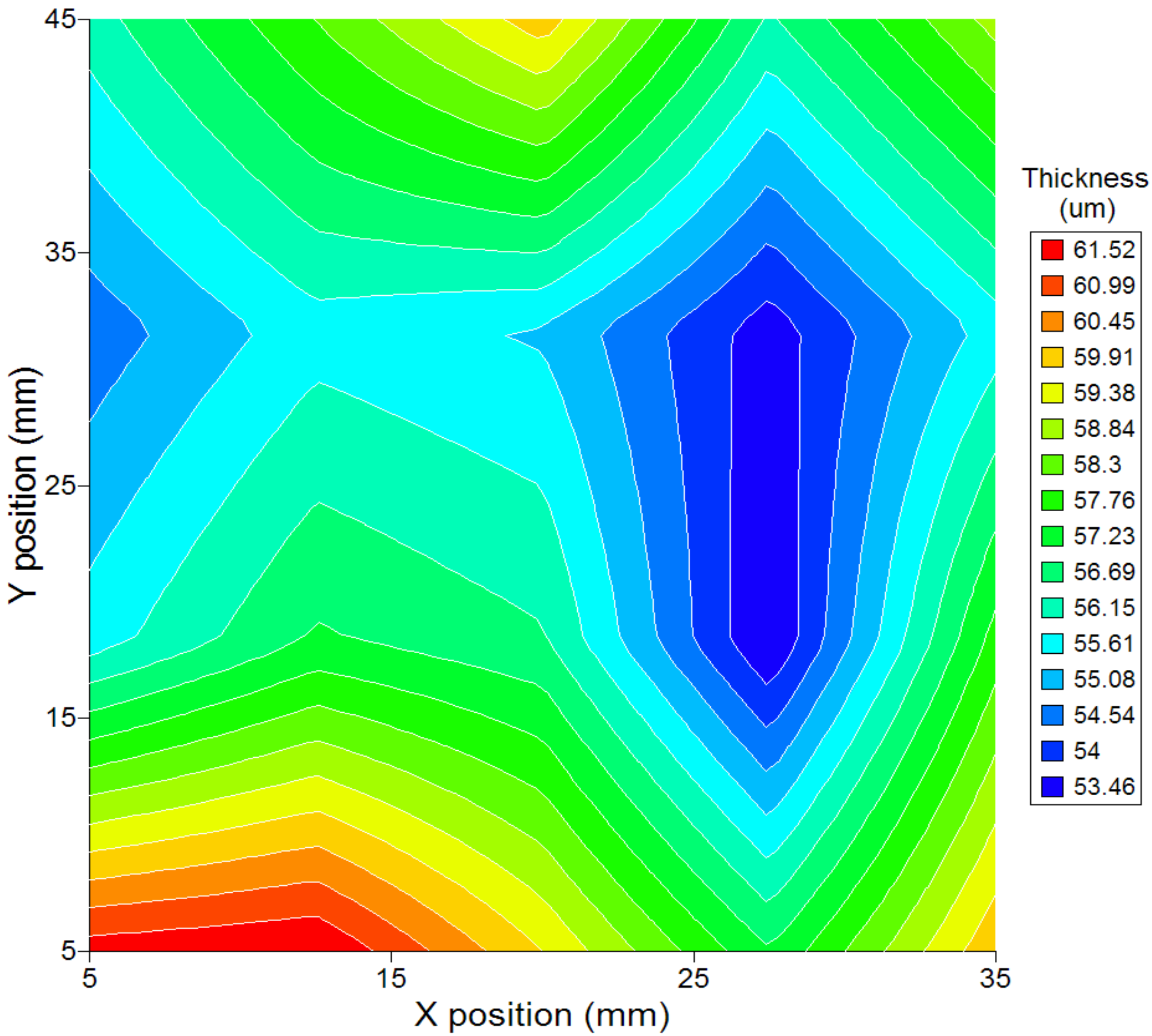
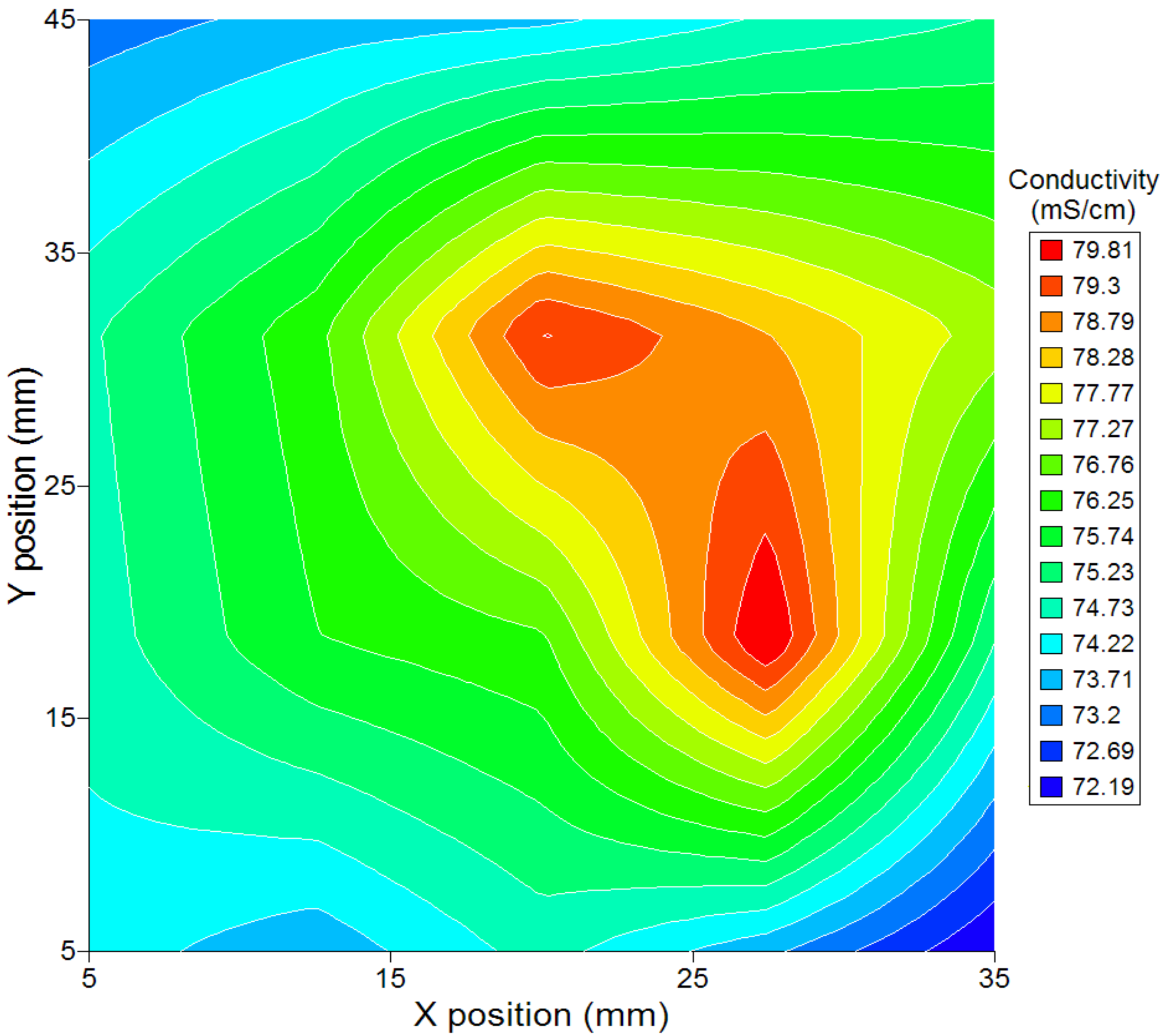


Uniform Nafion® 112 film exhibiting uneven membrane swelling

HTC: Property Maps (Nafion® 112)



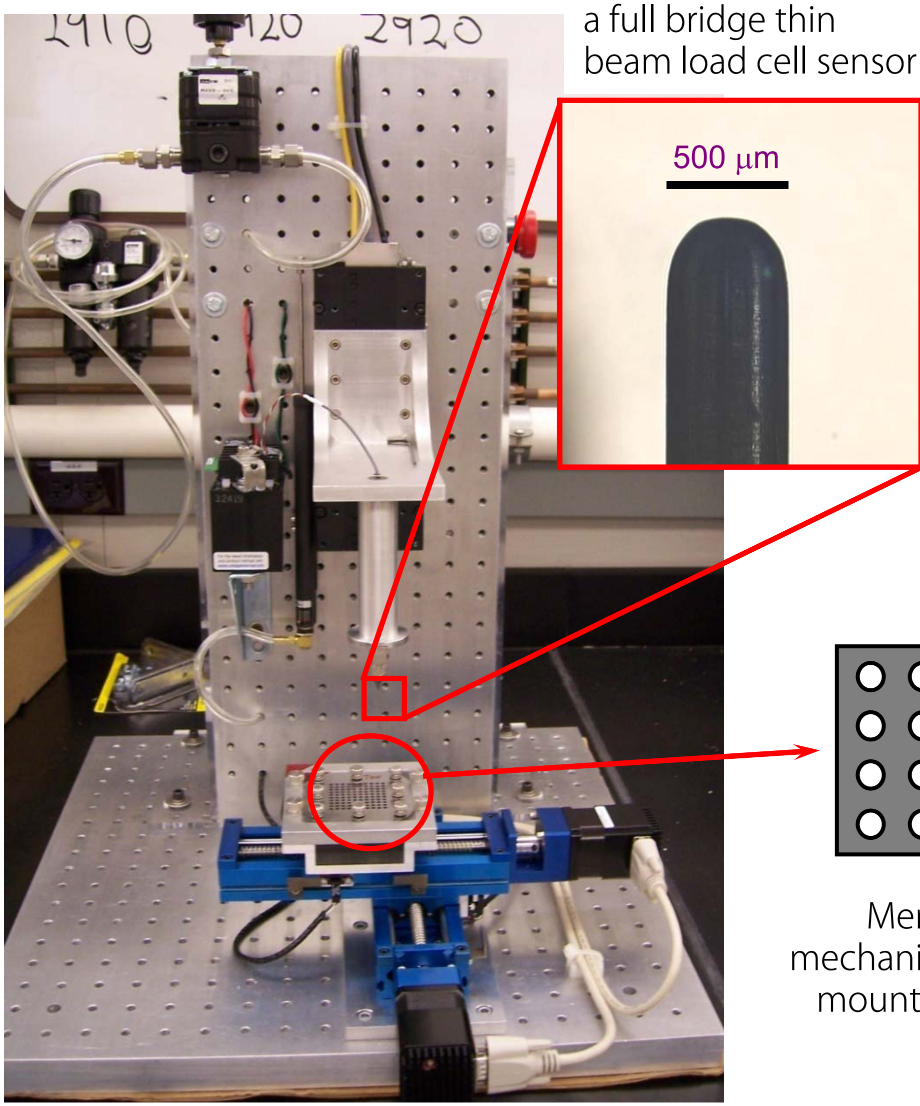
Uniform Nafion® 112 film exhibiting uneven membrane swelling

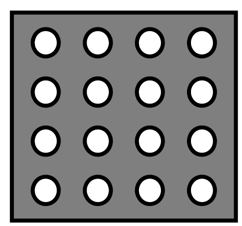
↓

Imbalance of sulfonic acid groups distribution (membrane anisotropy)

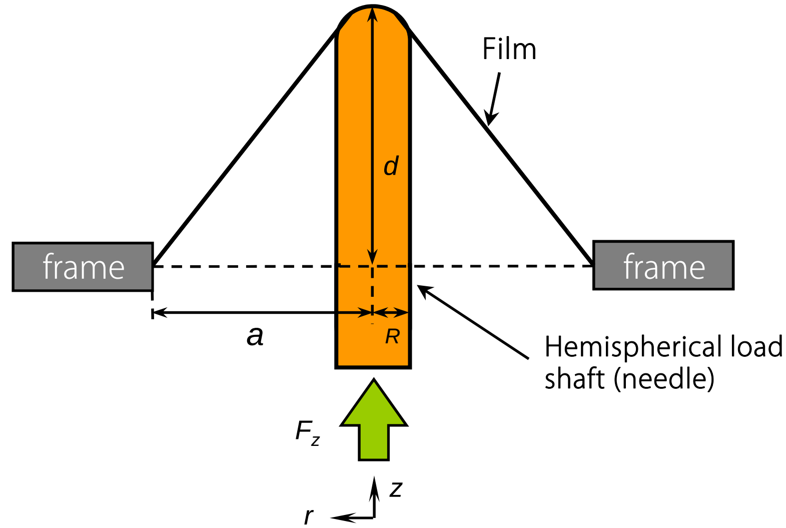
HTMECH: Design Overview

Load shaft attached to a full bridge thin beam load cell sensor





Membrane mechanical isolation mount schematic



- Contact tip: Steel hemispherical load shaft
- Biaxial film deformation
- Wide range of strain rates: 0.01mm/s to 1000mm/s
- Rapid test rate: up to 200 stress-strain profiles per hour

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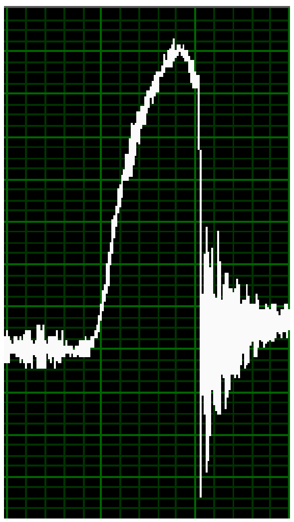
HTMECH: Data Manipulation and Analysis

Original signal

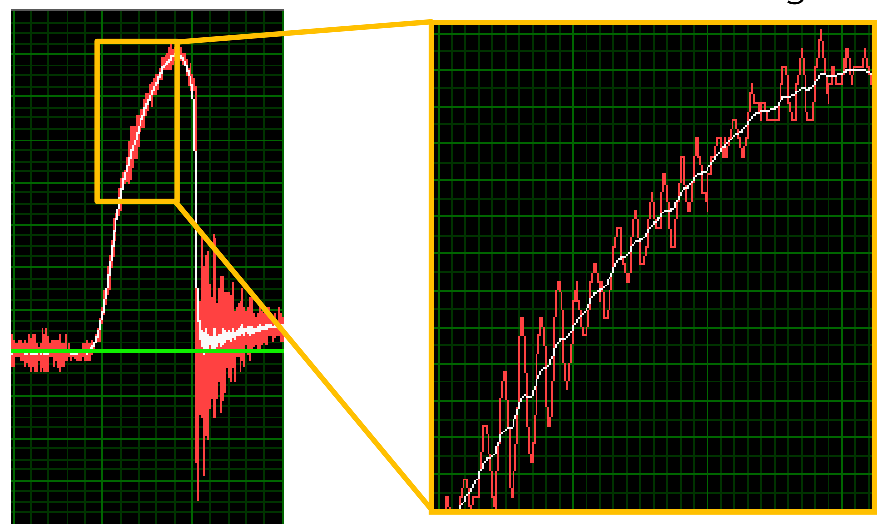


Signal conditioning

- Undecimated wavelet transform (UWT)
- Zero-phase IIR filtering

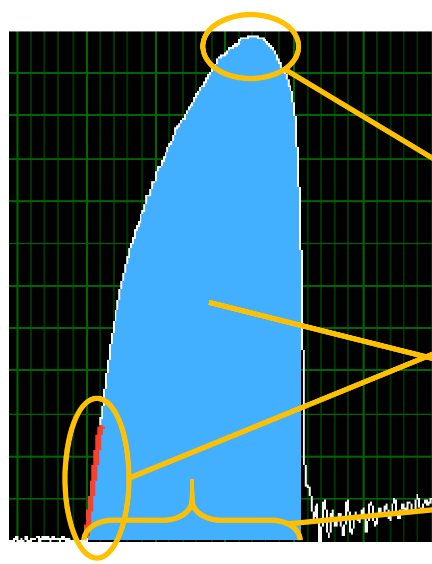
Denoised signal

Detail of filtered signal



Analysis of filtered signal

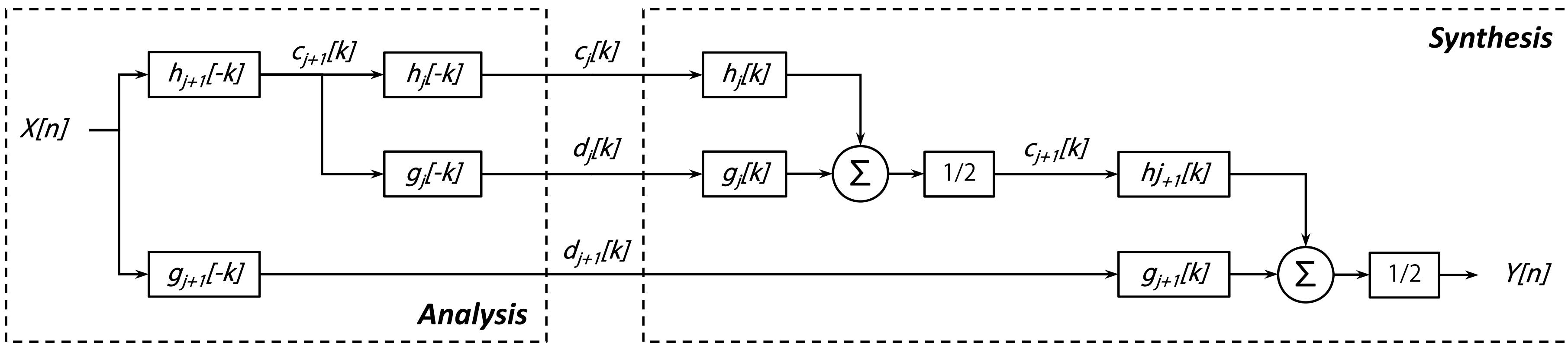
- Signal scaling
- Composite trapezoidal numerical integration
- Inverse bi-square slope fitting



- Properties
  - Maximum Force
  - Young's Modulus
  - Ultimate tensile strength
  - Breaking strength
  - Toughness
  - Strain at break

HTMECH: Data Manipulation and Analysis

- Undecimated wavelet transform (UWT)



$$h_j[k] = h_{j+1}[k] \uparrow 2$$
$$g_j[k] = g_{j+1}[k] \uparrow 2$$

Low and high pass filters upsampling

$$c_j[k] = \left(c_{j+1}[k] * h_j[-k]\right)$$
$$d_j[k] = \left(c_{j+1}[k] * g_j[-k]\right)$$

Approximation and detail coefficients (analysis)

$$c_{j+1}[k] = \frac{1}{2}\left(c_j[k] * h_j[k] + d_j[k] * g_j[k]\right)$$

Approximation coefficients (synthesis)

$$\sqrt{2Log(n)} \cdot \frac{\sigma}{\sqrt{n}}$$

Universal threshold

- Translation-invariant transform: avoid signal “shift”
- Orthogonal wavelets (energy conservative): minimize signal amplification or attenuation

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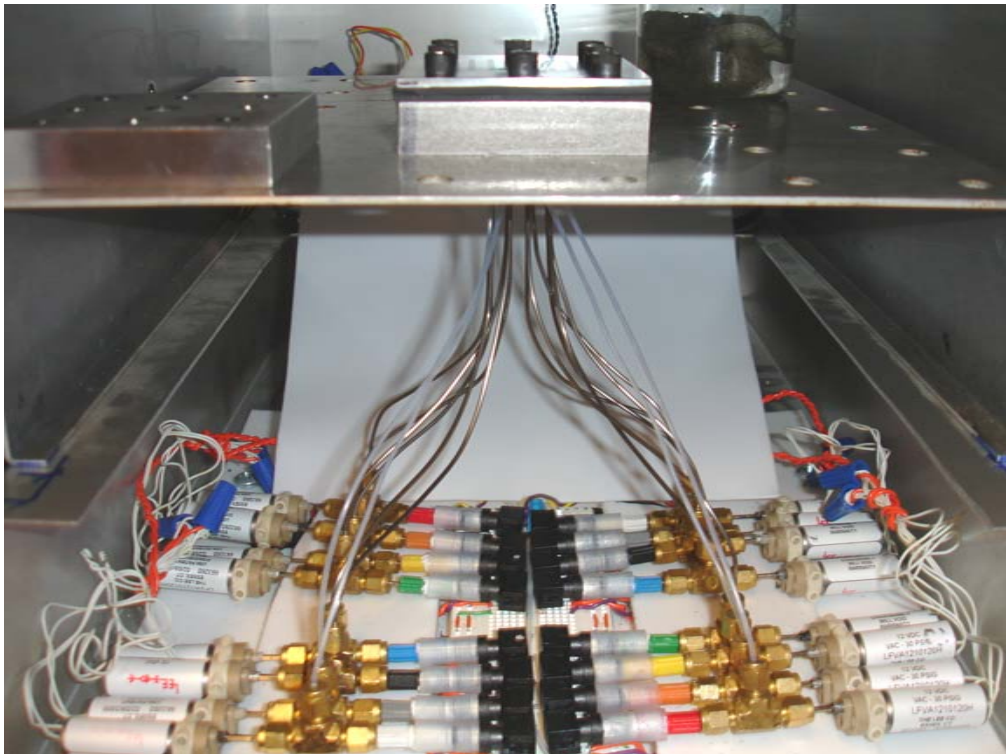
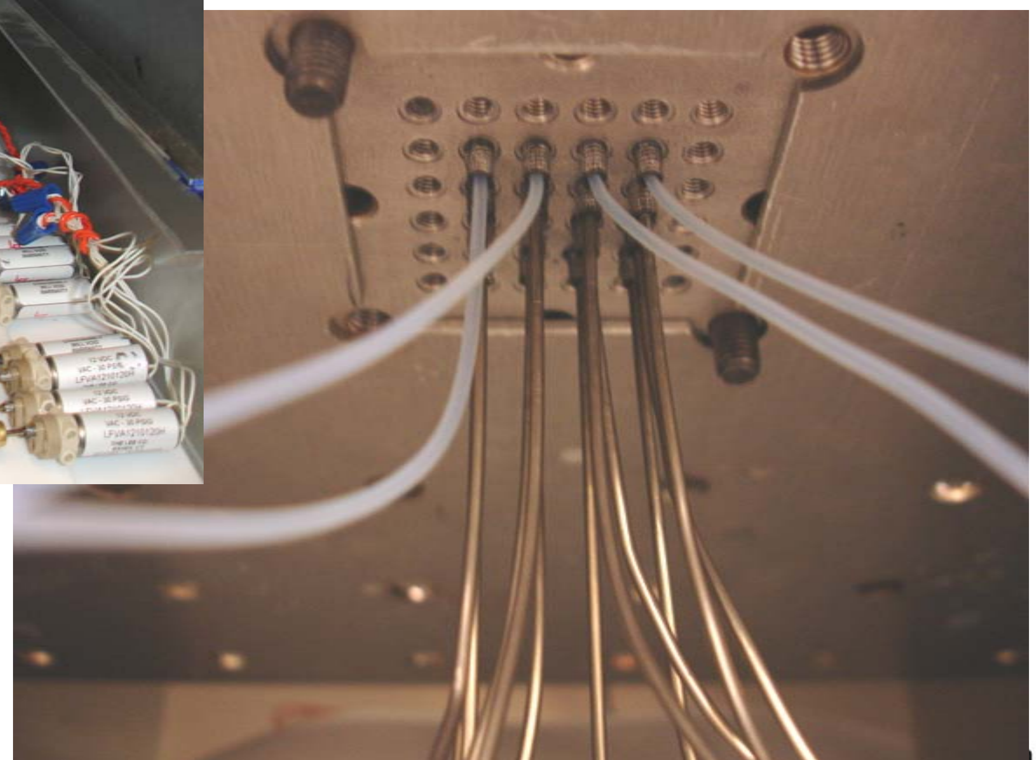
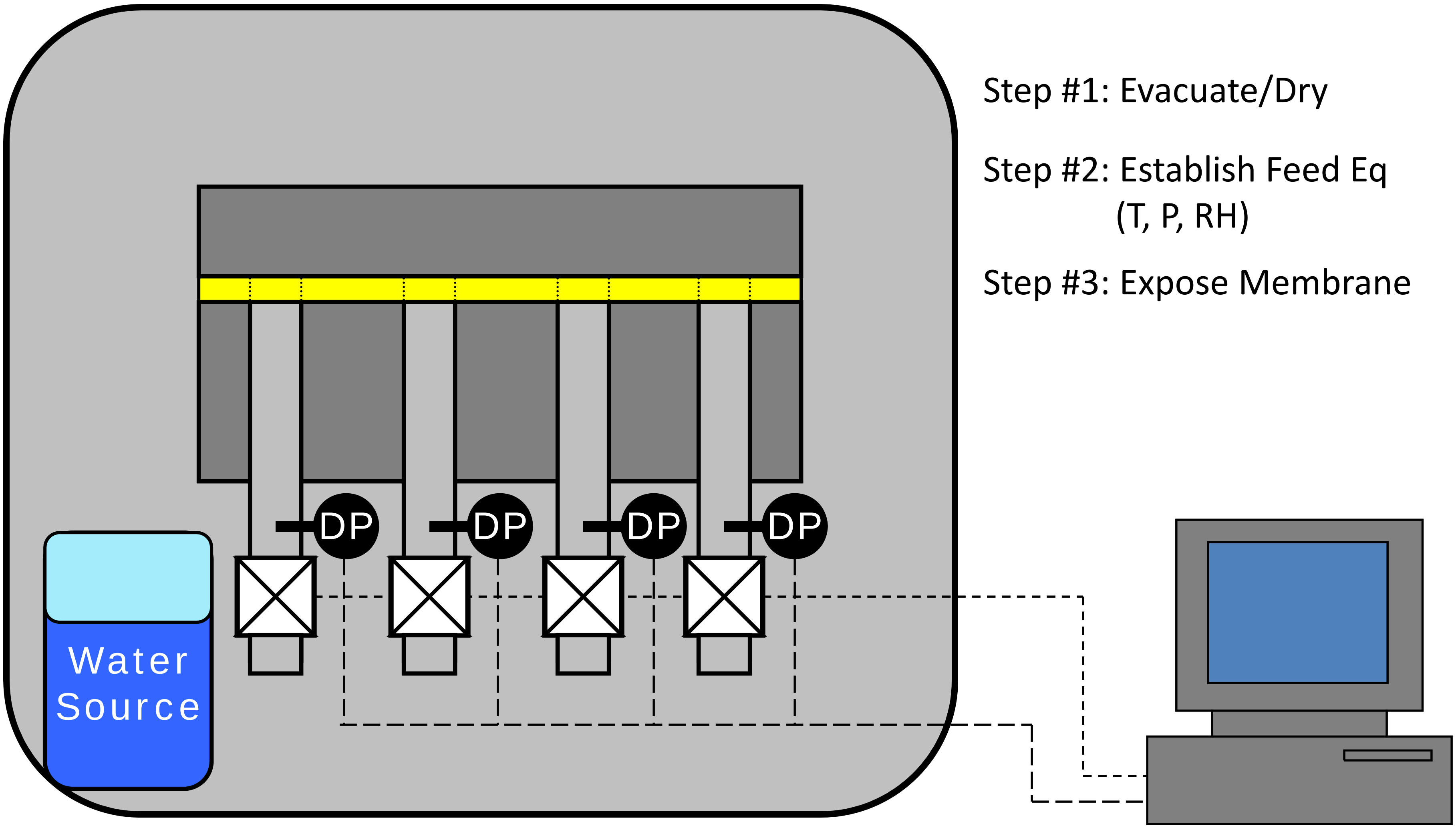
High-Throughput Permeability & Sorption Screen System





High-Throughput Sorption and Permeation



Step #1: Evacuate/Dry

Step #2: Establish Feed Eq (T, P, RH)

Step #3: Expose Membrane

Mass Transfer Theory

Assuming negligible air sorption, dP(t) → M(t) using Ideal Gas Law

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left(\frac{-(2n+1)^2\pi^2 Dt}{\ell^2}\right)$$

Converges rapidly at long times

$$\frac{M_t}{M_\infty} = \frac{4}{\ell}\left(\frac{Dt}{\pi}\right)^{0.5} + \frac{8}{\ell}(Dt)^{0.5}\sum_{n=1}^{\infty}(-1)^n \operatorname{ierfc}\left(\frac{n\ell}{2(Dt)^{0.5}}\right)$$

Converges rapidly at short times

Single term approximations to approximate **Diffusivity**:

$$\ln\left(1 - \frac{M_t}{M_\infty}\right) = \ln\left(\frac{8}{\pi^2}\right) - \frac{\pi^2 Dt}{\ell^2}$$

for sufficiently long times

$$\frac{M_t}{M_\infty} = \frac{4}{\ell}\left(\frac{Dt}{\pi}\right)^{0.5}$$

for sufficiently low times

Solubility: $S = \frac{M_\infty}{m_{poly} * P_{H_2O}^{sat}(T) * RH}$

Permeability: P=DS

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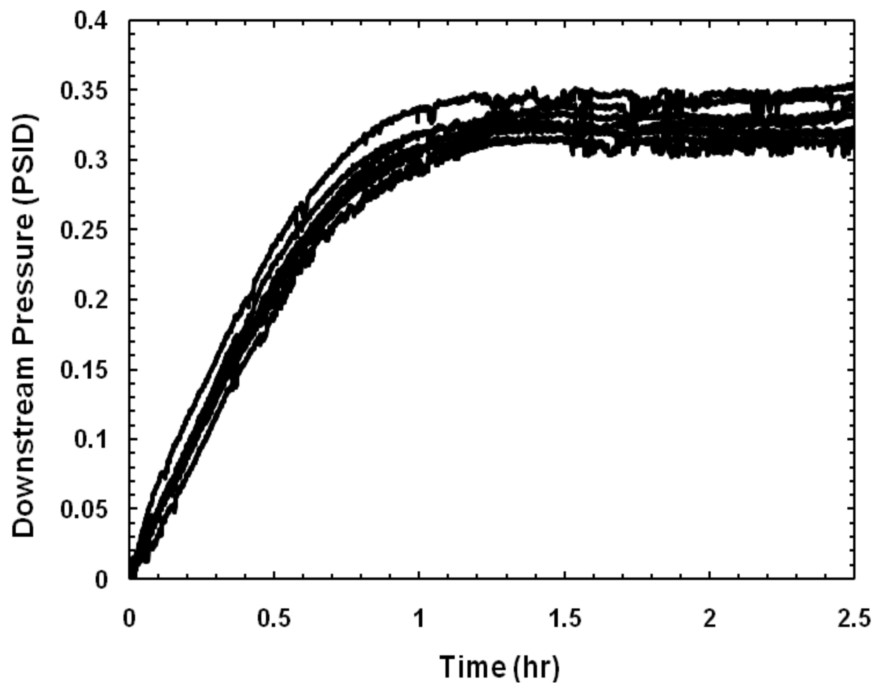
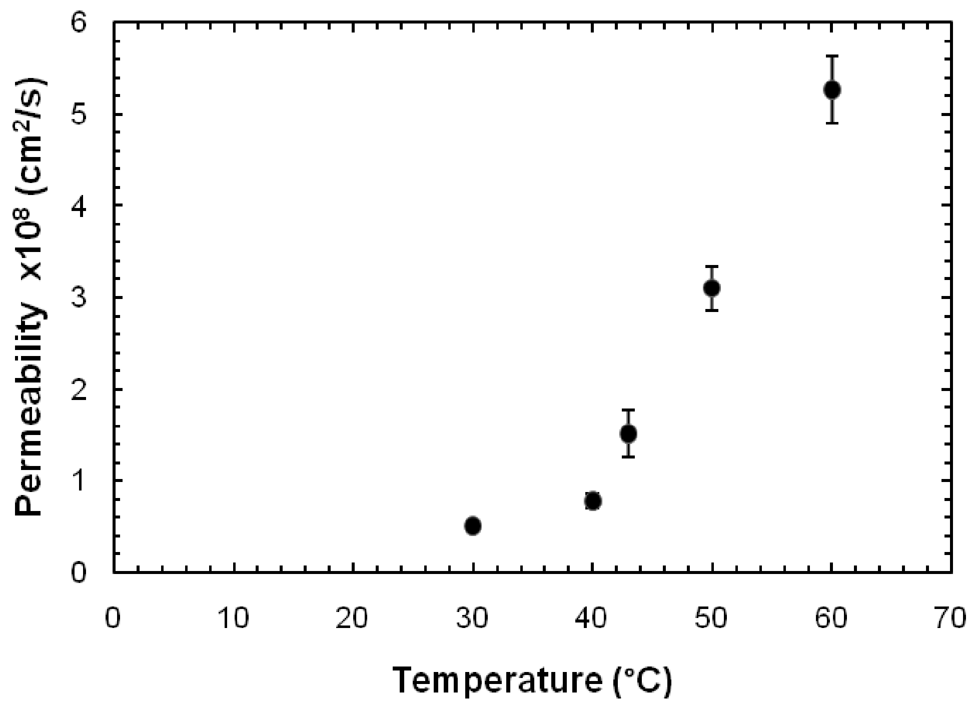
HT Permeability: Nafion 112





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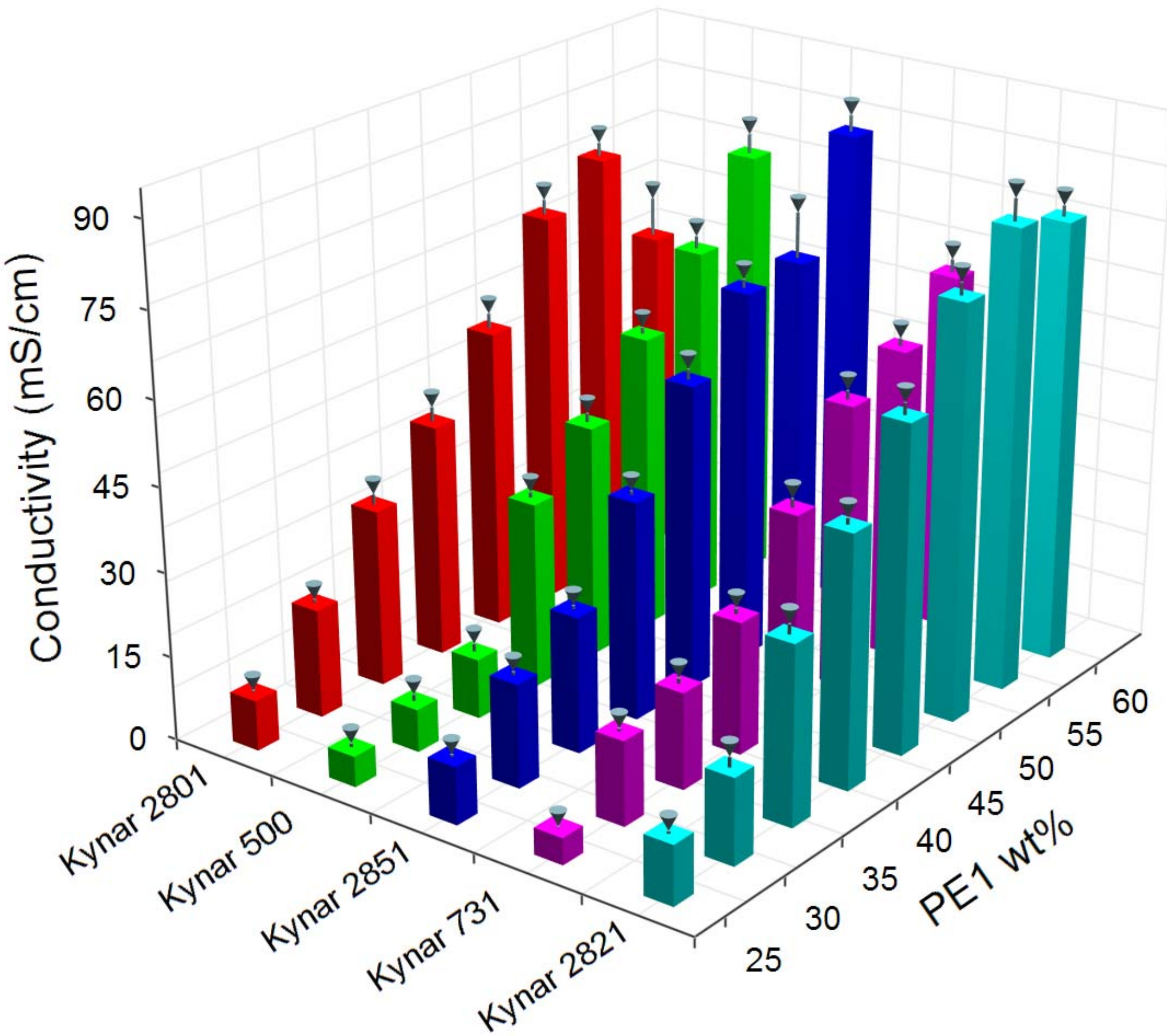
Screening Experiments: PVDF/Acrylic PE

HTC: PVDF/PE1 membranes

Polyelectrolyte 1 (PE1)



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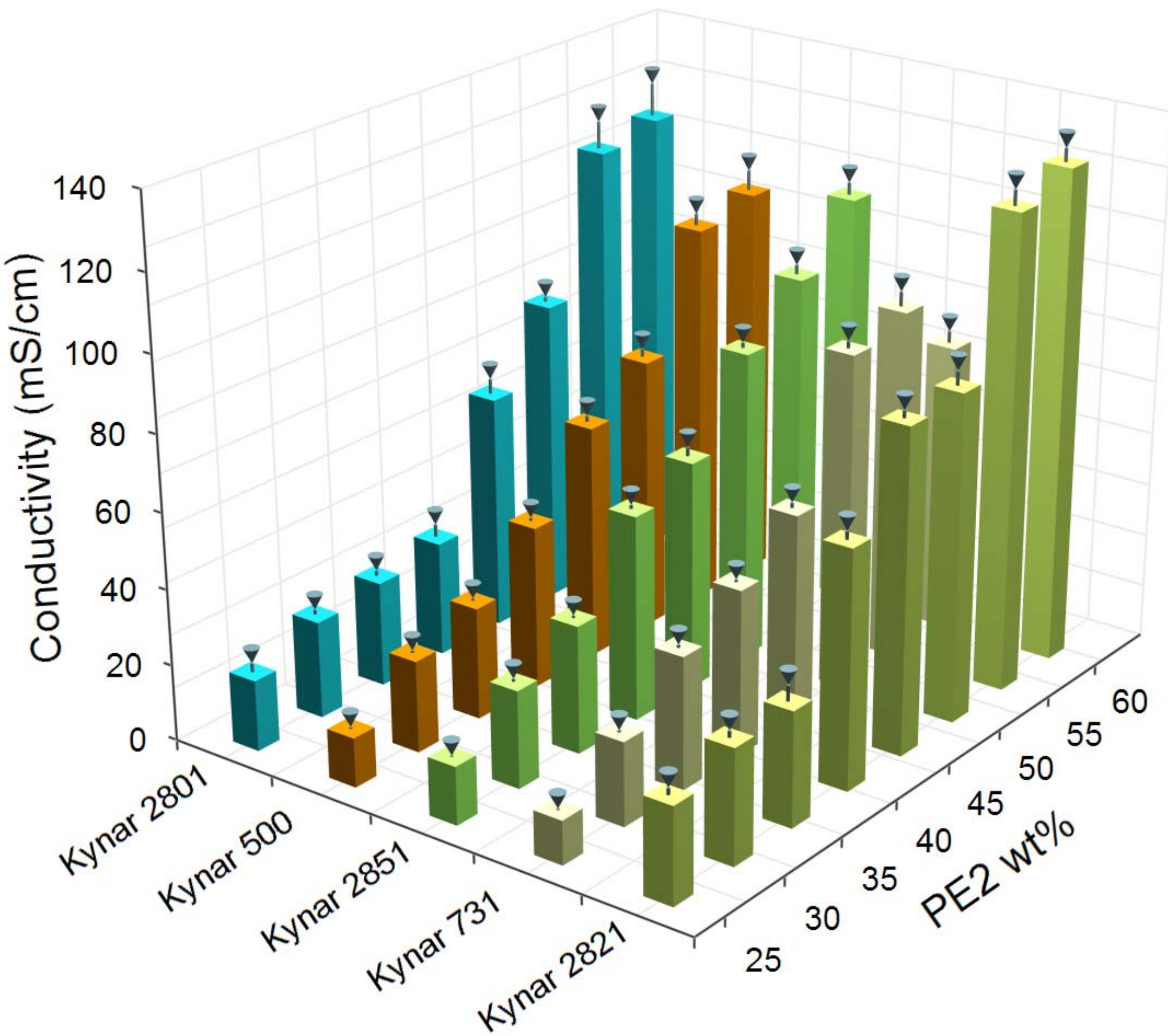
HTC: PVDF/PE2 membranes



Polyelectrolyte 2 (PE2)

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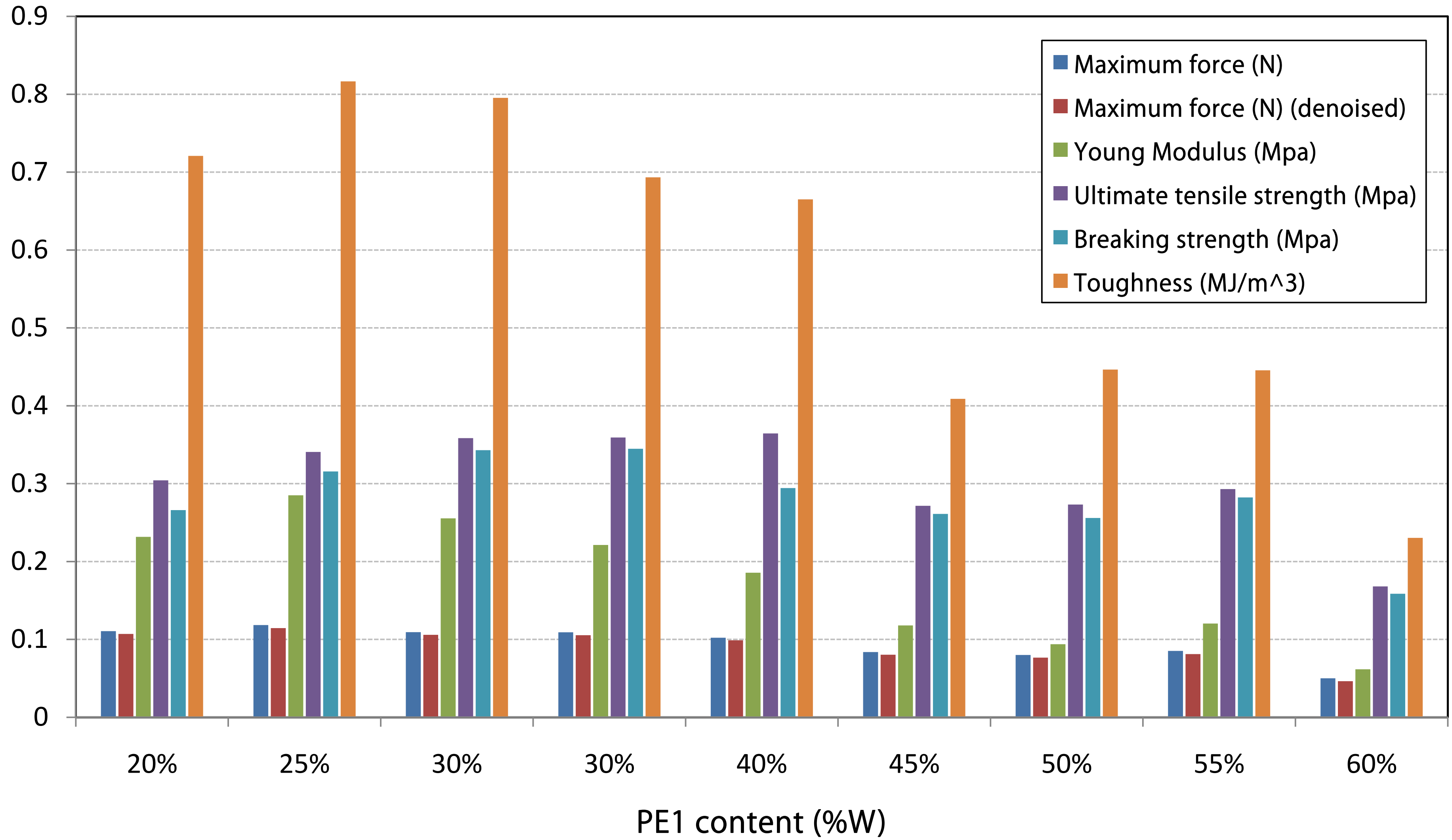
HTMECH: Preliminary Results (Kynar®500/PE1)



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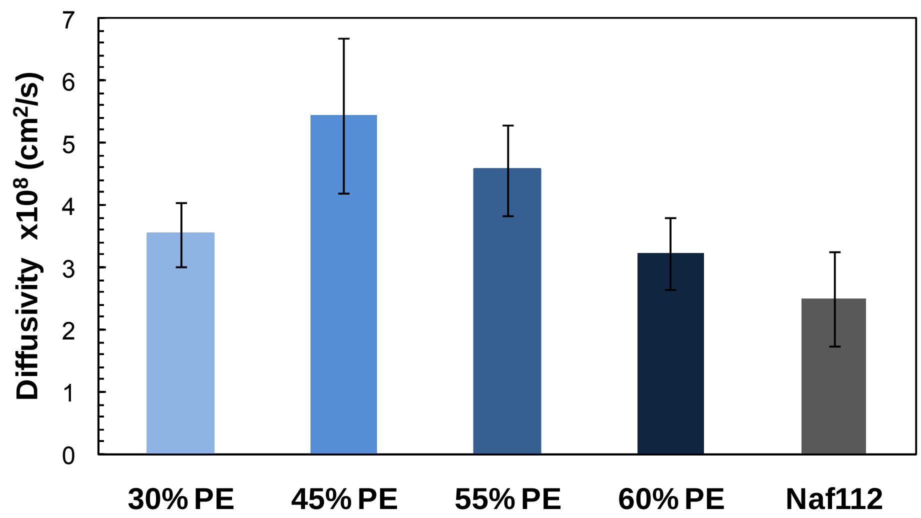
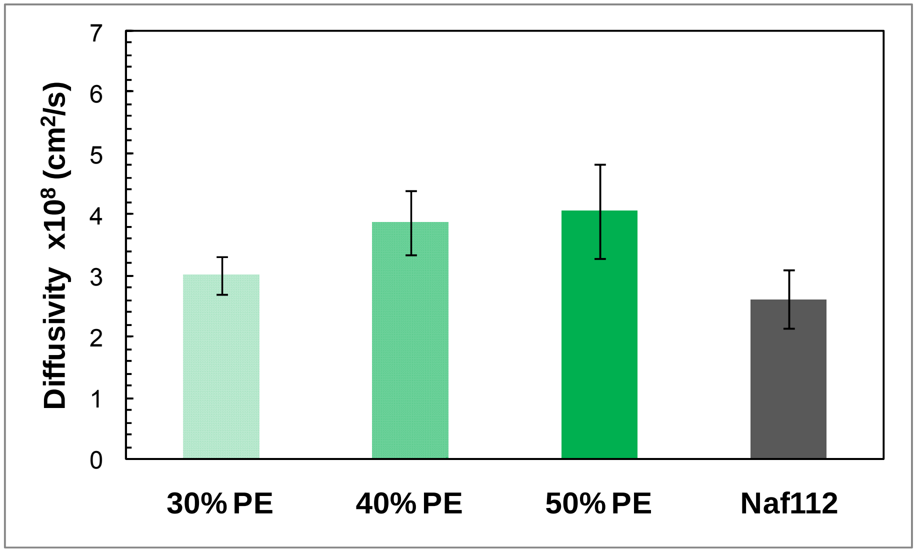
HT Permeability: PVDF/PE





Statistical Analysis: PVDF/PE Conductivity

- Data categorization
- Find non-evident correlation patterns

- Methods:
  - Unbalanced univariate general linear model (type III sums of squares)
  - One-way ANOVA
  - Levene's test
  - Tamhane's T2 post-hoc test (pairwise comparisons, unequal group size)

Statistical Analysis: PVDF/PE Conductivity

- Simple effects:
  - Non-statistically significant difference in conductivity at a PE1 content of 25%wt, and below a PE2 content of 30% regardless of PVDF grade

- Within groups comparison:
  - Non-statistically significant difference in conductivity between PE (both types) contents of 55%wt and 60%wt for most PVDF grades

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Statistical Analysis: PVDF/PE Conductivity

- Tamhane's T2 post-hoc test: Homogeneous subgroups

PVDF/PE1 Membranes		
Kynar® 500	Kynar® 731	Kynar® 2801
		Kynar® 2821
		Kynar® 2851

PVDF/PE2 Membranes			
Kynar® 500	Kynar® 731	Kynar® 2801	Kynar® 2821
		Kynar® 2851	

- Possible dissimilar PVDF-PE interaction effects between PVDFx/PE1 and PVDFx/PE2
  - Kynar® 500 and Kynar® 731 = Homopolymers
  - Kynar® 28x1 = PVDF:HFP copolymers

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Summary

- Univariate general linear model
  - Identified main significant effects: PVDF grade, PE content, and PVDF*PE interaction
- Simple effects and within groups comparison
  - PVDF effect minimized at low PE contents: Statistically identical conductivity at low PE%wt regardless of PVDF grade
  - Maximum effective PE content suggested: Increment in PE content from 55%wt to 60%wt shows no statistically significant effect
- Tamhane's T2 post-hoc test and marginal means
  - Homogeneous subgroups of statistically identical mean conductivity by PVDF family (i.e., 500, 700, 2800 families) for PE1 membranes
  - Structure-property effect suggested: Variation in the Kynar® 28x1 homogeneous subgroup between PE1 and PE2 membranes
- DSC tests
  - Correlation between crystallinity level and marginal conductivity values: low crystallinity = high conductivity (possible improvement on the phase separation process and ion-conducting channel formation)

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