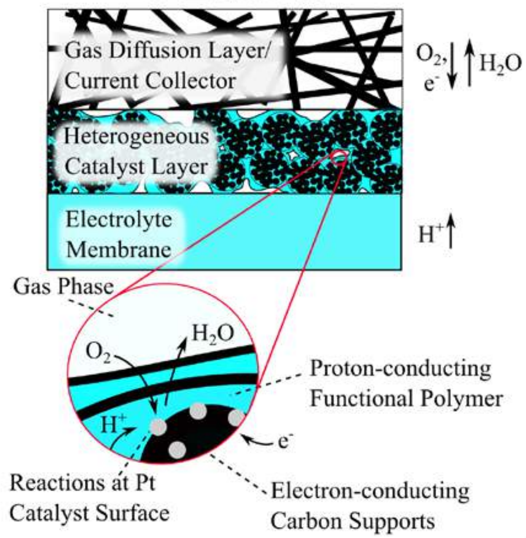
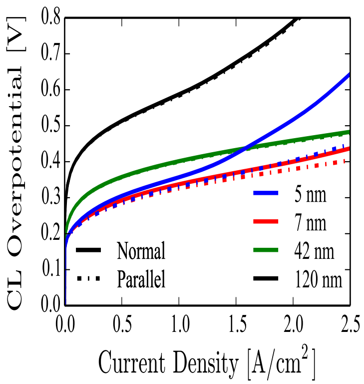
In situ NR Depth Profiles for Analysis of Transport Limitations in PEMFC Catalyst Layers

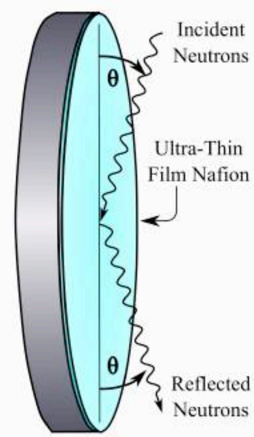
PEMFC Design & Fab

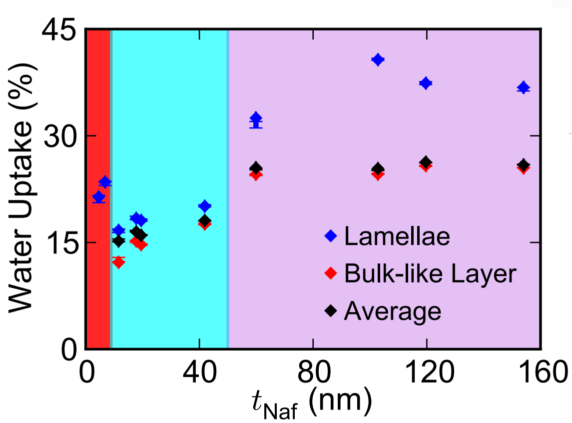


Fuel Cell Simulations



Neutron Reflectometry Measurement





Steven C. DeCaluwe

Colorado School of Mines
Department of Mechanical
Engineering, Golden, CO

Gordon Research Conference on Fuel Cells
August 1, 2018

Earlier today…

Promotion and Tenure Package

Steven C. DeCaluwe

Assistant Professor
Department of Mechanical Engineering
Colorado School of Mines

Acknowledgements

Collaborators

At the NCNR:

- Paul Kienzle – Refl1D
- Chuck Majkrzak

At Colorado School of Mines:

- John Fischer – UG Research Fellow
- Corey Randall – Masters Student
- Center for High Performance Computing

- **Undergraduate researchers (SURF) at NCNR:**
- Andrew Baker (U. Delaware / Los Alamos National Lab)
- Pavan Bhargava (UC Berkeley)

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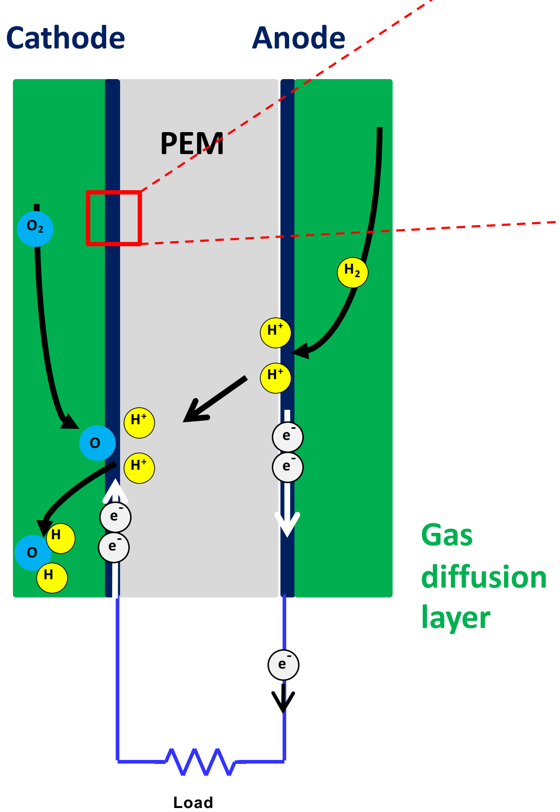
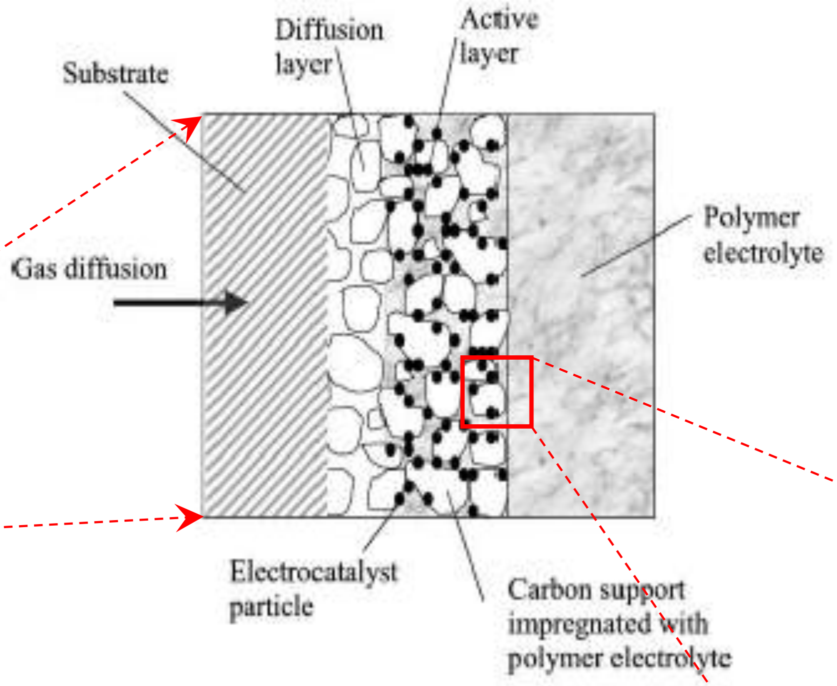
- **NIST Summer Undergraduate Research Fellowship program: Center for High Resolution Neutron Scattering (NSF/NIST partnership)**
- **DOE Early Career Award #DE-SC0018109 Program Manager: Dr. Pappannan Thiyagarajan**

Fuel Cell Interfaces

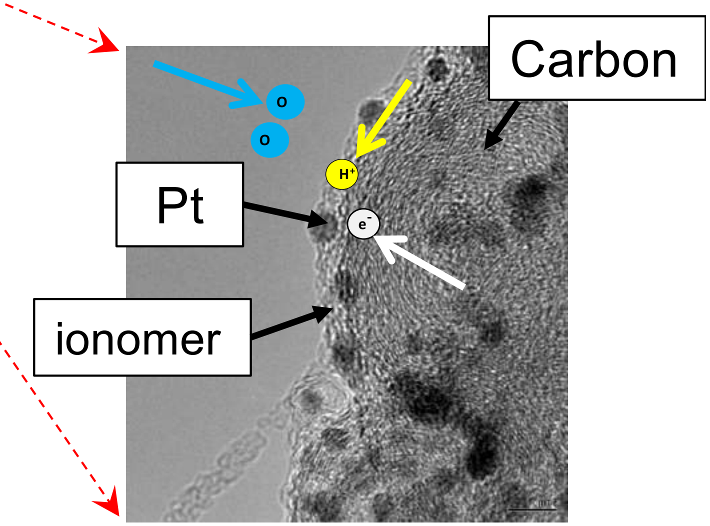
Membrane Electrode Assembly





Three Phase Region

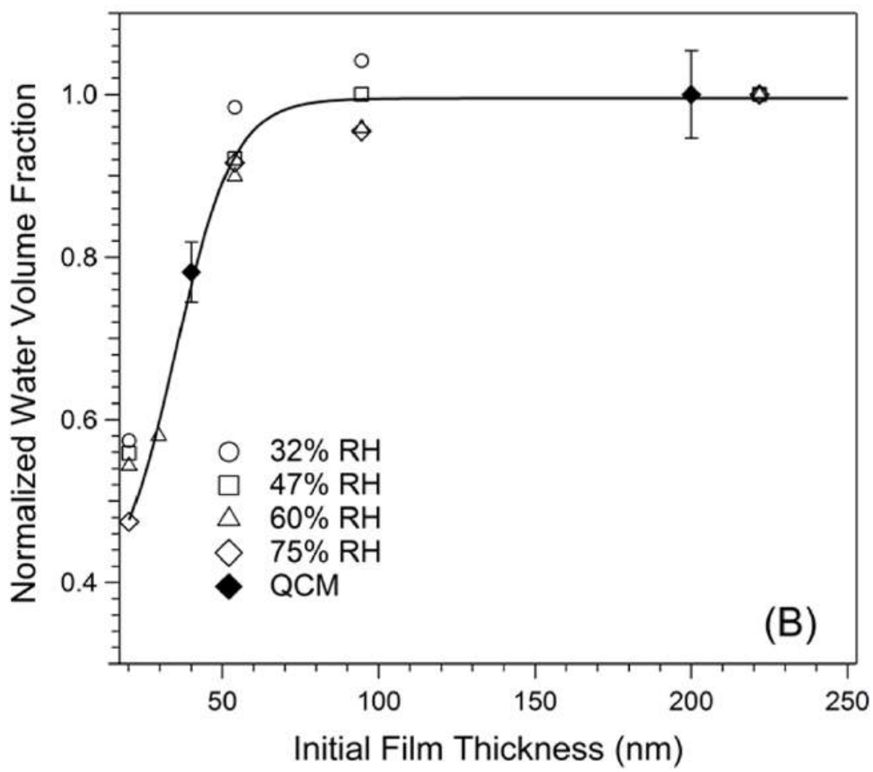
(where gasses electrode and PEM come together to allow the electrochemical reaction)



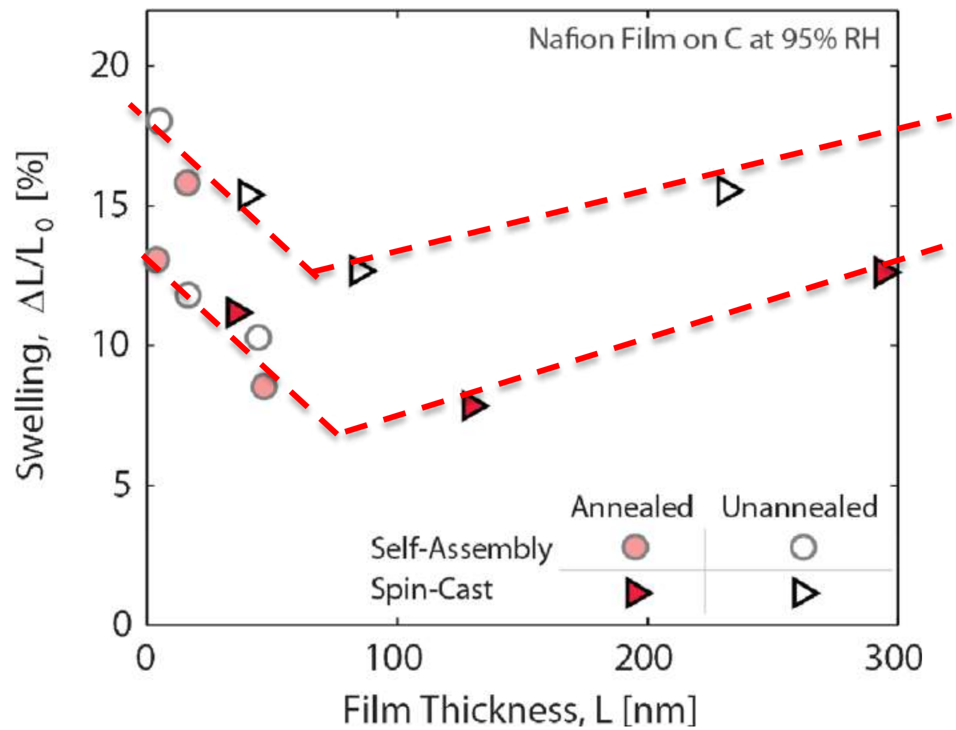
K. L. More, et al., *ECS Transactions* (2006)

Finite thickness effects in PEMFC Catalyst Layer Nafion

- Decreasing water uptake for films ≤ 60 nm
- Increasing uptake at very low thickness.
- Increasing stiffness, confinement.

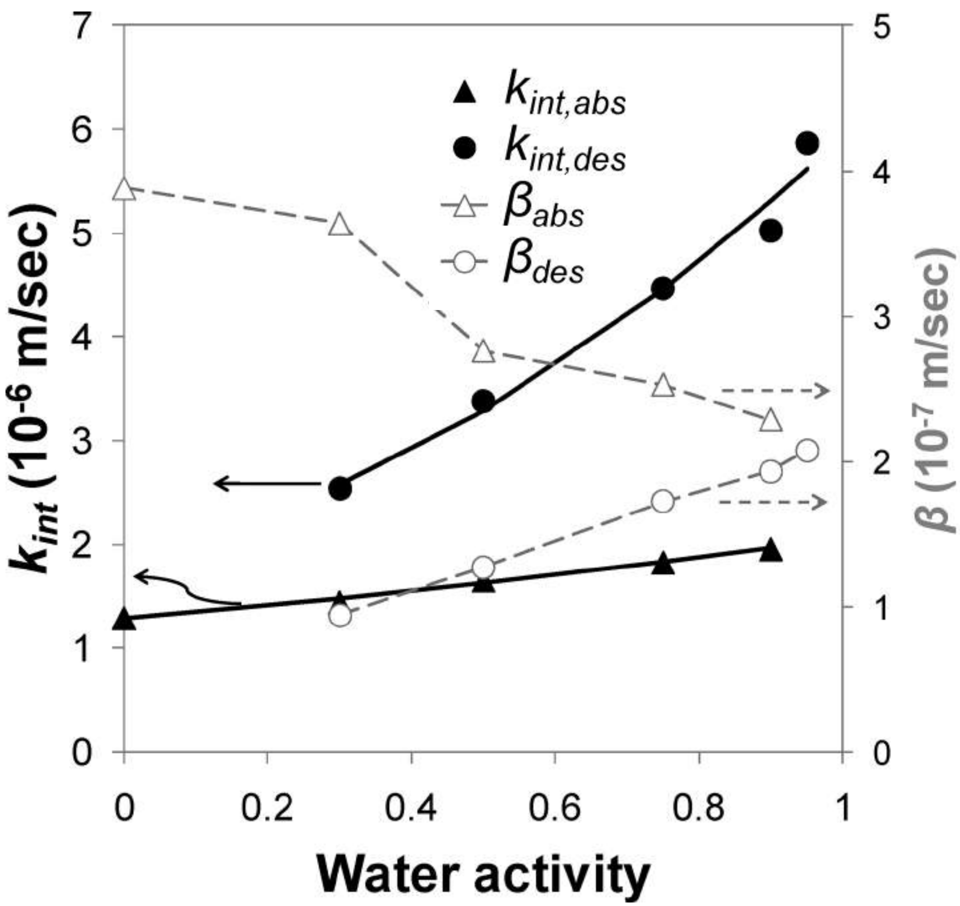


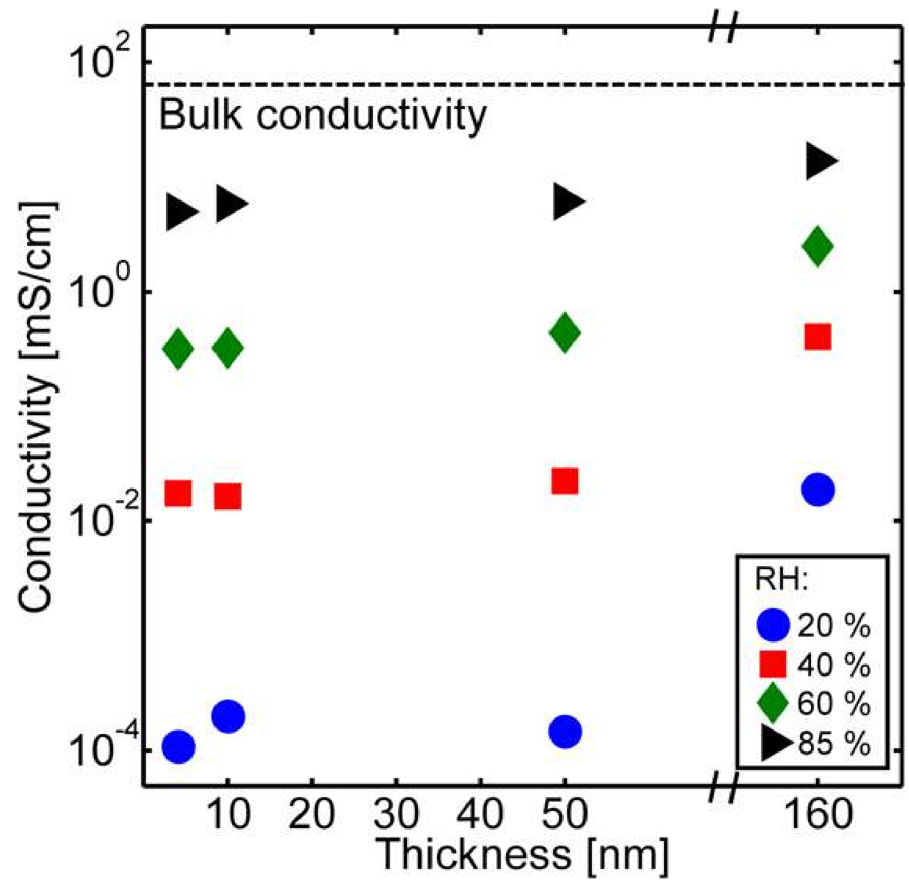
Eastman, et al., *Macromolecules*, 2012



Kusoglu, et al., *Adv. Func. Mat.*, 2014

Finite thickness effects in PEMFC Catalyst Layer Nafion





Kongkanand, *J. Phys. Chem. C*, 2011

Modestino, et al., *Macromol*, 2013

Finite thickness effects in PEMFC Catalyst Layer Nafion

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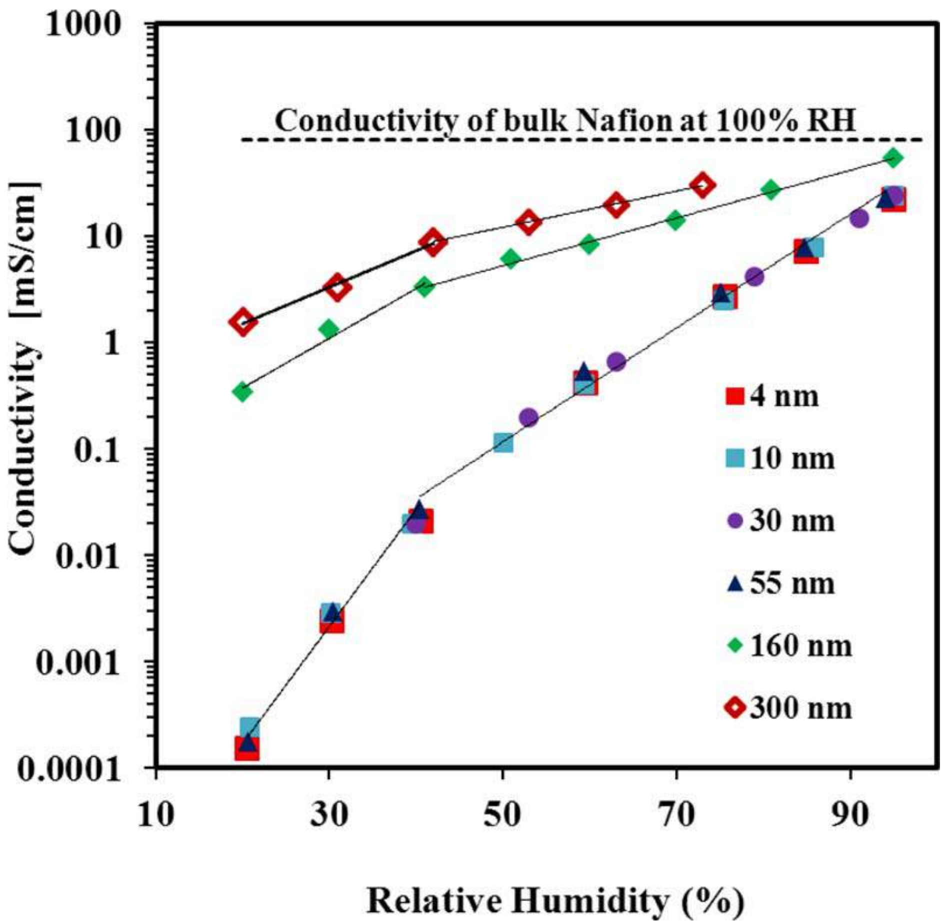
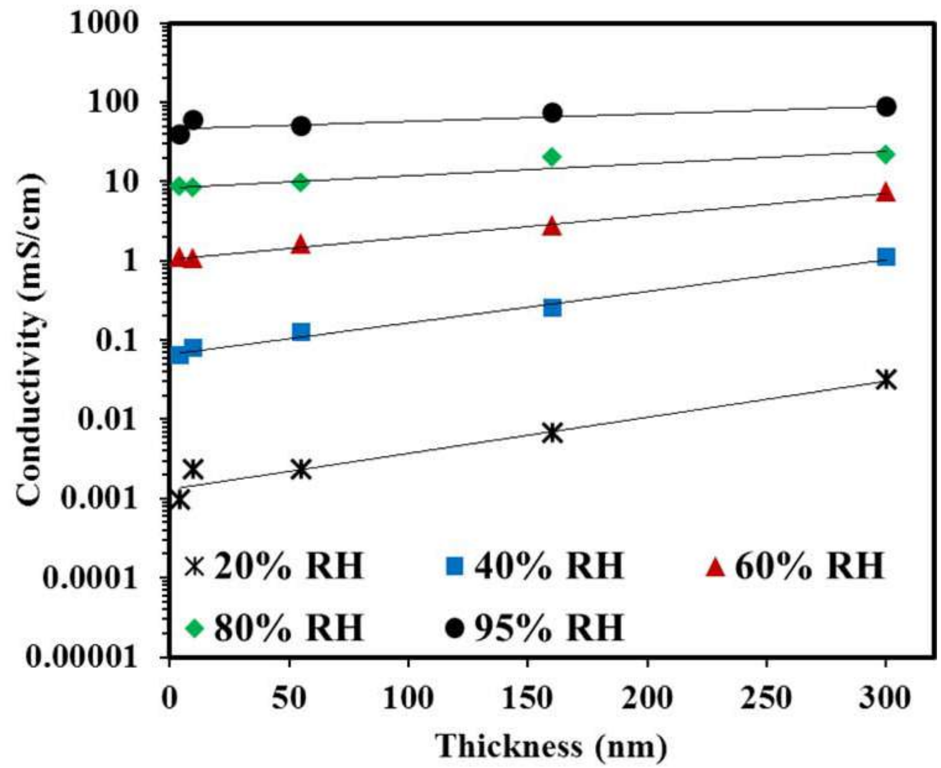
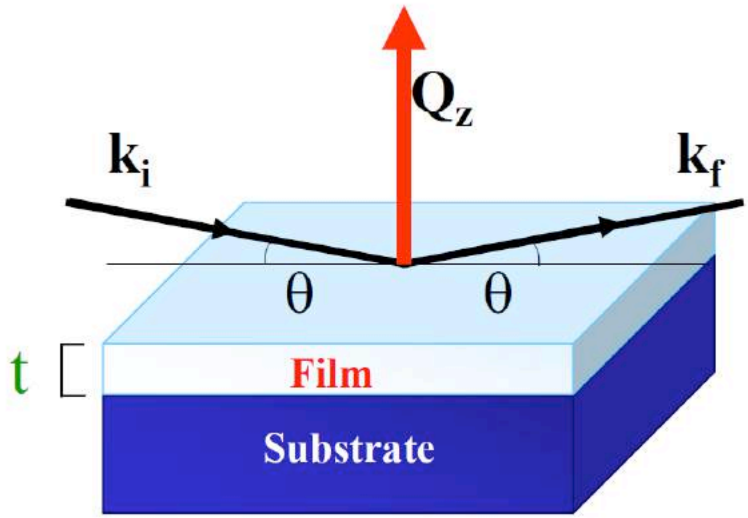




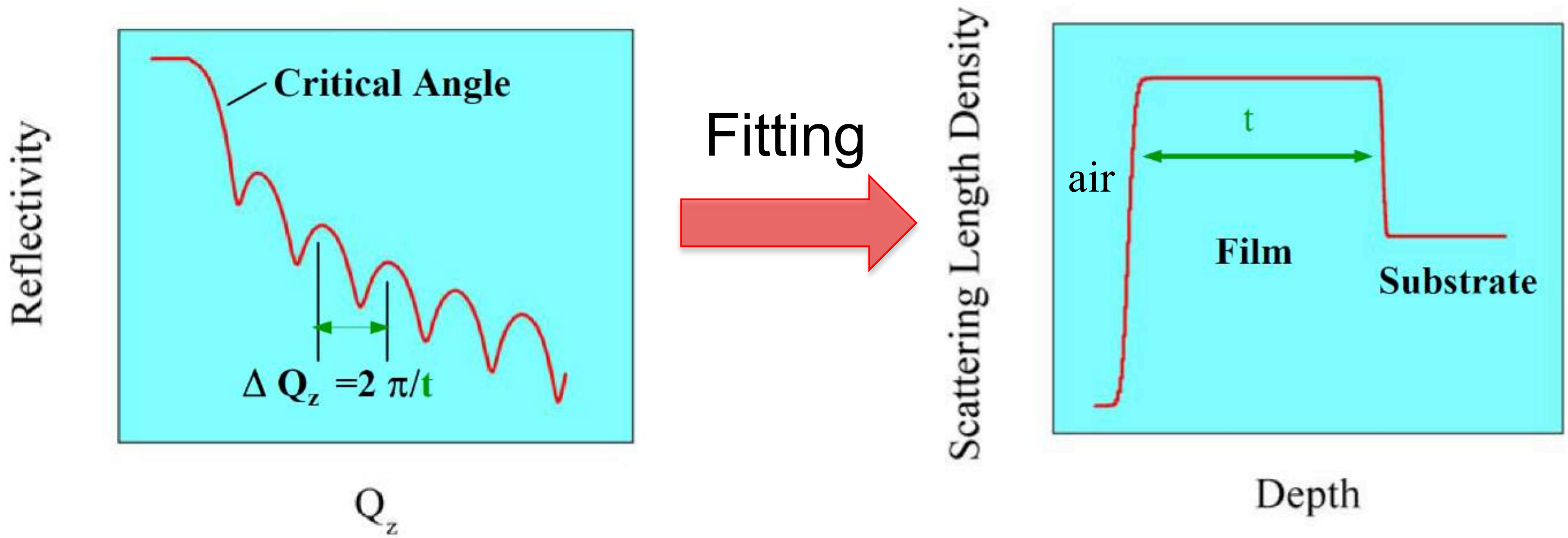
Paul, McCreery, Karan, *J. Electrochem Soc.*, 2014

Neutron Reflectometry (NR)

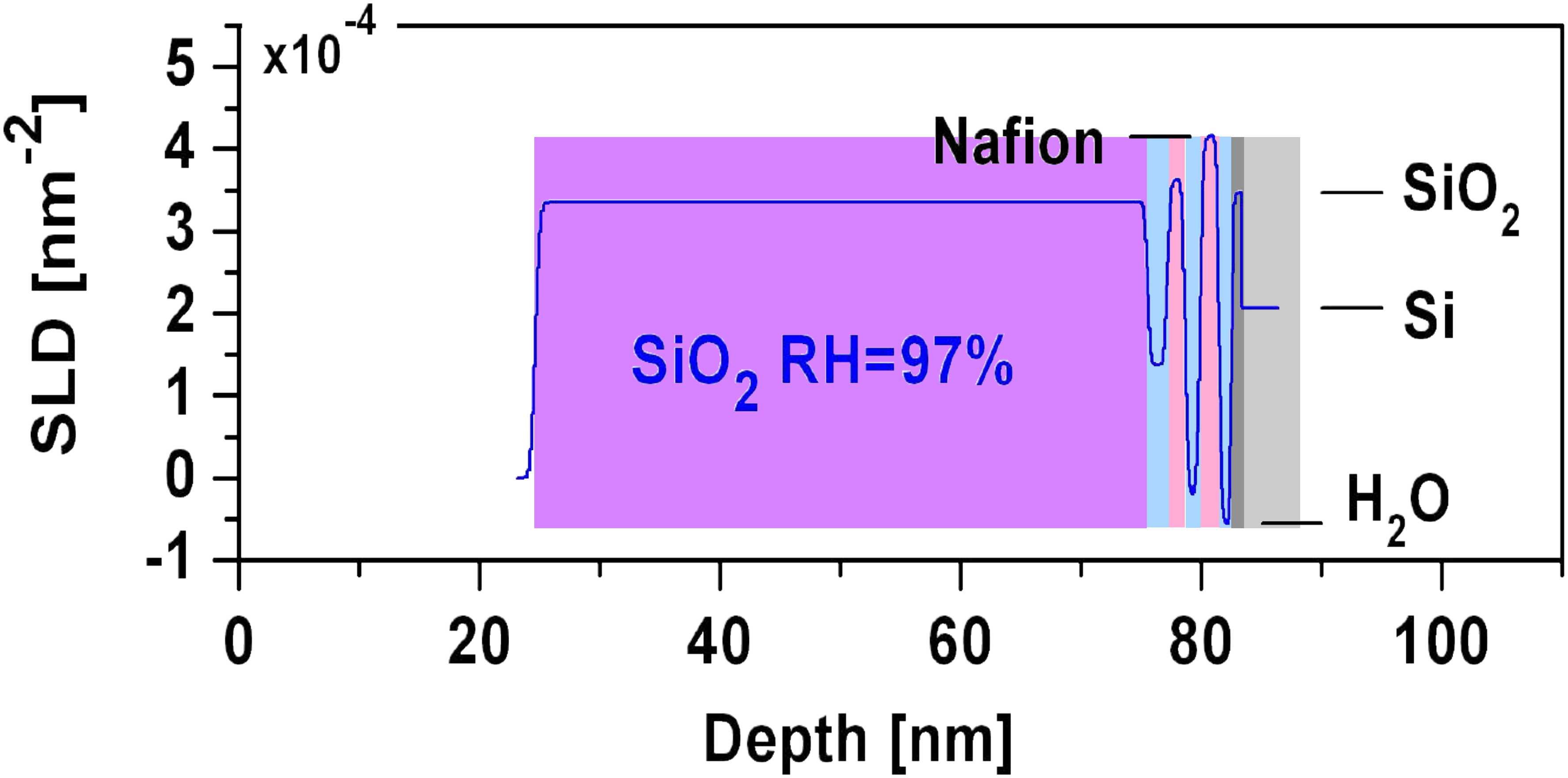


- Specular NR measures Reflected Intensity vs. grazing angle θ or Q_z
- Oscillations with period 2π / layer thickness
- NR Provides Depth Profile of the SLD
- SLD related to Composition by volume fractions V_j

$$SLD(z) = \Sigma_j SLD_j V_j$$



Multi-Lamellar Structures at Nafion-support Interfaces



Dura, et al., *Macromolecules*, 2009

Lamellar phase segregation at Nafion-support Interfaces

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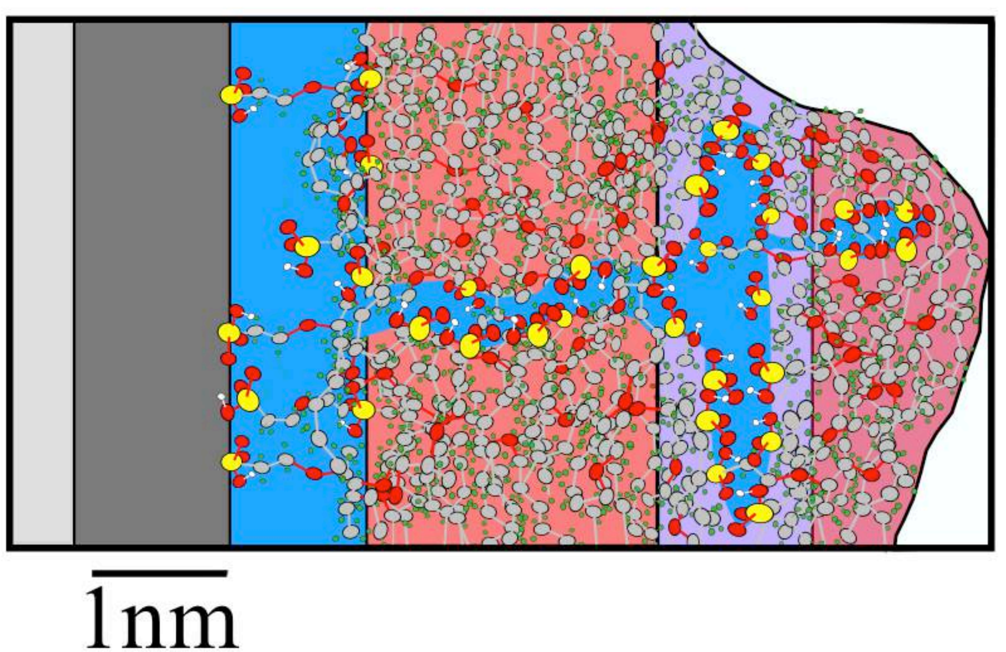
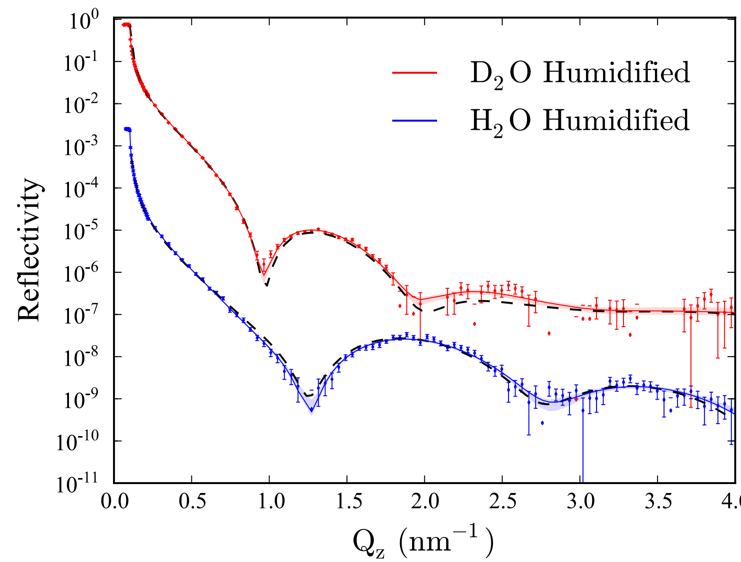
Observed phase segregation of Nafion constituents (sulfonic acid side chains and fluorocarbon backbones) at hydrophillic interface.

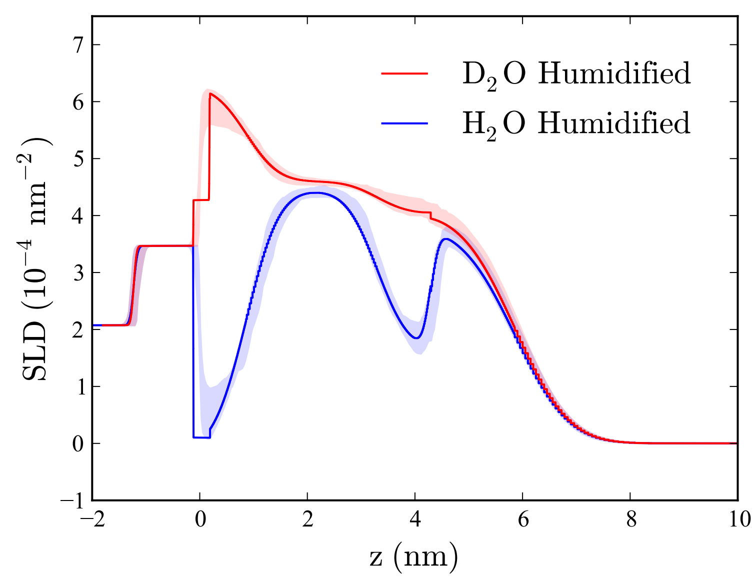
Consistent with:

- Global stoichiometry of Nafion 1100
- Nafion molecule length scales
- Known Nafion/water chemical interactions

Roughly consistent with NR data.







DeCaluwe, et al., *Soft Matter*, 2014

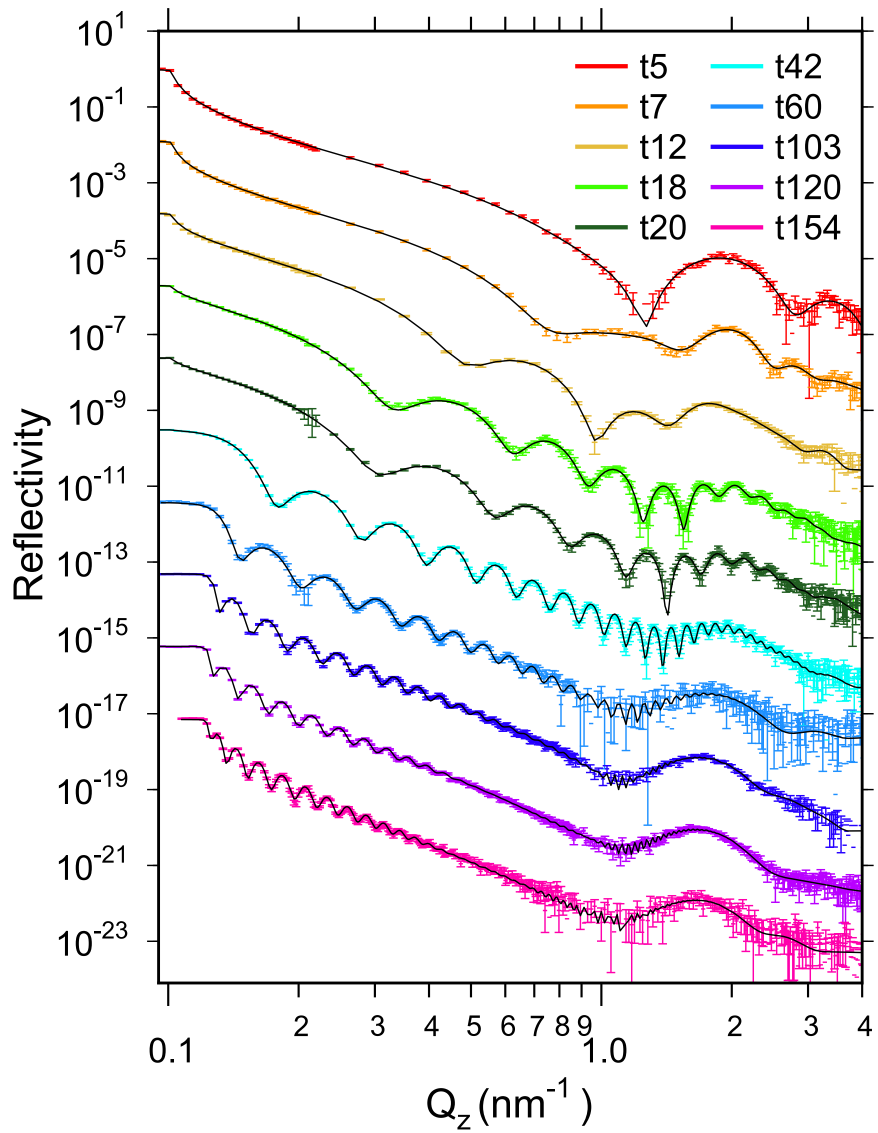
Thickness Effects on Nation Interface Structure and Water Uptake

- 10 films, t_{Naf} = 5 nm—154 nm

$$t_{\mathrm{Naf}} = \sum_j t_j V_{\mathrm{Naf},j}$$

- Samples named according to equivalent Nafion thickness: tXX = t_{Naf} = XX nm

- NR measured at
  RH = 92% RH
  T = 29.6 C



DeCaluwe, et al., *Nano Energy*, 2018

Increasing Water Uptake With Increasing Film Thickness

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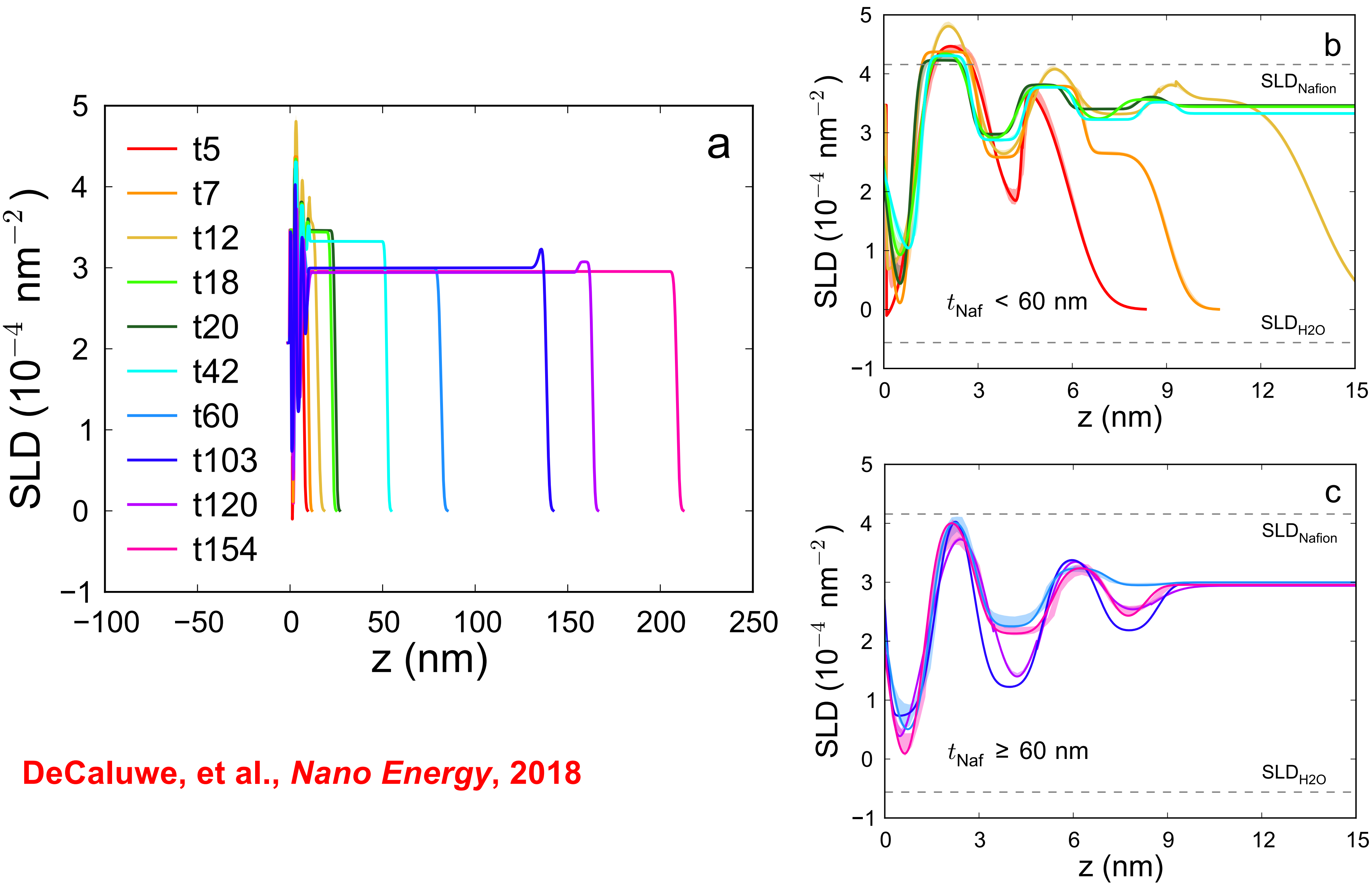
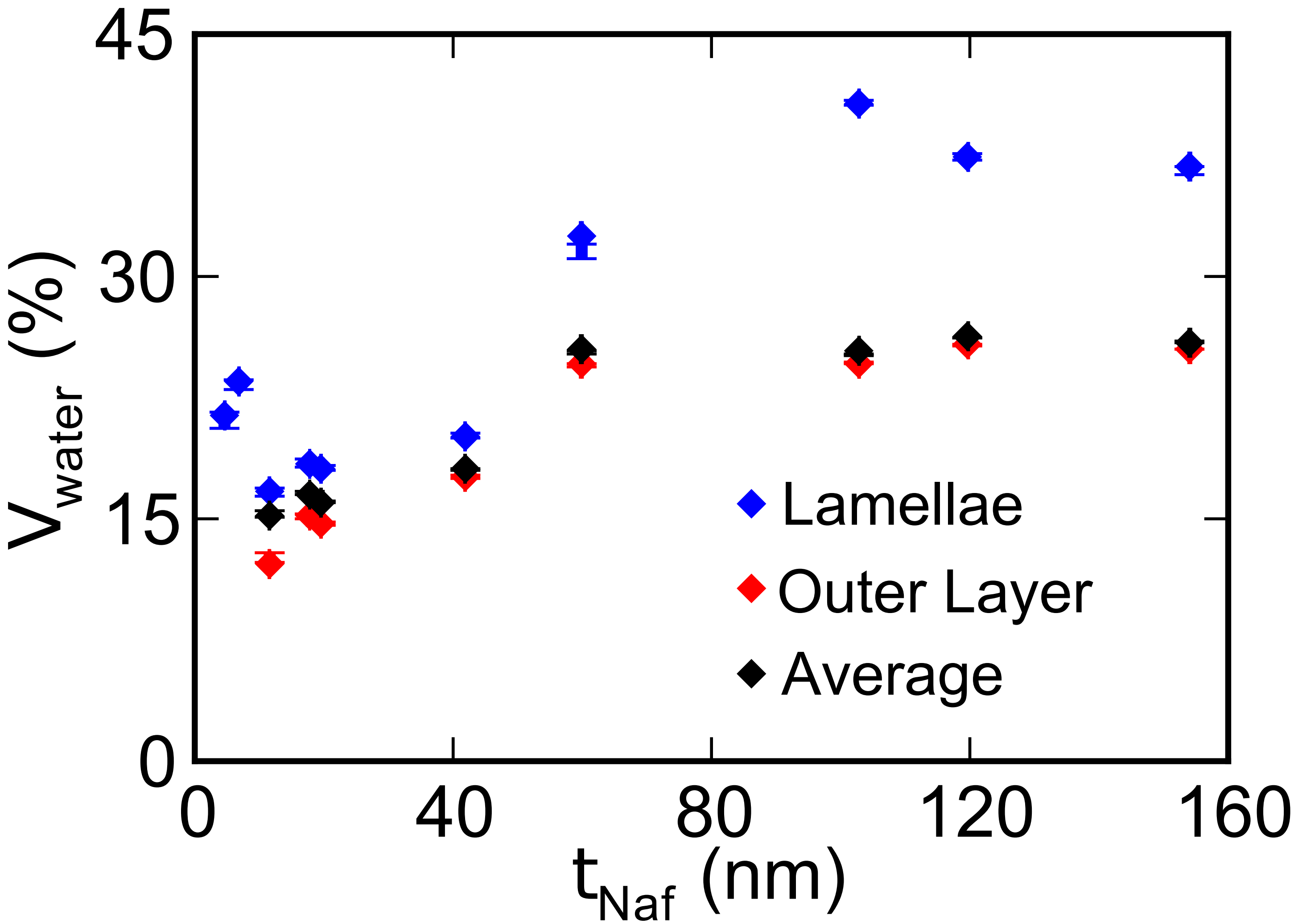


DeCaluwe, et al., *Nano Energy*, 2018

Non-monotonic Water Uptake Trends



“Moving Average” Water Uptake

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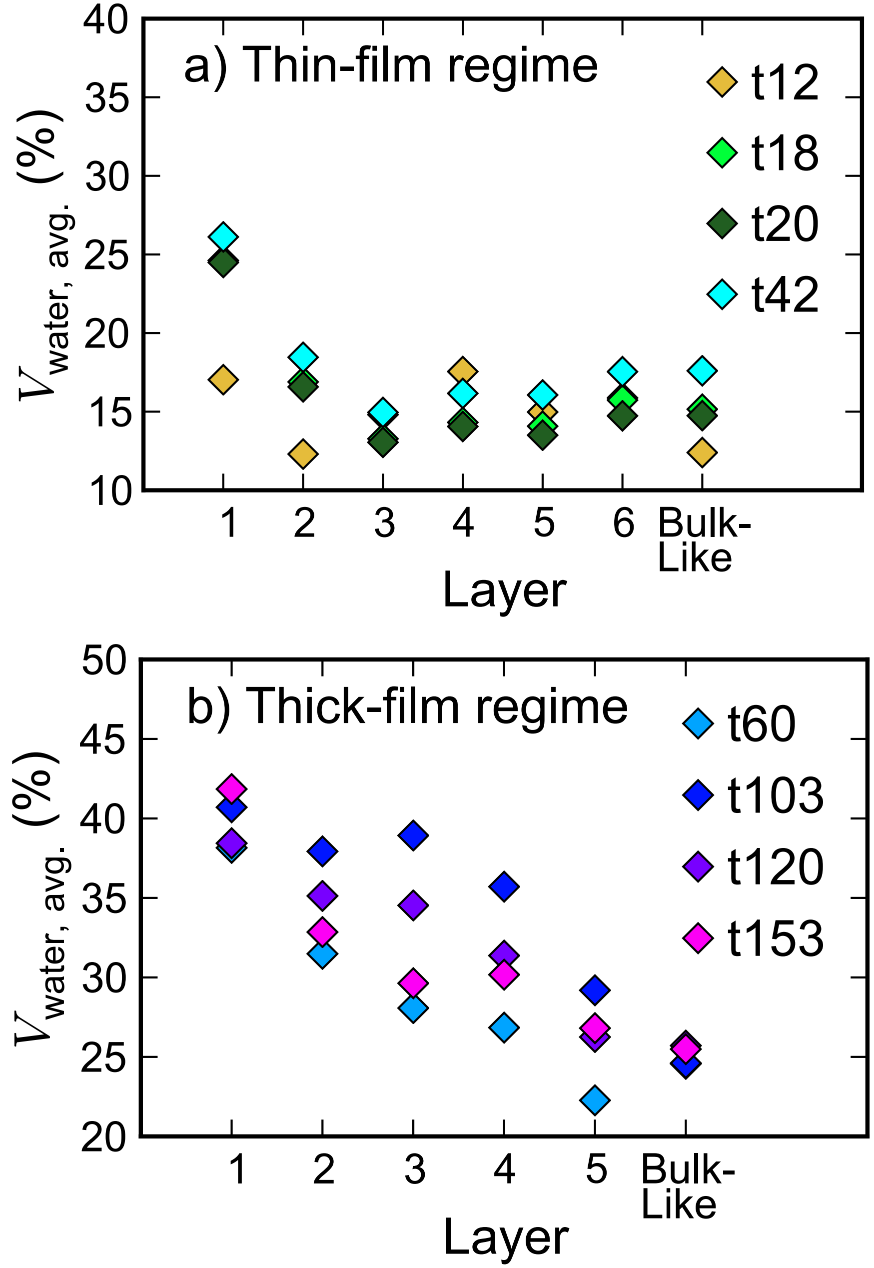

Toward Structure-property relations: Ionic Conductivity Predictions

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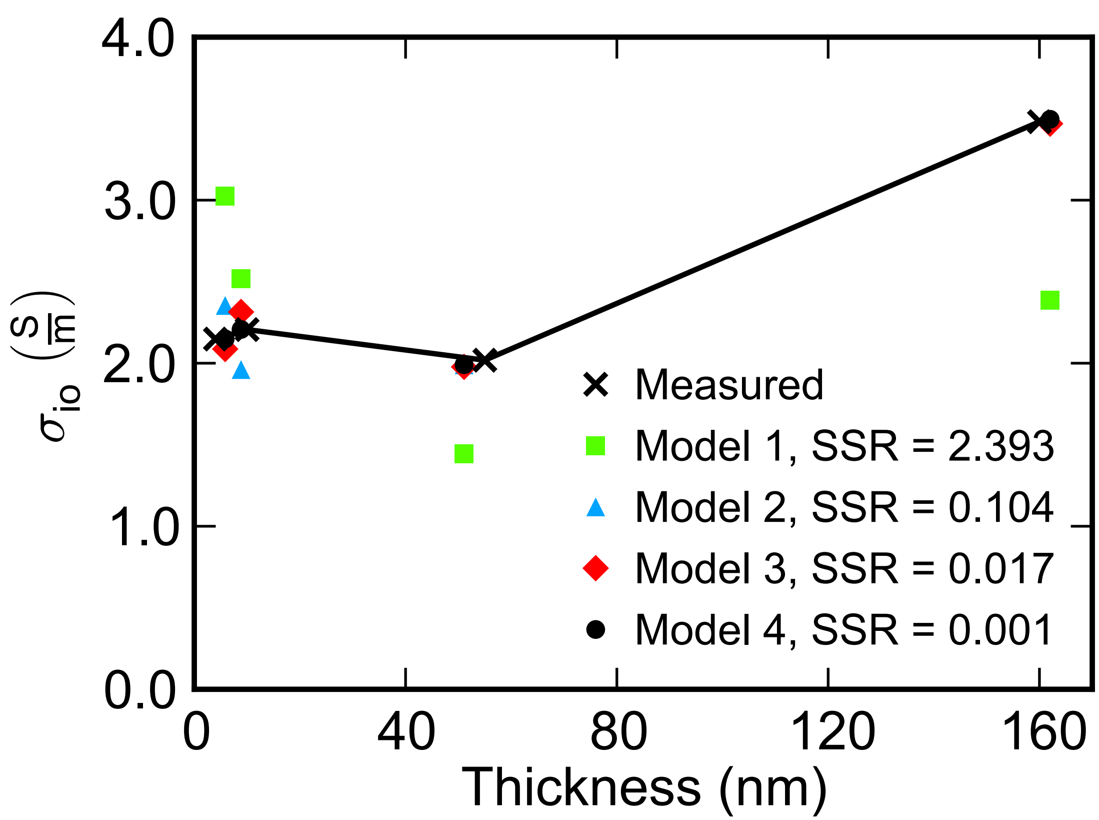
- Compare predictions to exp data (Paul, et al., *J. Electrochem. Soc*., 2014).
- Adopting standard $\sigma_{io} - \lambda$ relationships significantly over-predicts σ_{io} .
- Best model incorporates lamellar structure, linear gradient in ion mobility
- Mobility is lower, closer to the substrate.



Scaling Factors:

At SiO_2: 0.22

At outer layer: 0.51

Outer Layer: 0.67

Implications for Operating PEMFCs

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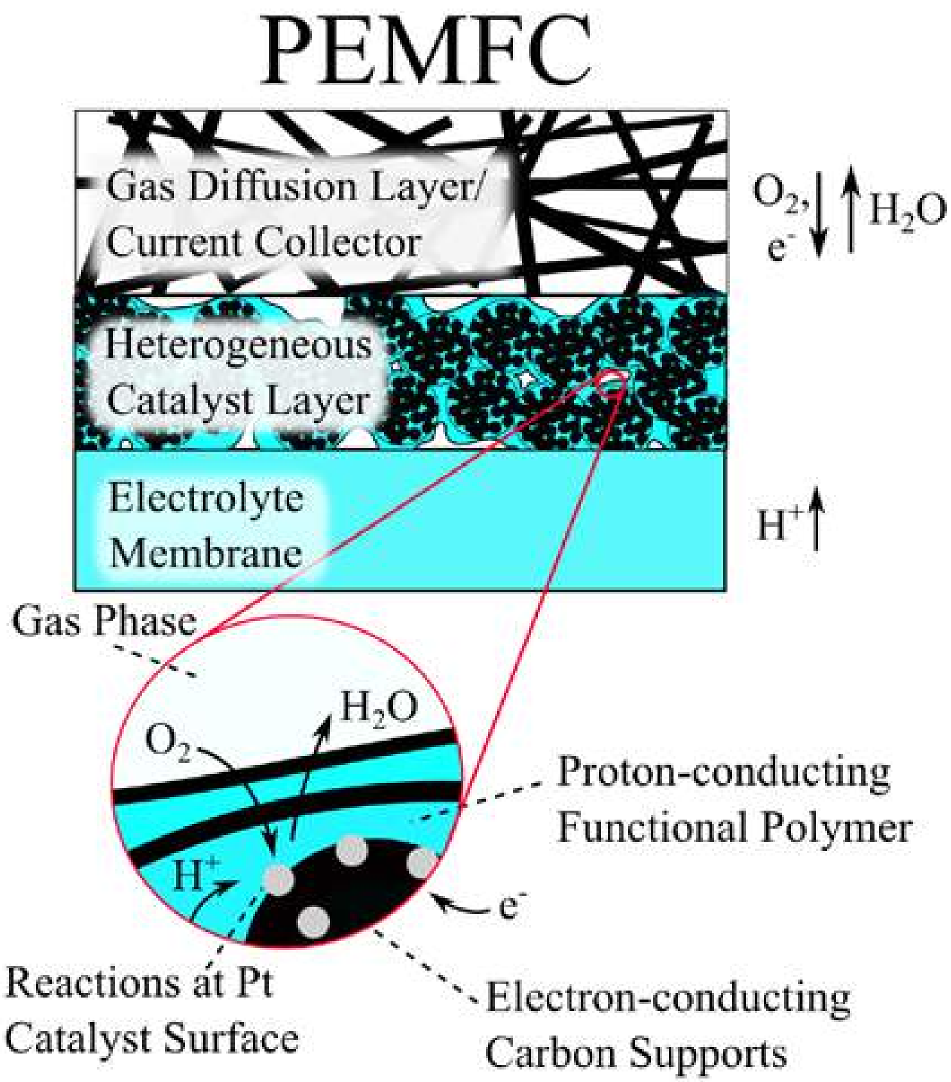
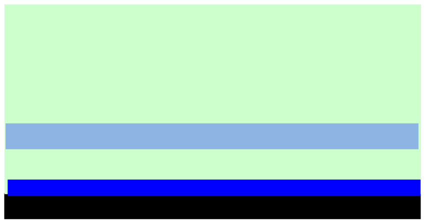
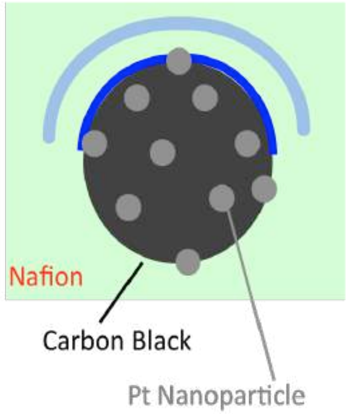




NR structure measured



Possible real structure

- Nafion structure at Pt/Carbon interface significantly impacts catalyst layer degradation:
  - -Nafion acidity varies
  - -Delamination
  - -Pt dissolution, C corrosion

- Affect transport to/from the Pt
  - -To/from the bulk membrane.
  - -To/from gas phase.

Implications for Operating PEMFCs

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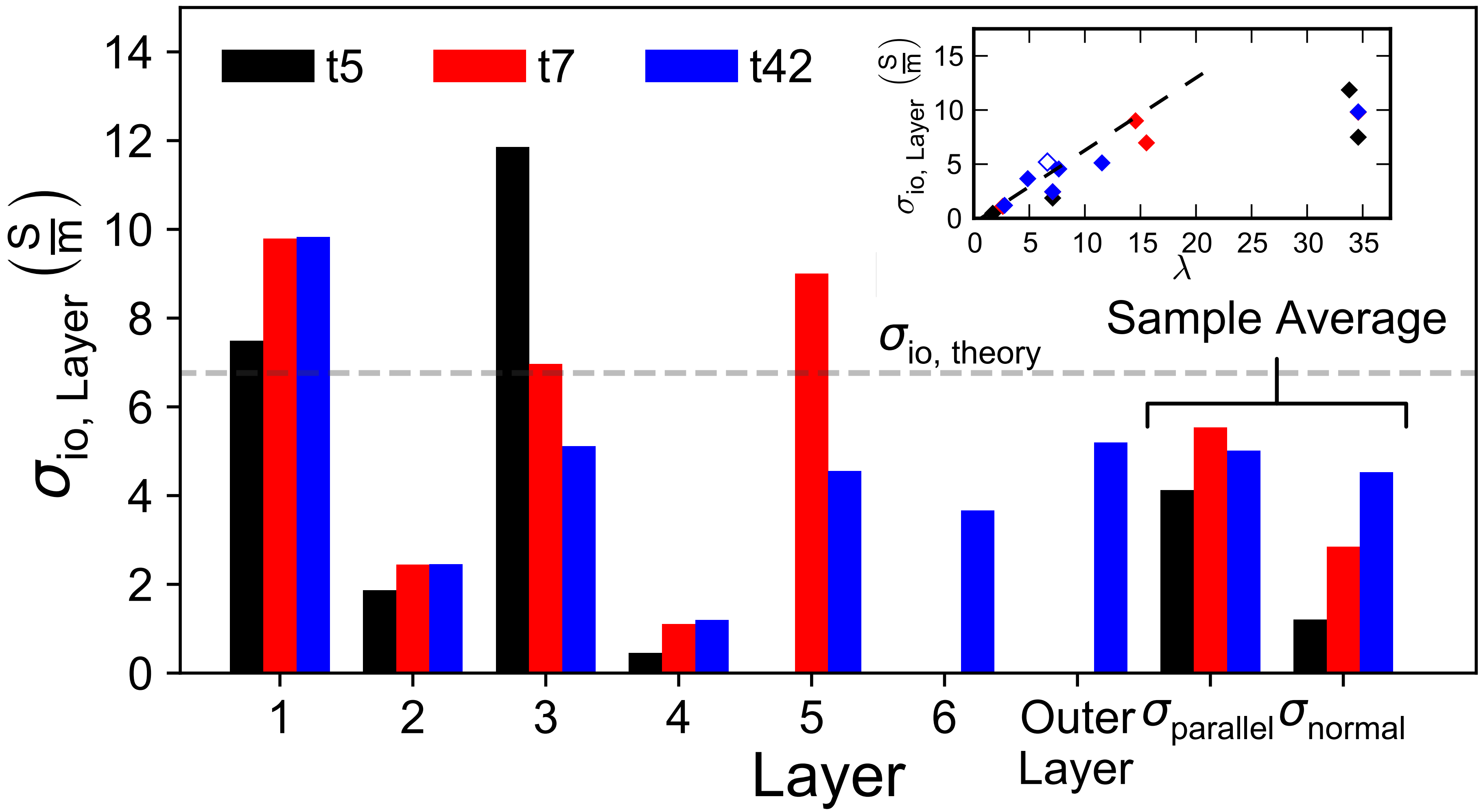


Toward Process-Structure-Property: PEMFC Catalyst Layer Model

Flooded agglomerate model used, simply as a convenient framework to explore property covariation and trends.

CANTERA used for all thermo-kinetic calculations.

Assumptions:

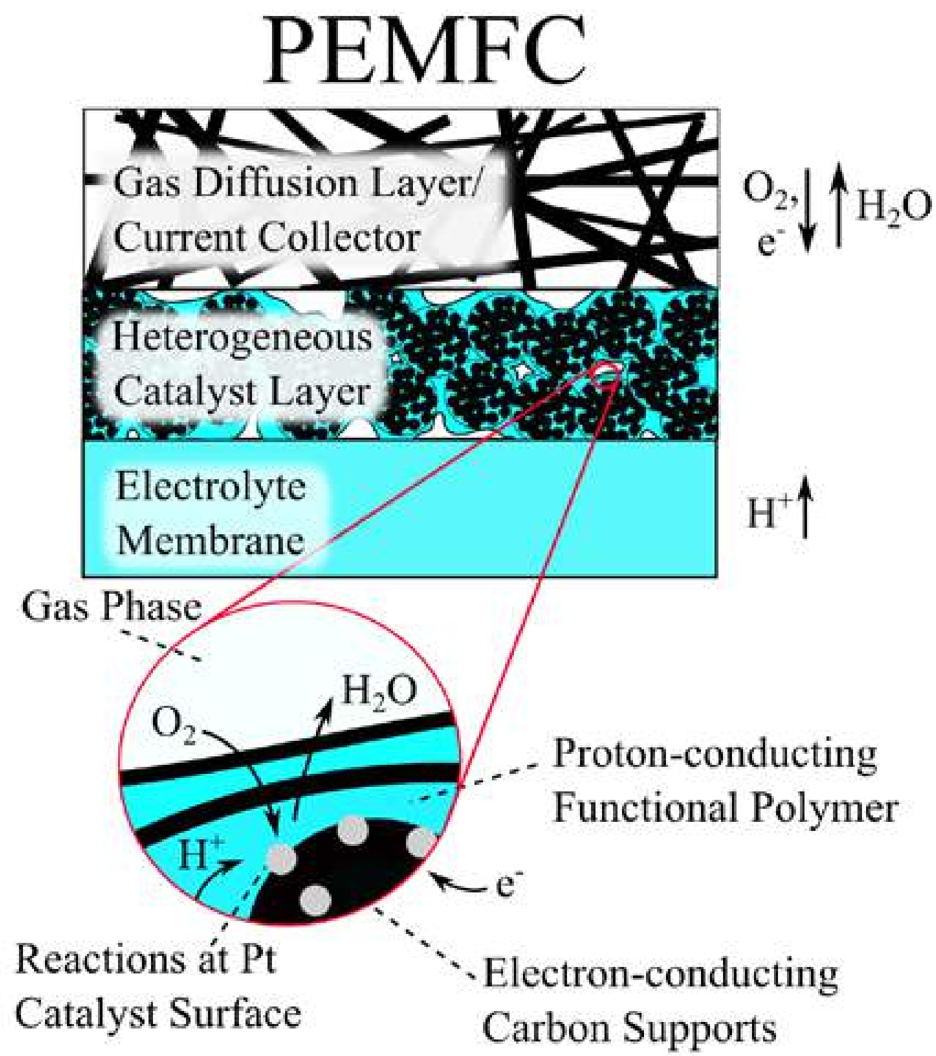
1. Effective conductivities $\sigma_{parallel}$ and σ_{normal} used as limiting cases.

2. Diffusion coefficients D_{O2}, D_{H2} scale linearly with V_{water}.

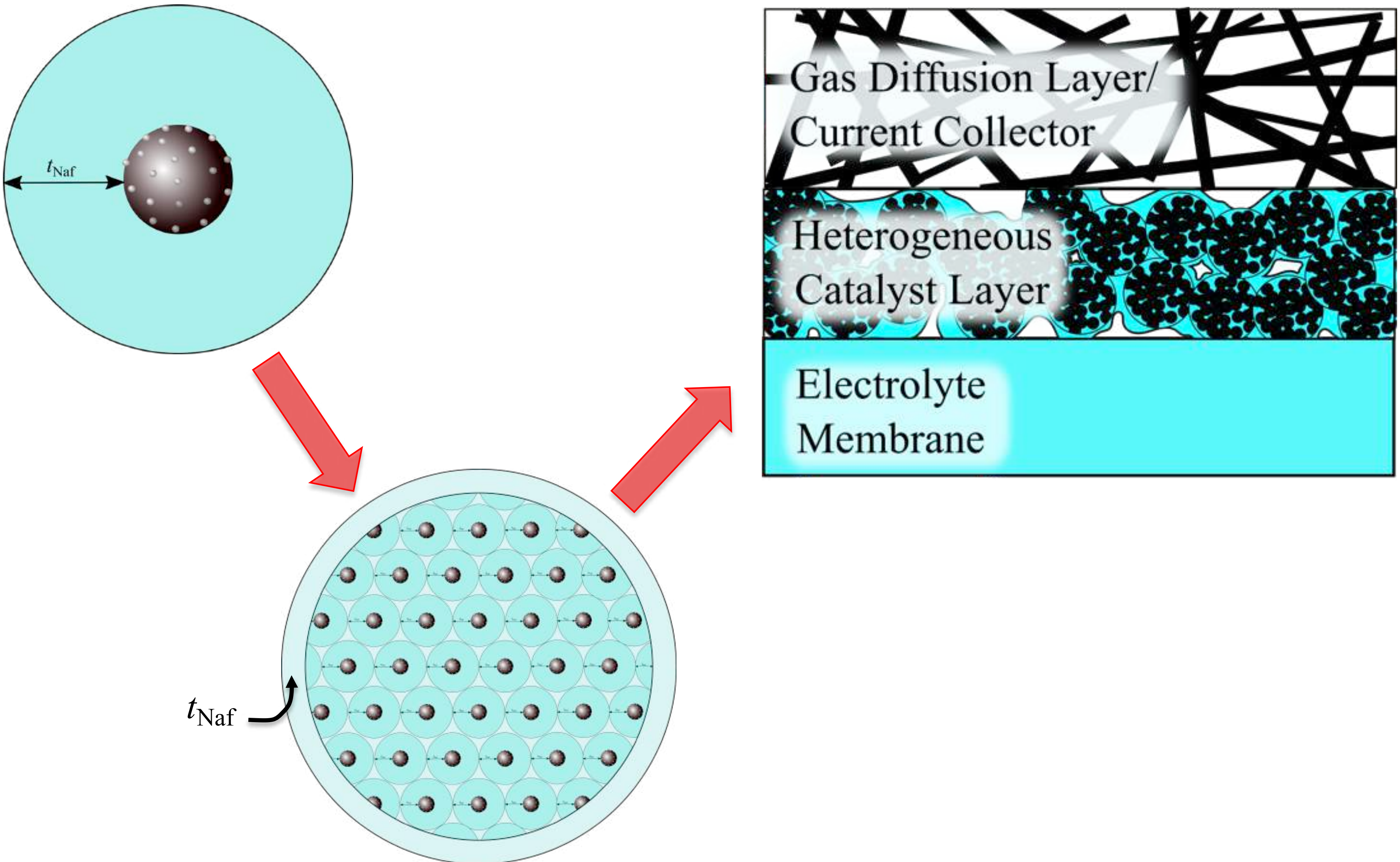
3. Agglomerates fully saturated by H_2O

4. No gas transport limitations.

5. No membrane effects.



Agglomerate Models – Case 1



Fixed Porosity ($\phi_g = 0.10$)

- m_{Pt} decreases significantly with increasing t_{Naf}.

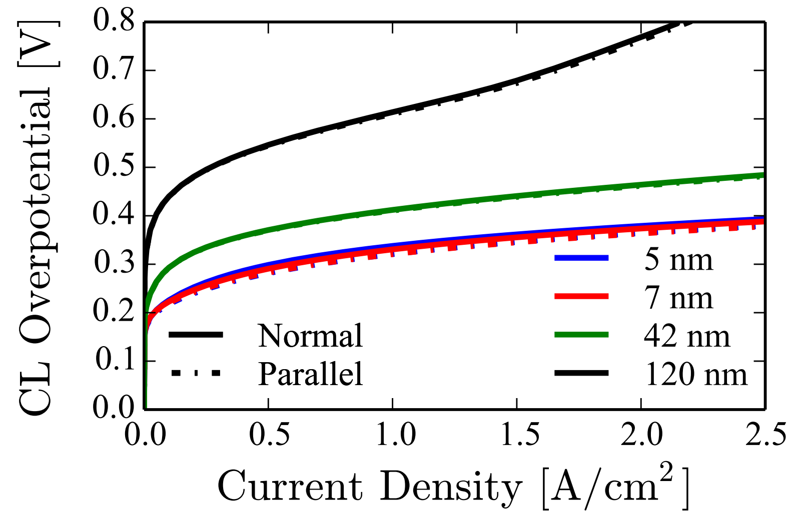
Proton conductivity below ~2 S/m impacts catalyst utilization.

Limiting for large agglomerates (O_2 diffusion into agglomerate is difficult).

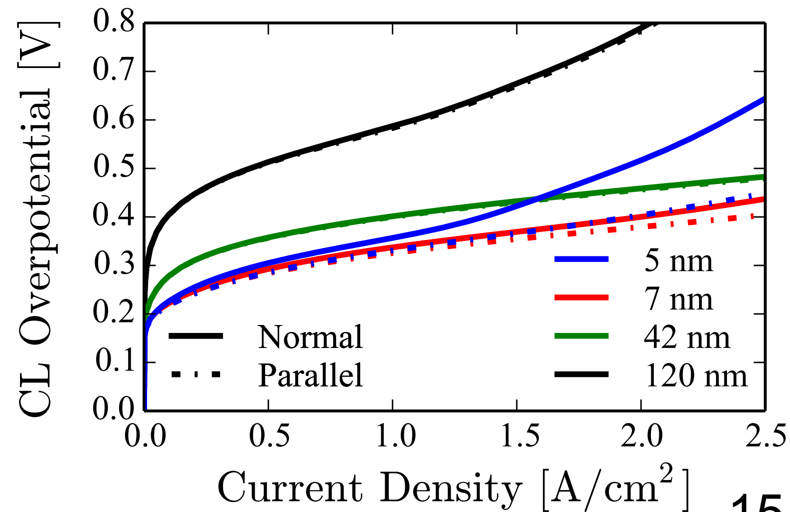
→ Complex interrelationship between properties and micro/nano-structure.

Thickness [nm]	σ_{normal} [S/m]	$\sigma_{parallel}$ [S/m]	V_{water} (relative to bulk)
5.9	1.21	4.12	0.83
8.9	2.85	5.54	0.92
51.1	4.53	5.01	0.70
162.0	6.92	8.04	1.01

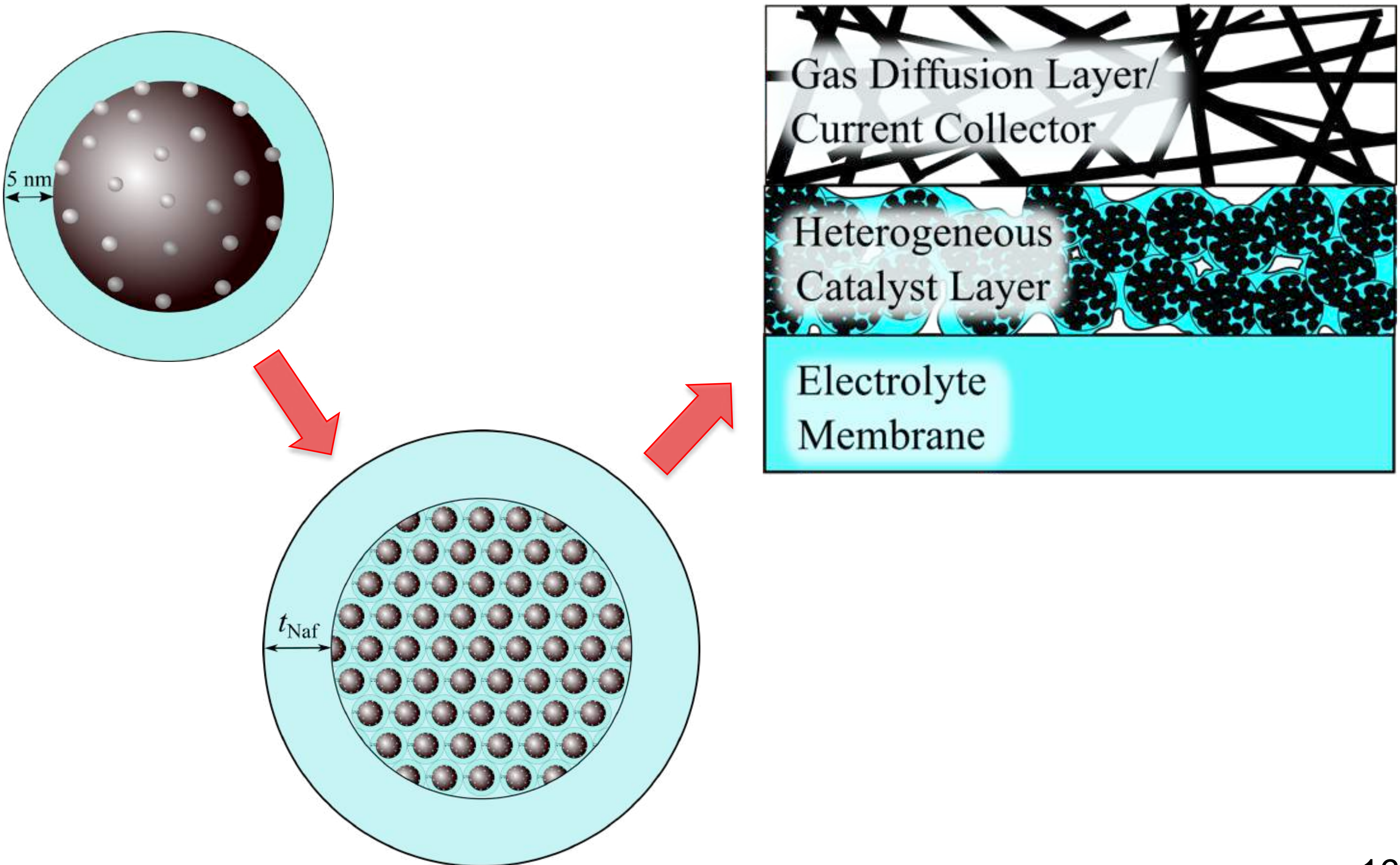
200 nm Agglomerates



500 nm Agglomerates



Agglomerate Models – Case 2



Varying “coating” thickness

m_{Pt} = 0.4 mg/cm^2

Thick coatings impede intra-agglomerate O_2 diffusion (duh).

For large agglomerates, micro/nano-structure (volume fraction, tortuosity) impedes intra-agglomerate O_2 diffusion.

For thin coatings, proton conductivity becomes limiting in large agglomerates.

Thickness [nm]	σ_{normal} [S/m]	$\sigma_{parallel}$ [S/m]	V_{water} (relative to bulk)
5.9	1.21	4.12	0.83
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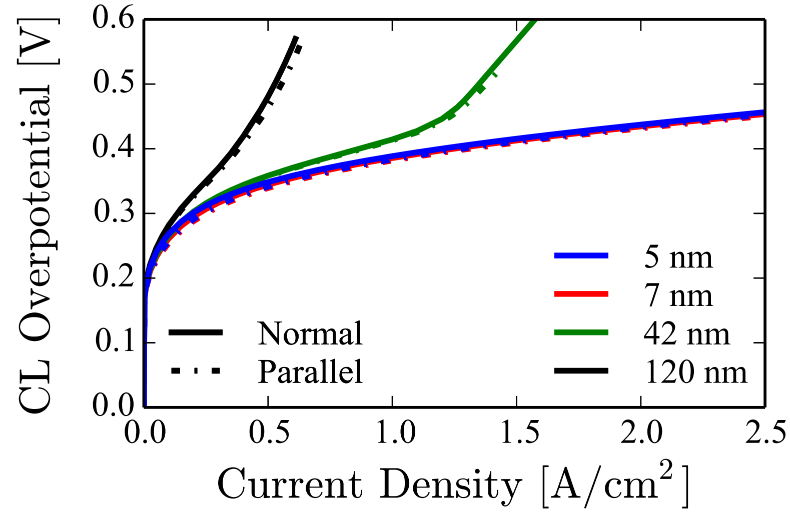
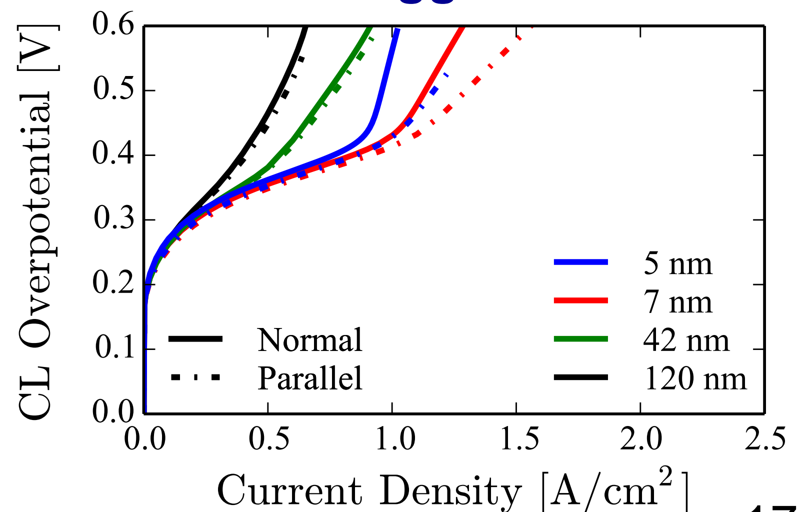
200 nm Agglomerates



500 nm Agglomerates



Next Steps:

Depth profiling Improvements

- Realistic Materials
- Realistic Microstructures
- Non-equilibrated structures

Correlating multiple measurements

Multi-scale simulation Improvements

Next Steps:

Depth profiling Improvements

- Realistic Materials

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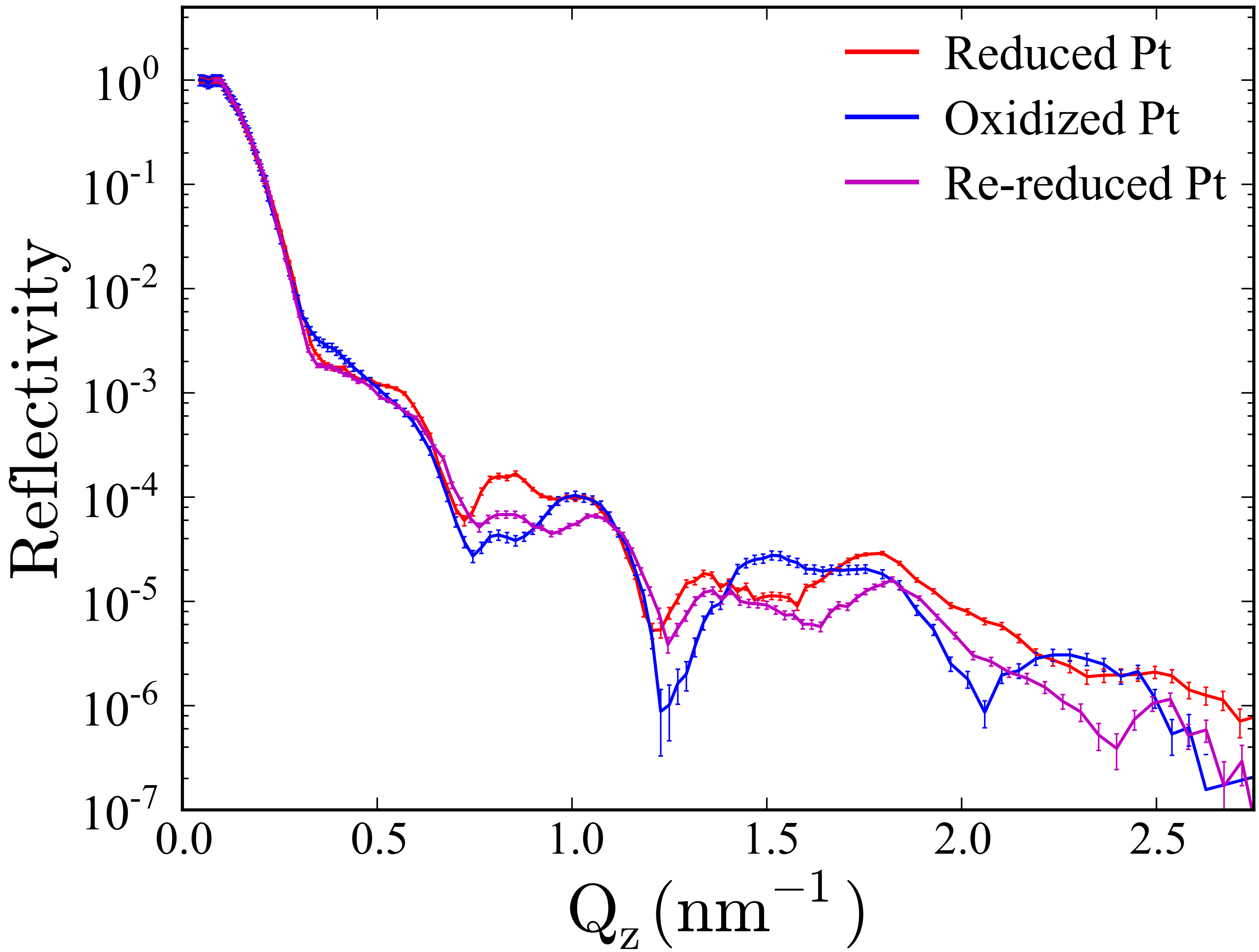
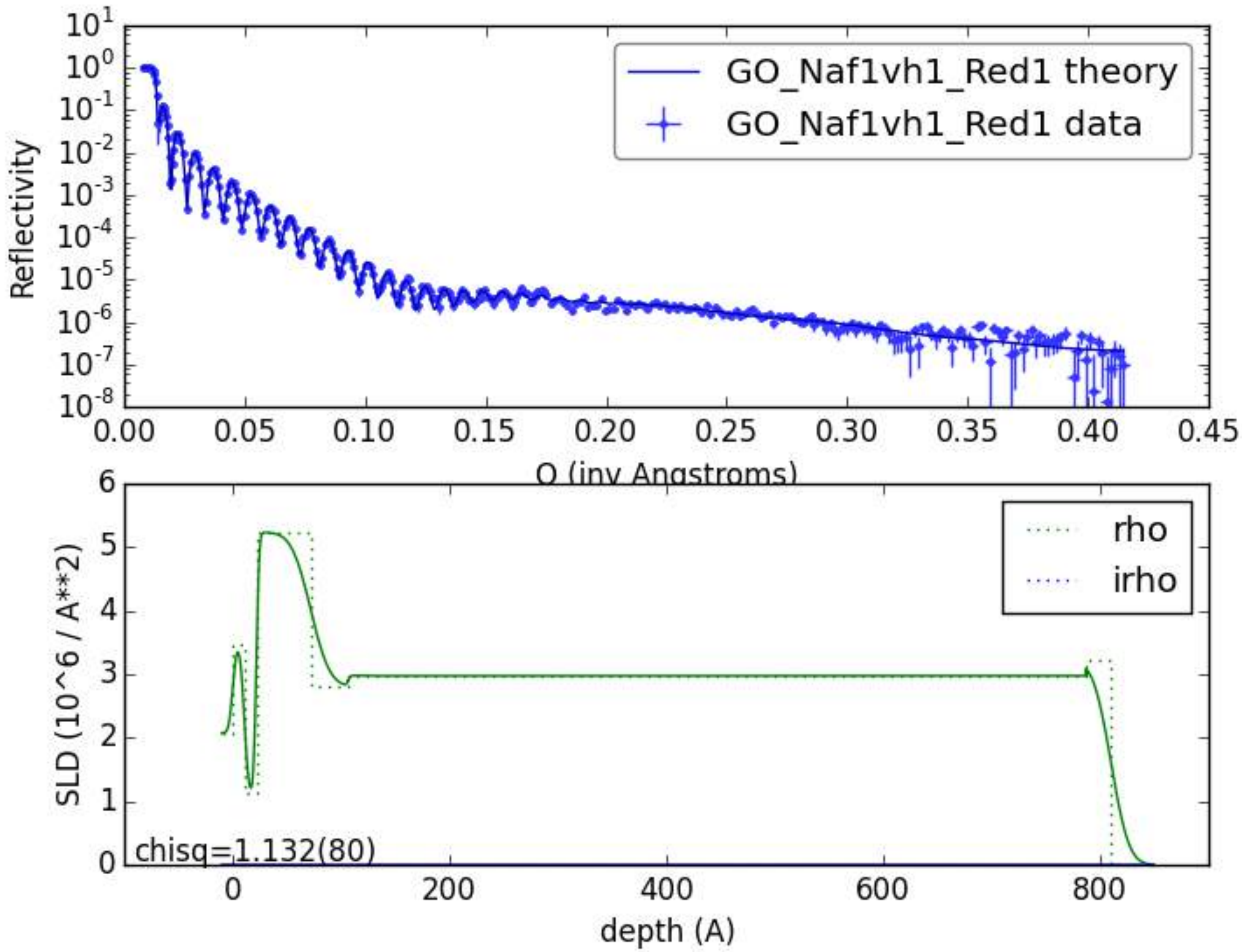
Nafion on Pt


Reduced Pt
Oxidized Pt
Re-reduced Pt
Reflectivity
10^{0}
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
0.0
0.5
1.0
1.5
2.0
2.5
$Q_z\,(nm^{-1})$

Nafion on Carbon



Next Steps:

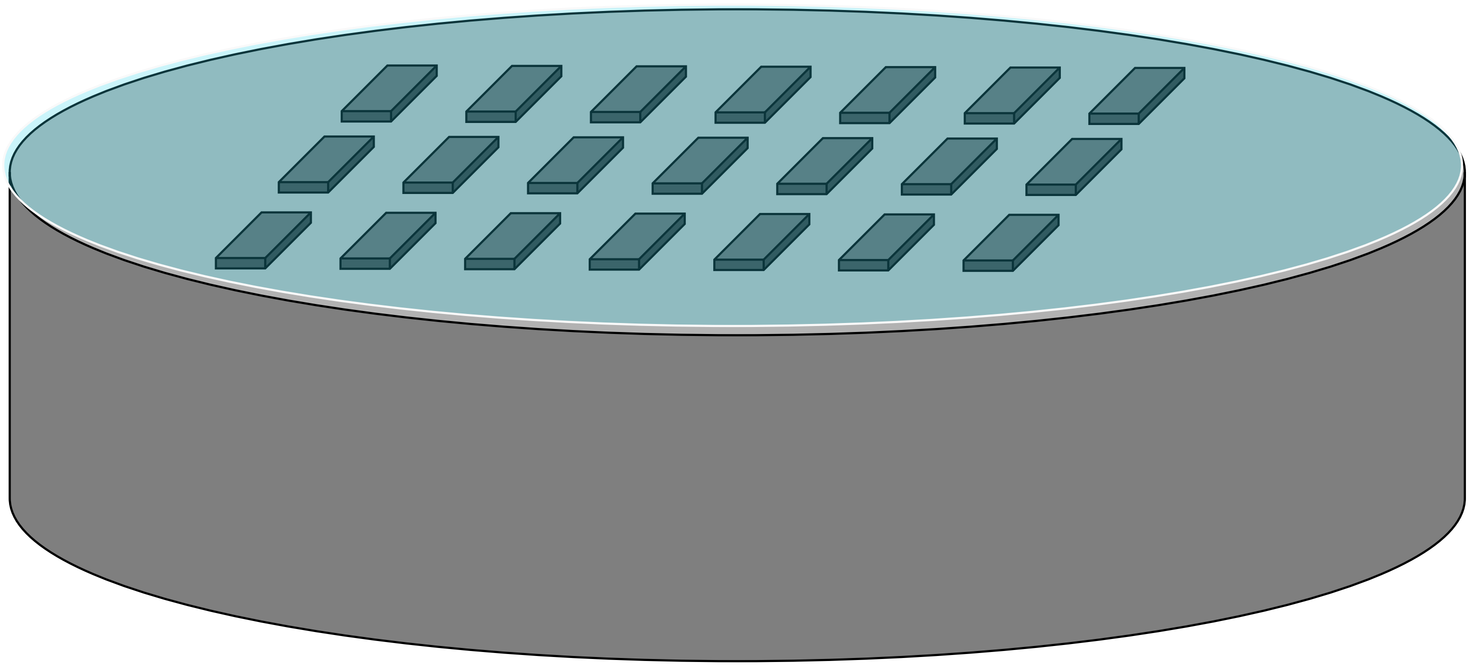
Depth profiling Improvements

- Realistic Materials
- "Realistic" Microstructures
- Non-equilibrated structures

Correlating multiple measurements

Multi-scale simulation Improvements

Off-specular NR on Patterned Pt



Next Steps:

<u>Depth profiling Improvements</u>

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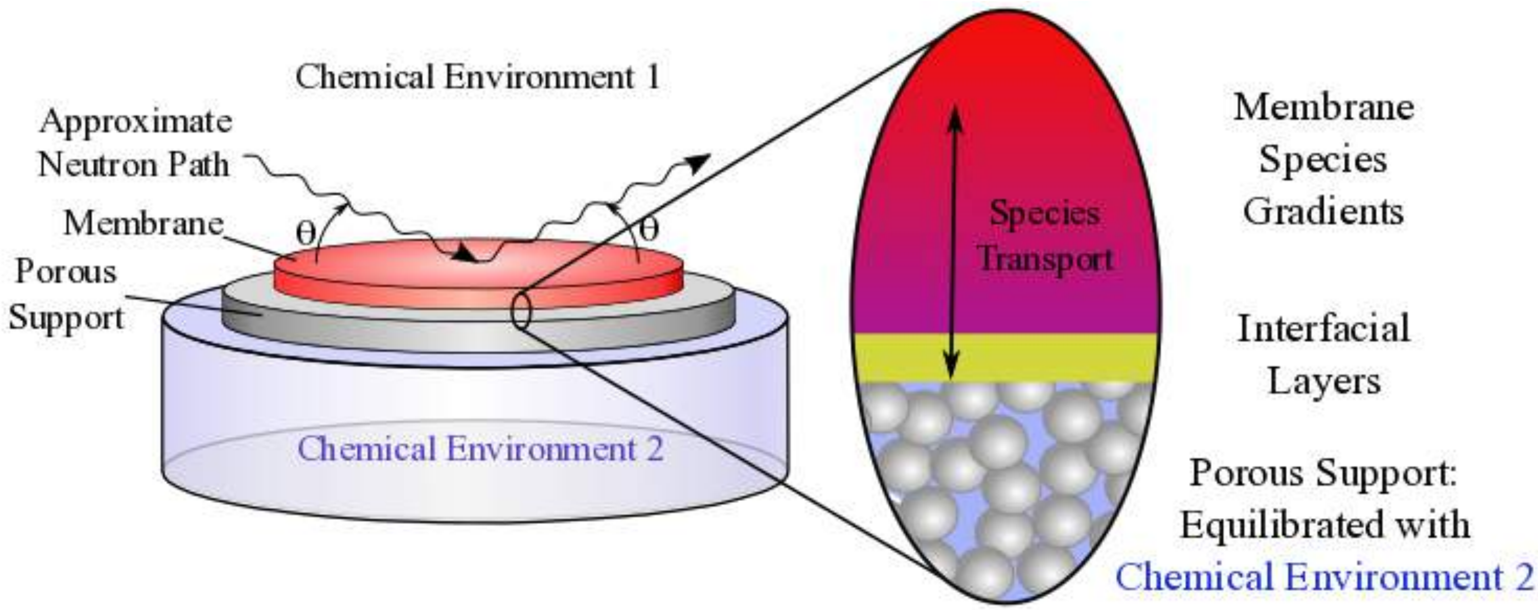
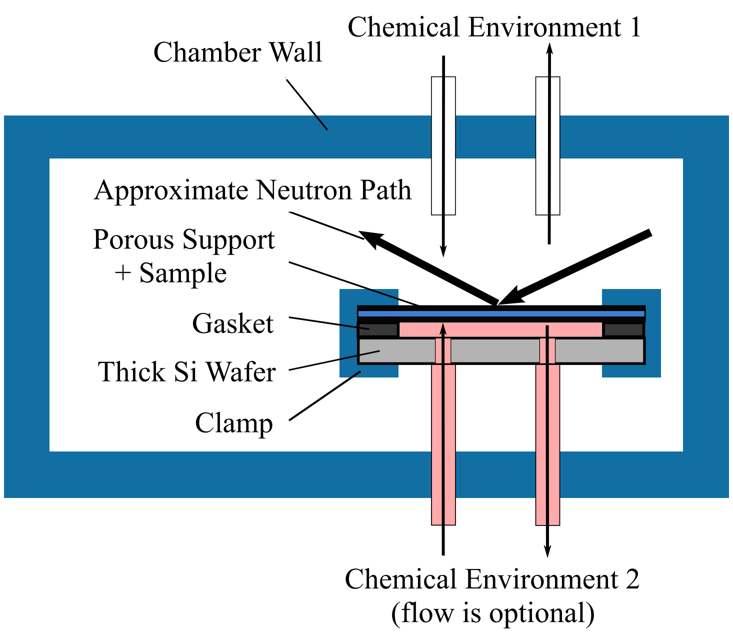
Multi-scale simulation Improvements

"Flow-Through NR"





Non-equilibrated samples with trans-membrane fluxes.

Species gradients
Interfacial layers and structures

Next Steps:

<u>Depth profiling Improvements</u>

- Realistic Materials

- “Realistic” Microstructures

- Non-equilibrated structures

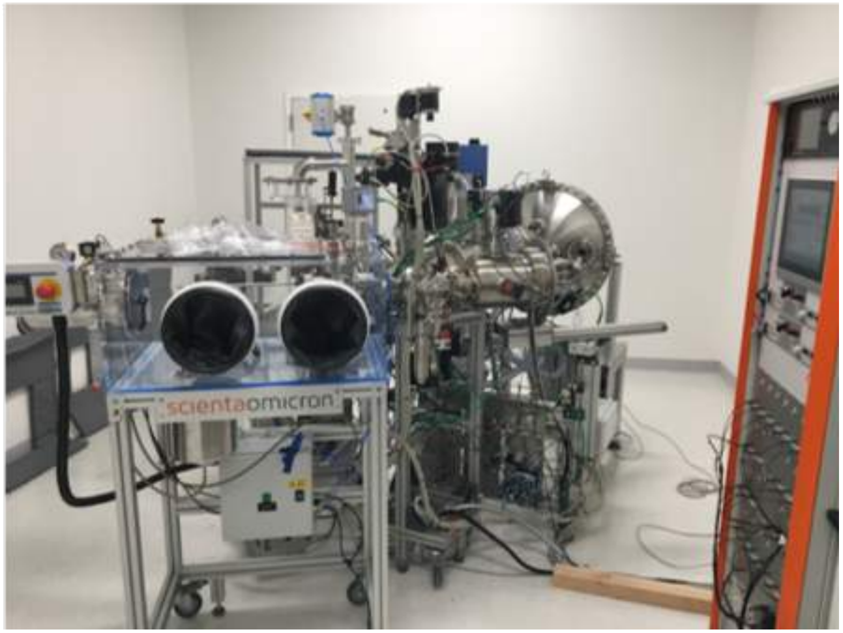
Correlating multiple measurements

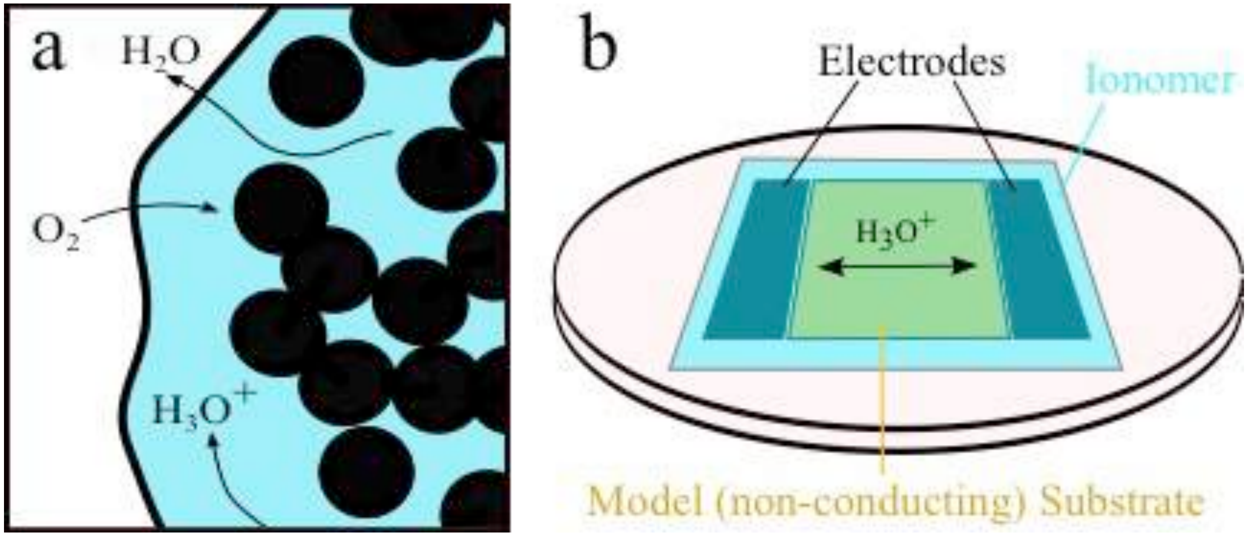
Multi-scale simulation Improvements

Rocky Mountain Environmental XPS

Colorado School of Mines

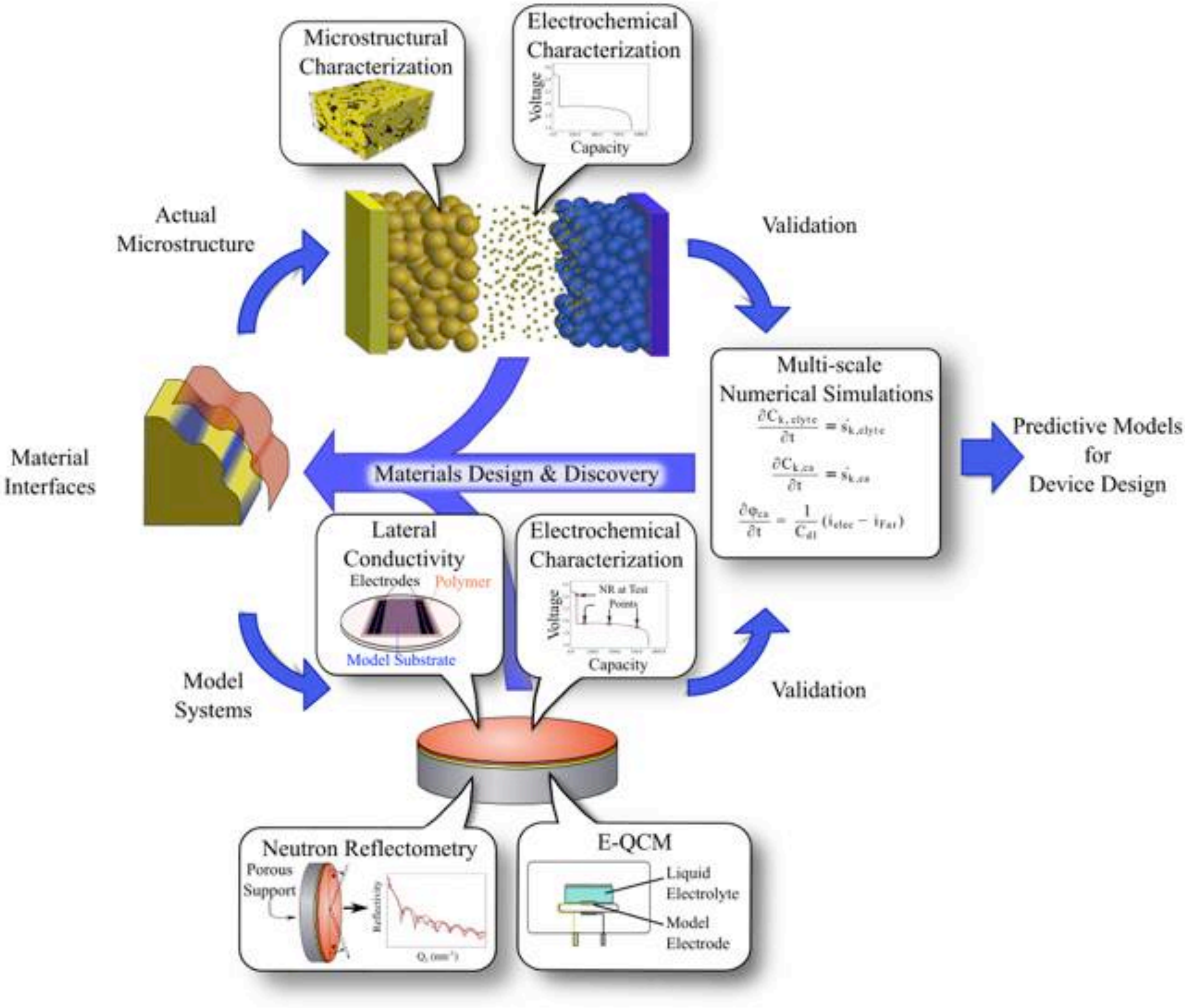
- Range of systems
  (model ←→ actual)
- Pressures up to 50 mbar
- Electric biasing (*non-equilibrium*)
- Temperature control
- ARPES – *moderate* depth profiling
- Lab-based system: suitable for examining polymer interfaces.





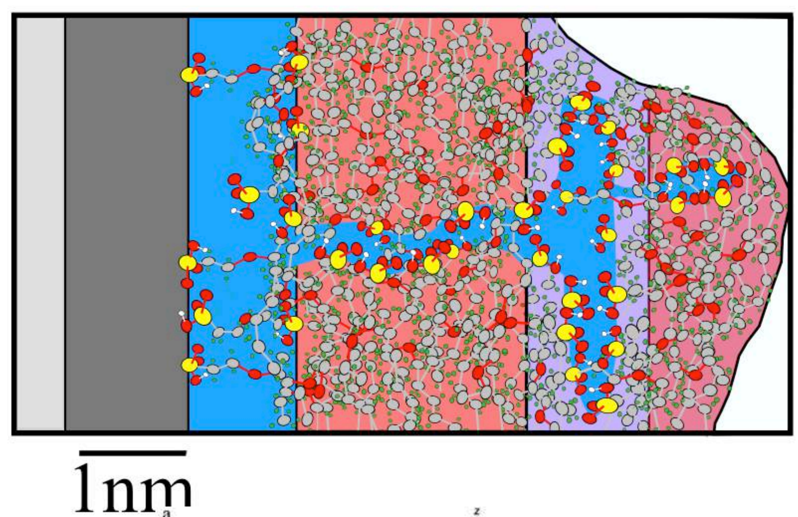
Operating as a user facility (soon)

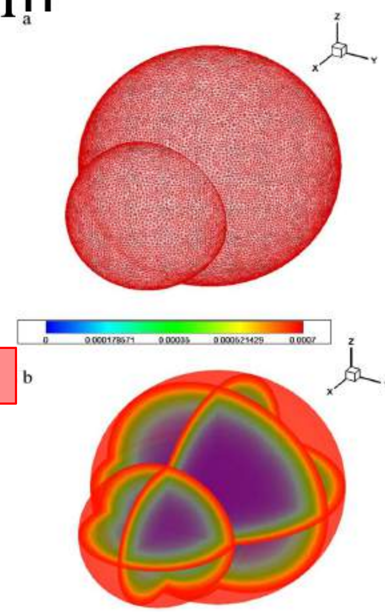
See Steven DeCaluwe or Svitlana Pylypenko

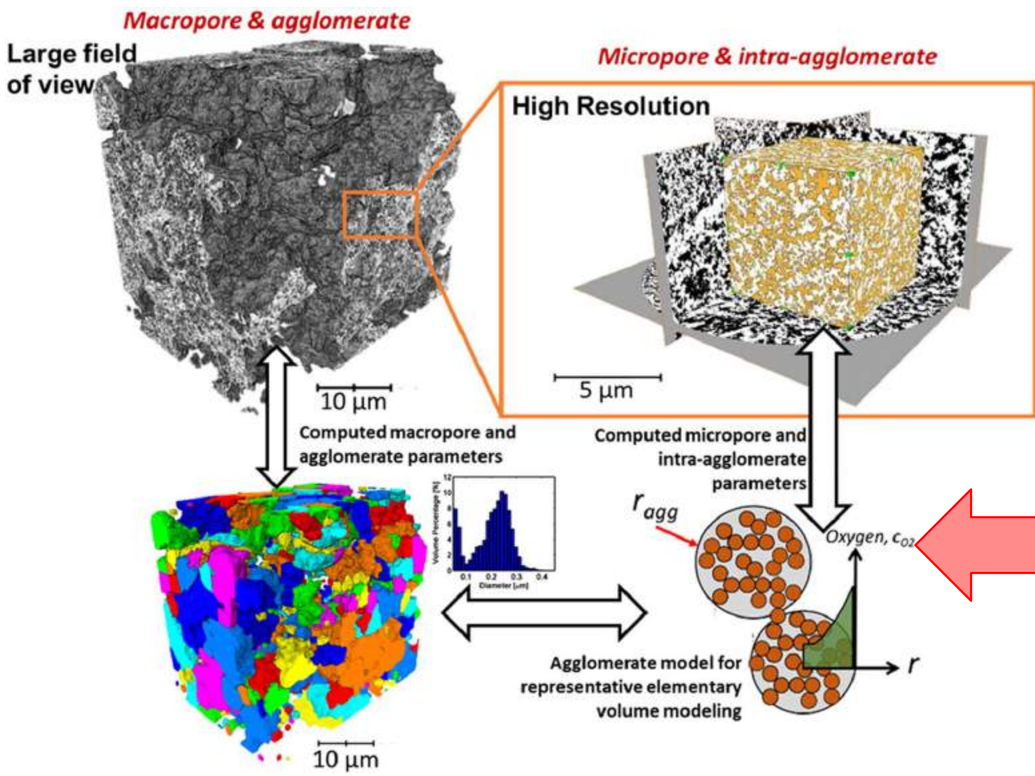


Microstructural Characterization
Electrochemical Characterization
Voltage
Capacity
Actual Microstructure
Validation
Multi-scale Numerical Simulations
$\frac{\partial C_{k,elyte}}{\partial t} = \dot{s}_{k,elyte}$
$\frac{\partial C_{k,ca}}{\partial t} = \dot{s}_{k,ca}$
$\frac{\partial \varphi_{ca}}{\partial t} = \frac{1}{C_{dl}}(i_{elec} - i_{Far})$
Predictive Models for Device Design
Material Interfaces
Materials Design & Discovery
Lateral Conductivity
Electrodes
Polymer
Model Substrate
Electrochemical Characterization
NR at Test Points
Voltage
Capacity
Model Systems
Validation
Neutron Reflectometry
Porous Support
Reflectivity
E-QCM
Liquid Electrolyte
Model Electrode

Multi-scale modeling







Babu, et al, *J. Electrochem Soc.*, 2017

Kamarajugadda & Mazumder, *J. Power Sources*, 2012

Thank You