Multiscale Modeling of Fuel-Cell Membranes

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Project ID #
FC 149

Overview

Timeline

- Project started FY14
  - September 2014
- Project end date*

Barriers

- C. Performance
  - Stack Water Management
  - System Thermal and Water Management
  - System Start-up and Shut-down Time and Energy/Transient Operation

Budget

- Total Project Funding: $600k
- Funding Received in FY15: $200k
- Planned Funding for FY16: $200k

Partners

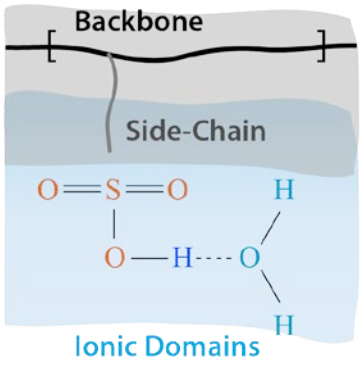
- Discussion with FC-PAD and other knowledgeable personnel
  - Material suppliers and those with unique diagnostic or modeling capabilities
- Interaction and work with LBNL, ASCR-funded computational researchers
- Initial work accomplished with McGill University

*Project continuation and direction determined annually by DOE

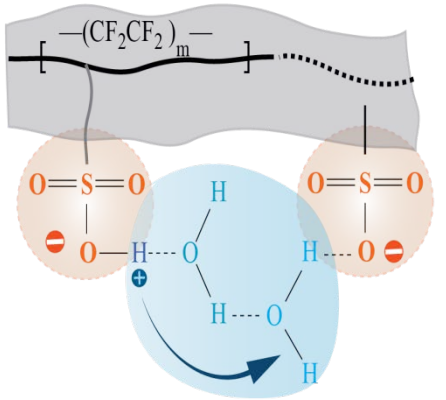
Relevance

- Despite broad use of ionomer membranes, such as Nafion, in energy research, *operando* behavior prediction is unavailable
- Understanding multi-ion transport in various ion-rich solvents would enable ionomer and system optimization
  - Optimize fuel-cell membrane performance
  - Understand contaminants and additives
  - Examine thin films
- Correlate nanostructural changes to macroscopic observables
  - Develop design rules by elucidating key ion-transport bottlenecks
    - Identify limits
- Provide behavior prediction information and mesoscale model of structure and transport phenomena in ion-conducting polymers
- Elevate advanced development of ionomers and enhance fundamental understanding of ion/ion and ion/ionomer interactions

Proton Conduction

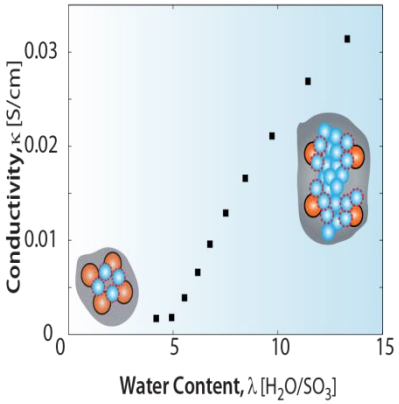


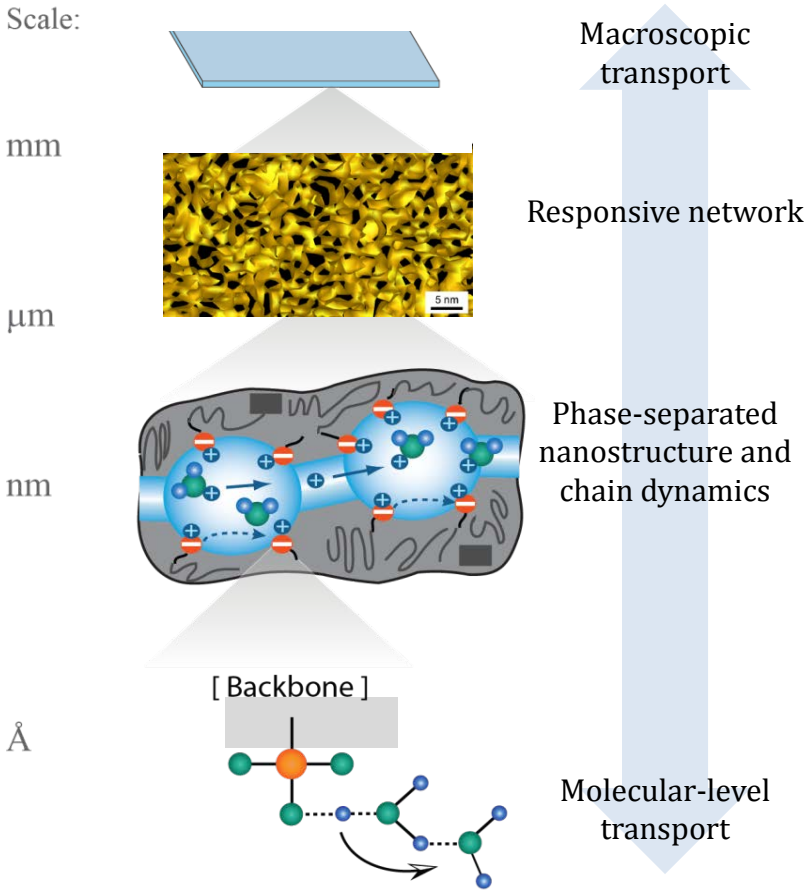
Solvation & Proton Transport



Water Hydration → Proton Hopping → Conductivity

Conductivity vs. Hydration





Phase-separated nanostructure is key to optimizing the membrane functionality in devices

F.I. Allen, L.R. Comolli, A. Kusoglu, M.A. Modestino, A.M. Minor, A.Z. Weber, **ACS Macro Letters,** 4, **2015**

Motivation

Macroscale Model

Macrohomogeneous concentrated-solution theory

Equilibrium uptake

Nanoscale Model

Atomistic simulations

Dilute-solution single-pore models

Double-layer models

Cannot capture smaller scale interactions

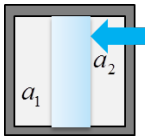
Limited chemistry predictions

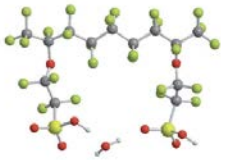
???

Very small domains and timescales

Cannot predict macroscopic observables

Hard to determine causality





Data

Nanostructure

Macro-scale (µm) transport

Equilibrium

Modeling Framework

Longer-range coupling of nanostructures for transport

Solutions impact on morphology

Highly non-ideal effects

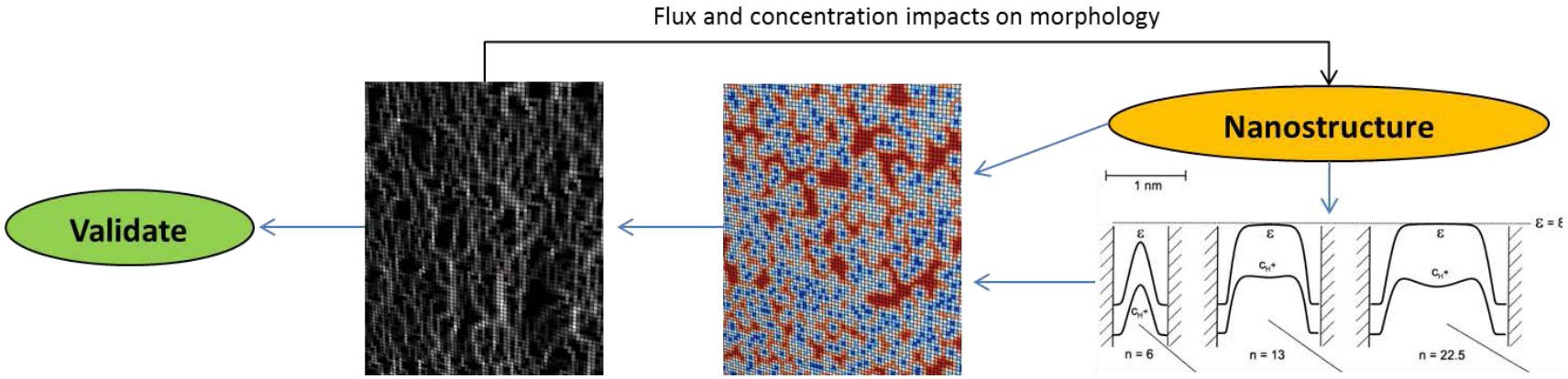
Detailed nanoscale phyiscs (mean-field theory)

Approach: Multiscale Model

Combine experimental and nano- and mesoscale physics models to bridge molecular understanding with macroscopic properties

A network model of mesoscale transport allows decoupling physics at multiple length-scales

Understanding is at a point where realistic physical models can be built



Calculate fluxes and effective properties

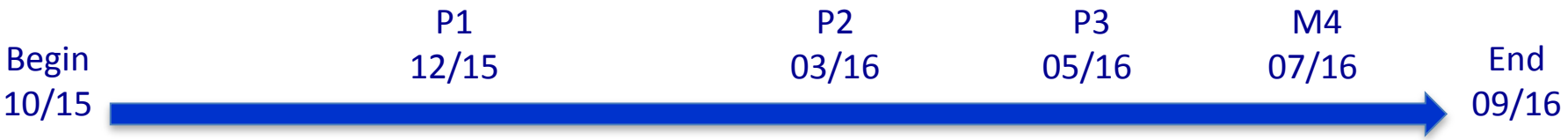
Upscale into network

Nanoscale physics

This approach moves beyond previous membrane modeling in that it focuses on how factors at each lengthscale impact macroscopic properties relevant for fuel-cell operation

Inclusion of nanoscale physics in the membrane domains provides insights into material design and mechanisms

FY16 Project Timeline



Major Milestones/Deliverables/Progress Measures

P1: Nanoscopic modeling based on sodium ion conductivity (*completed*)

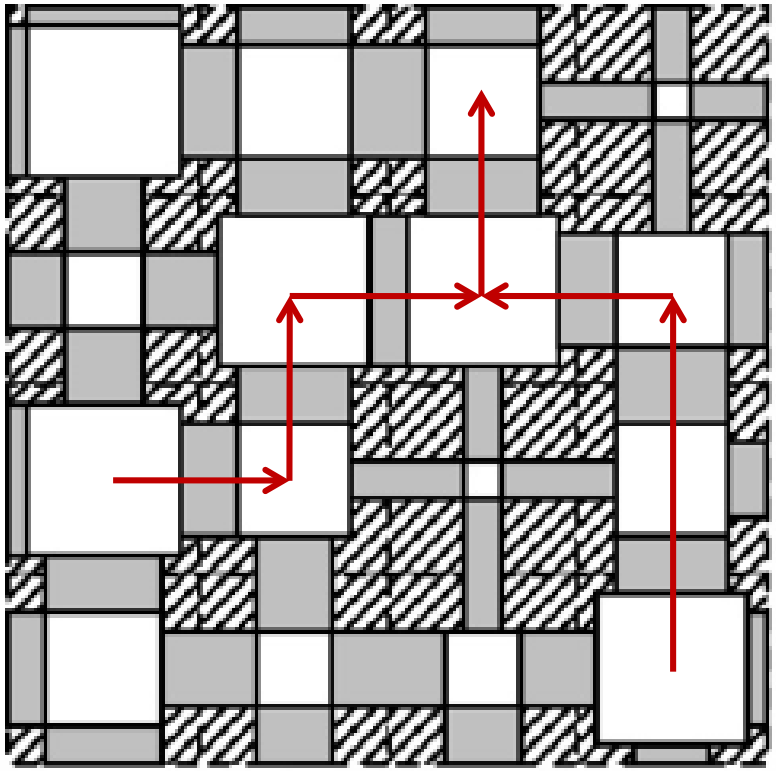
P2: Paper submitted for modeling results and methodology (*completed with paper submitted*)

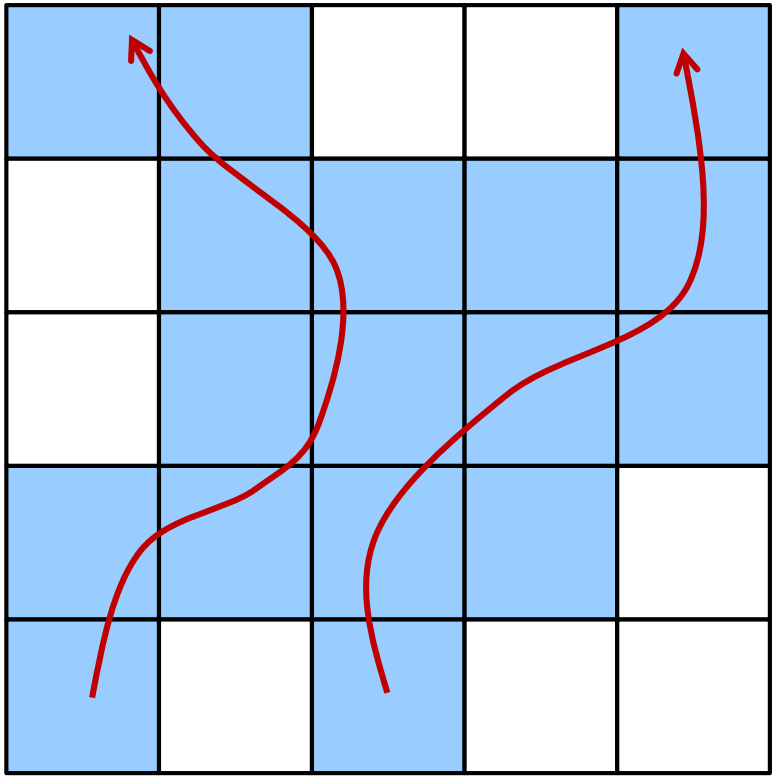
P3: Upscaling methodology and domain-scale solvent transport (*on track with different methodologies being examined*)

M1: Water flux through a Nafion membrane measured for 4 different RHs and 3 membrane thicknesses (*on track*)

Pore Network → Conductive Pathways

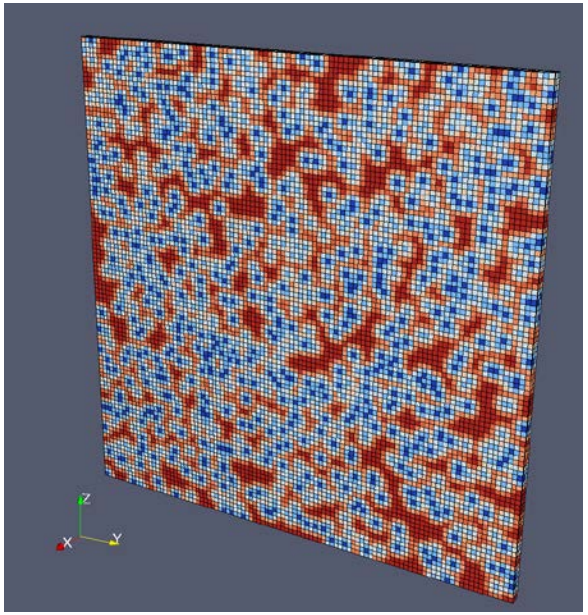
- Pore Network
  - Conductivity between pores is easily found in pore network
- PEM Network
  - Can we do conduction in the same fashion?



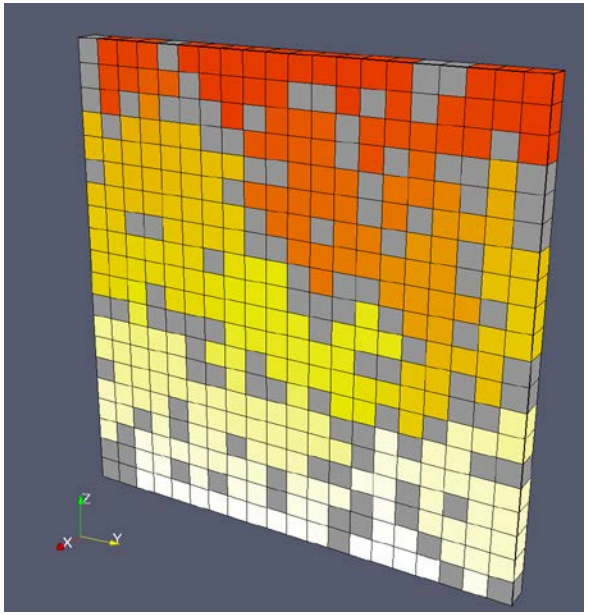


Conduction Network Modeling

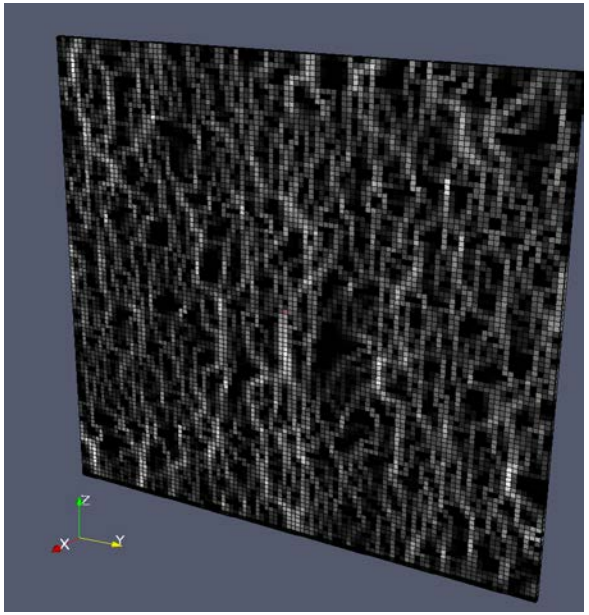
Conductivity



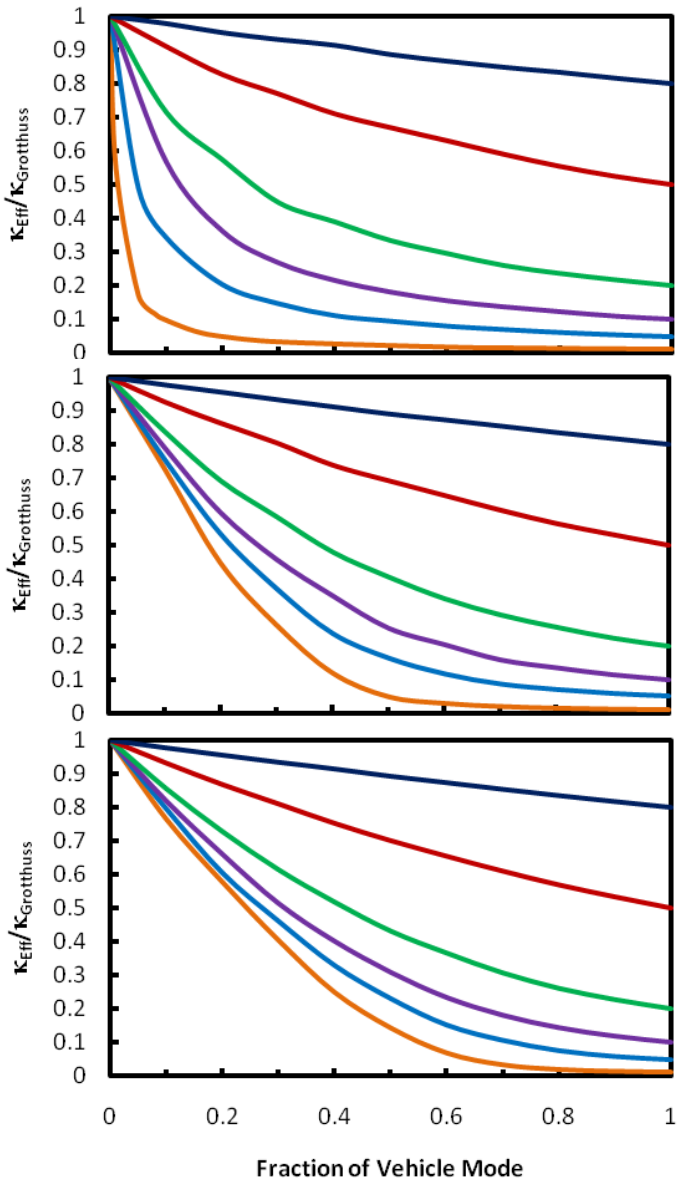
Potential

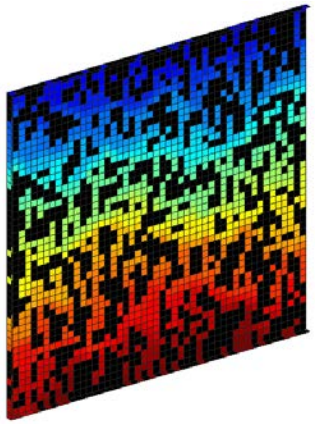


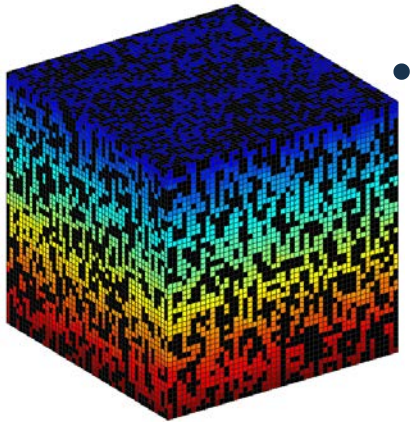
Current



Conduction Network Modeling





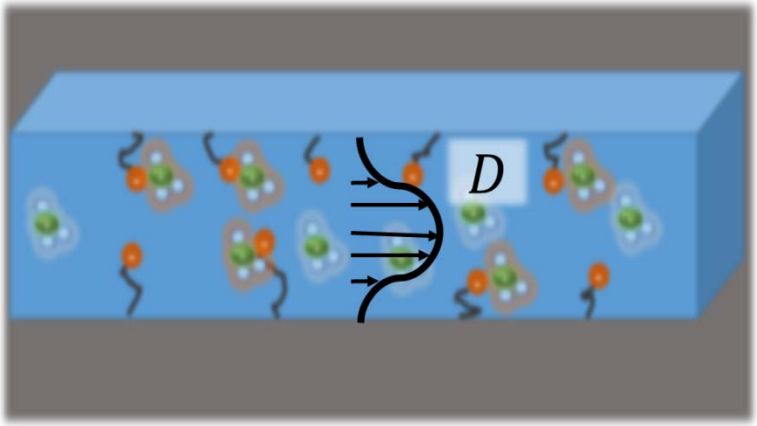


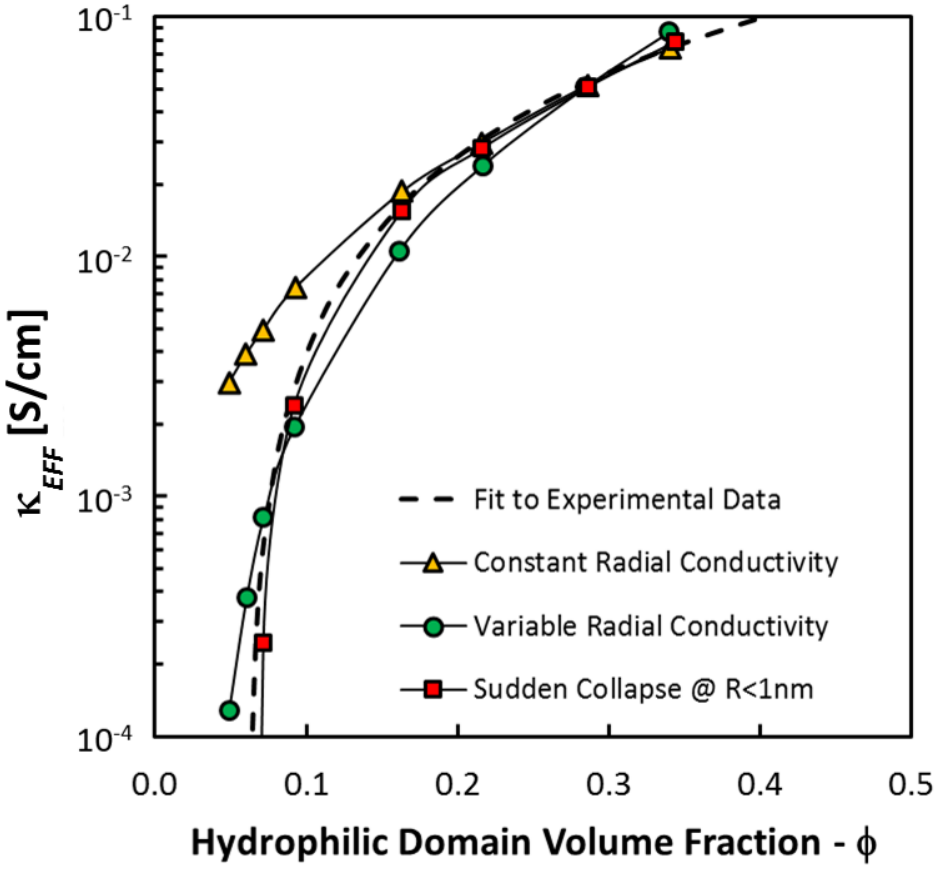
- 1D: Series Conduction
  - Only a few vehicle sites greatly reduce overall conductivity
  - Same as single pore
- 2D: Parallel Conduction
  - The ability to bypass vehicle sites enhances ion conductivity but percolation limitations remain
- 3D: Parallel Conduction
  - Additional paths around vehicle sites improves conductivity further and percolation threshold is increased over 2D

Network Simulation

- Use transport properties as a function of domain size
  - Simulations agree qualitatively with data

$$\sigma_{pore}(R) = \int_0^R \frac{F^2}{RT} c(r) D(r) dr$$



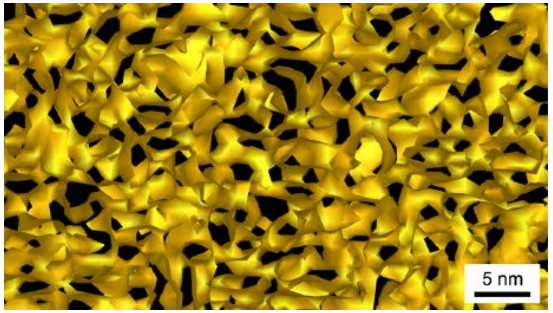


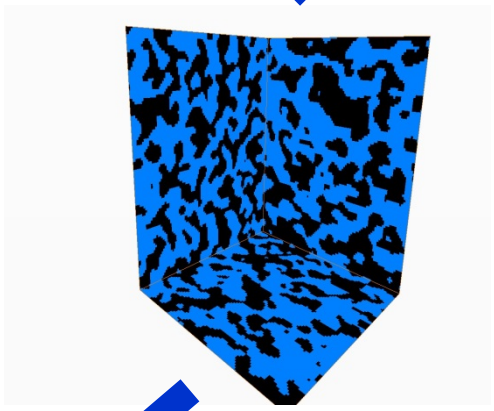
*Jeffrey T. Gostick and Adam Z. Weber, Electrochimica Acta, **179**, 137-145 (2015).*

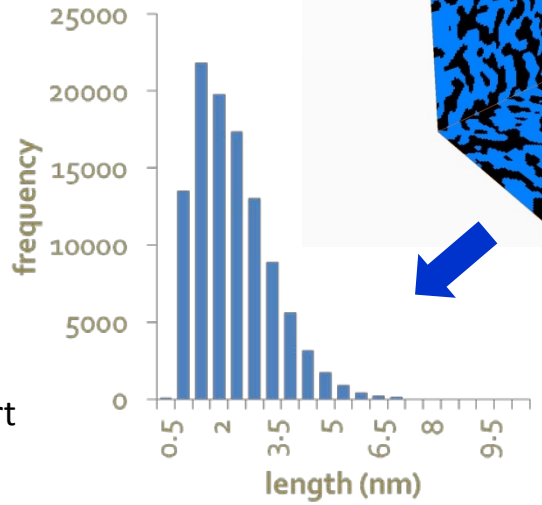
Nafion Network

- Network of conductive domains was extracted from real-space imaging of membrane
  - ↳ Model methodology used to simulate cation transport across the network

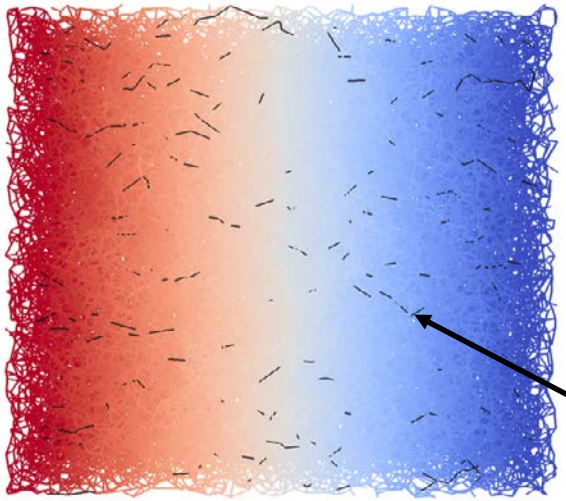
- Transport across the network is heterogeneous with a few pathways dominating transport







Network Simulation



Key transport pathways

Distance Across Membrane, Increasing Potential

Nanoscale Phenomena

- Nanoscale mean-field model used to model nanoscale physics
- Balance of energies specifies cation location inside pore

$$\mu_+ = \mu_+^0 + k_b T \ln\left(\rho_+(\bar{r})\right) + \mu_{fs}(\bar{r}) + z_+ e\Phi(\bar{r}) + \mu_{solv}(\bar{r})$$

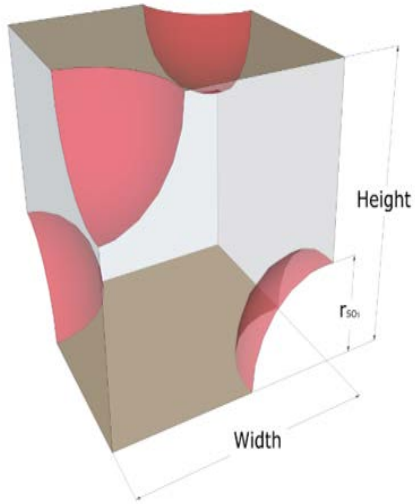
Concentration | Finite size | Electrostatic | Solvation

Coupled to

$$\nabla \cdot \varepsilon(\bar{r})\nabla\Phi(\bar{r}) = -\frac{e}{\varepsilon_0}\sum_i z_i c_i(\bar{r})$$

- Dielectric constant varies with field and confinement
- Solvation term due to variation in dielectric saturation
- Finite size term due to hard sphere interactions between catio
- Transport

$$\boldsymbol{J}_+ = \boldsymbol{u}_+ c_+ \boldsymbol{\nabla}\boldsymbol{\mu}_+$$



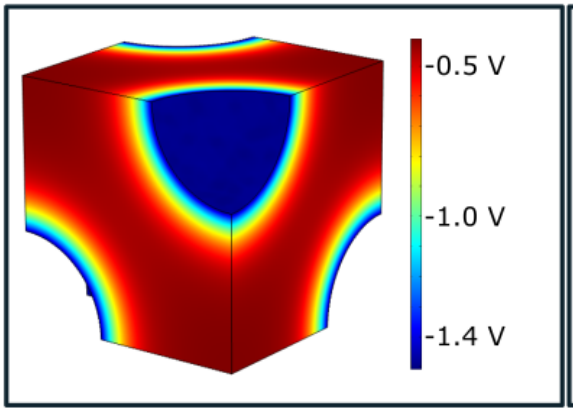
Nanoscale unit cell

Nanoscale Energies

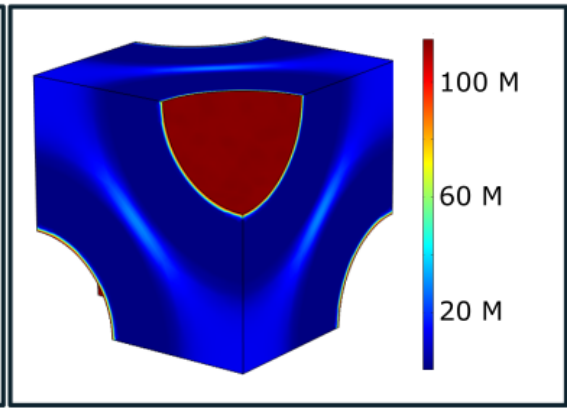
- Balance of energies specifies cation location inside pore

$$\mu_+ = \mu_+^0 + \underbrace{k_b T \ln\left(\rho_+(\bar{r})\right)}_{\text{Concentration}} + \underbrace{\mu_{fs}(\bar{r})}_{\text{Finite size}} + \underbrace{z_+ e \Phi(\bar{r})}_{\text{Electrostatic}} + \underbrace{\mu_{solv}(\bar{r})}_{\text{Solvation}}$$

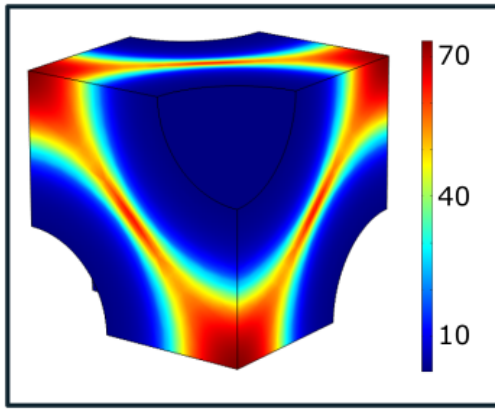
Ionic potential



Cation probability density



Dielectric



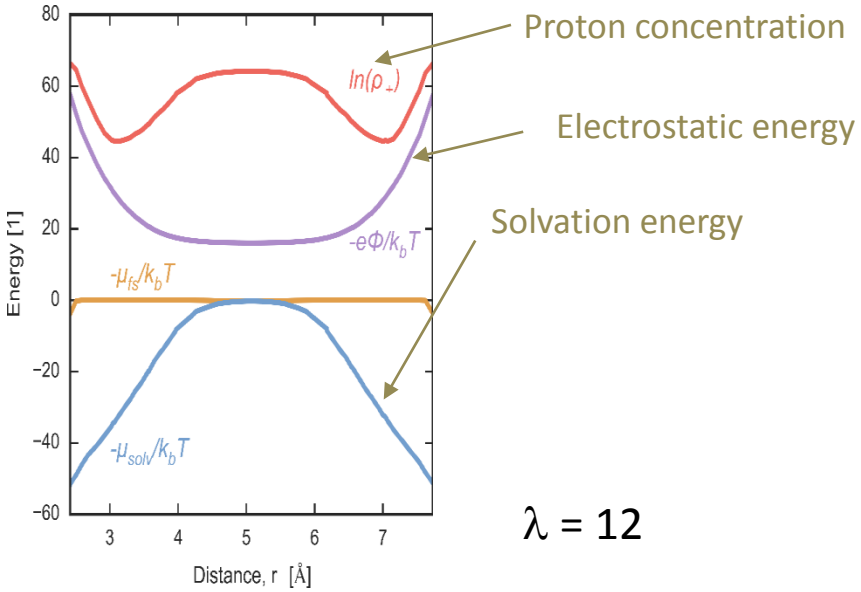
$\lambda = 9$

Nanoscale Energies

- Balance of energies specifies cation location inside pore

$$\mu_+ = \mu_+^0 + \underbrace{k_b T \ln\left(\rho_+(\bar{r})\right)}_{\text{Concentration}} + \underbrace{\mu_{fs}(\bar{r})}_{\text{Finite size}} + \underbrace{z_+ e\Phi(\bar{r})}_{\text{Electrostatic}} + \underbrace{\mu_{solv}(\bar{r})}_{\text{Solvation}}$$

Proton interaction energies between sulfonates

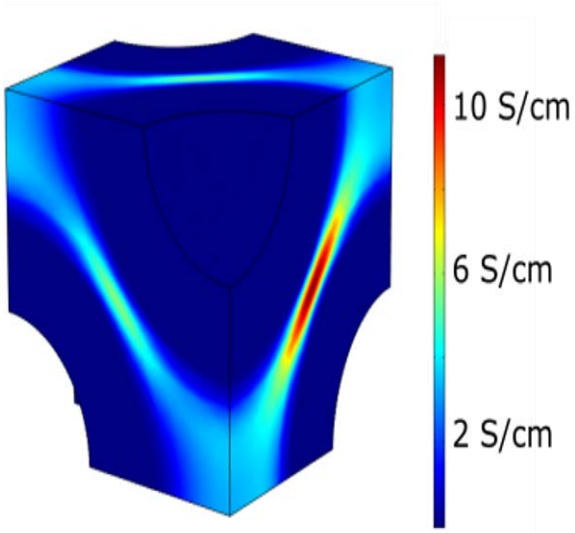


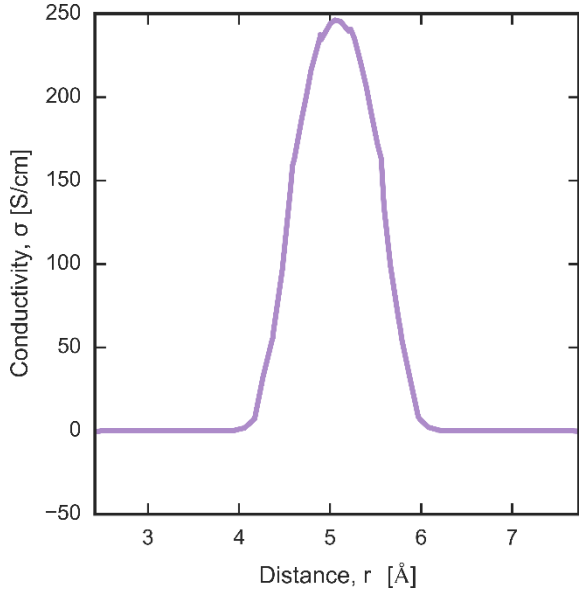
λ = 12

- **Solvation and electrostatic energies dominate and form competition**
  - **Only secondary solvation shell cations are truly mobile**

Nanoscale Conductivity

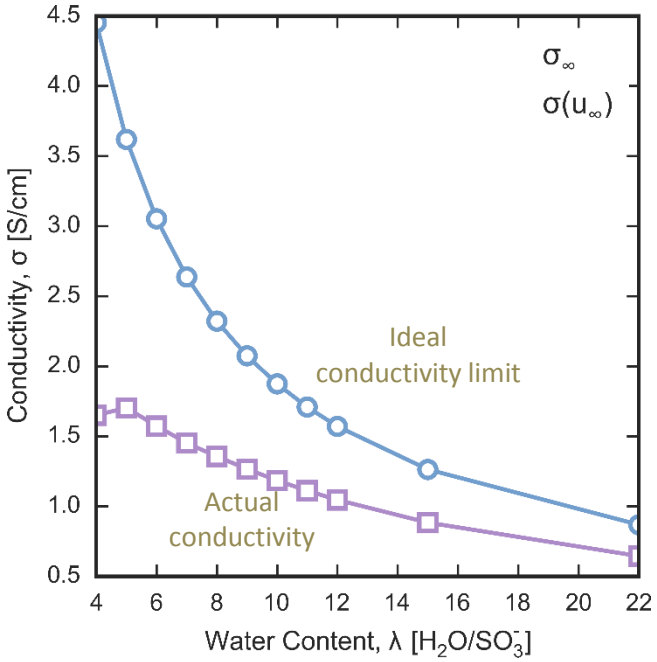
- Balance between electrostatic and solvation energies dictate proton behavior in the domain
- Conductivity occurs by movement of free, hydrated protons in center of domain
- Bound protons do not contribute to conduction
- These insight suggest avenues to increase pore-level conductivity

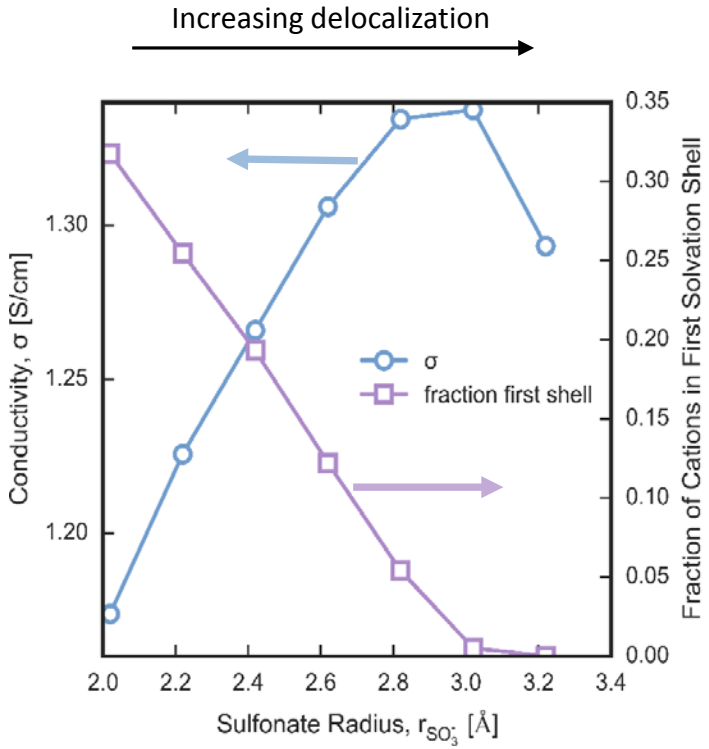




Nanoscale Resistances

- Electrostatic interactions reduce domain-scale conductivity by trapping protons bound to sulfonate groups
- Varying sidechain chemistry to delocalize negative charge reduces cation binding
- These insights show potential material design avenue to improved pore-level conductivity





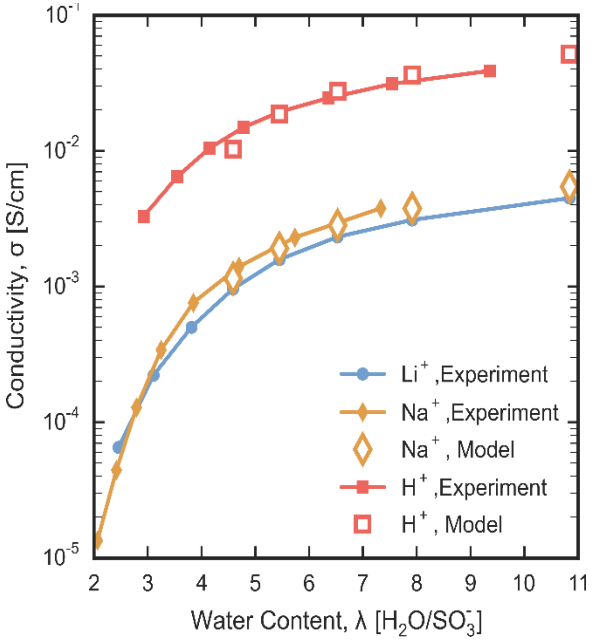
Macroscale Validation

- Upscaling pore-scale model effectively modeled macroscale conductivity from experiments

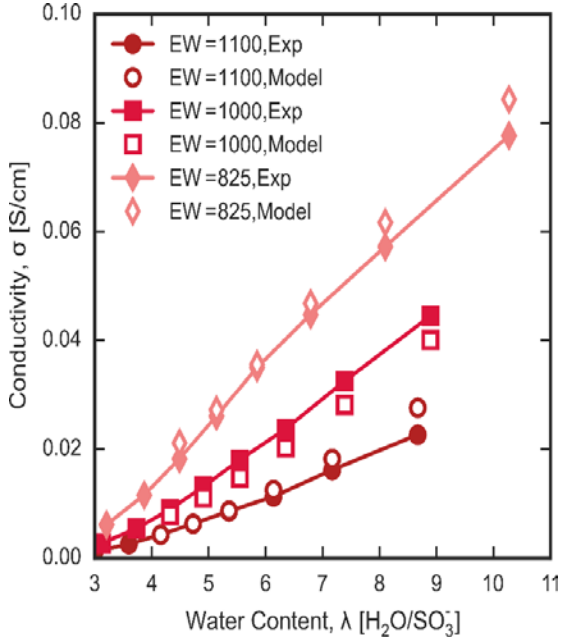
$$\tau = e^{k\left(\frac{1}{\phi}-1\right)}$$

  - Where k is a fitting parameter
    - Fit once to Li+ for 1100 EW membrane

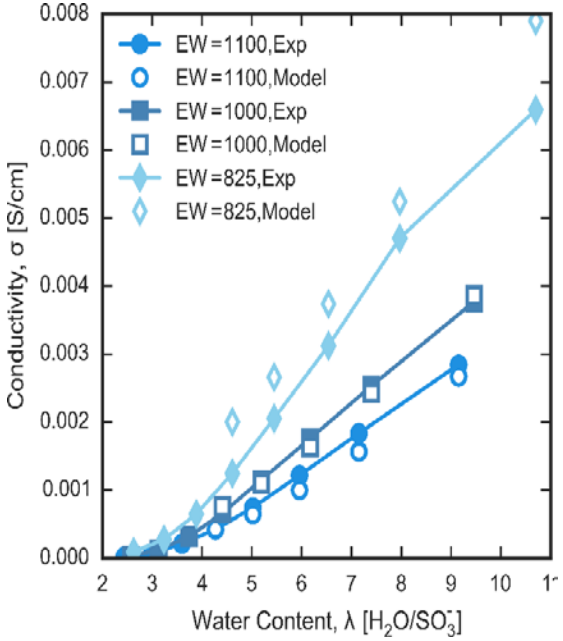
Ionic form for 1100 g/mol



Proton-form

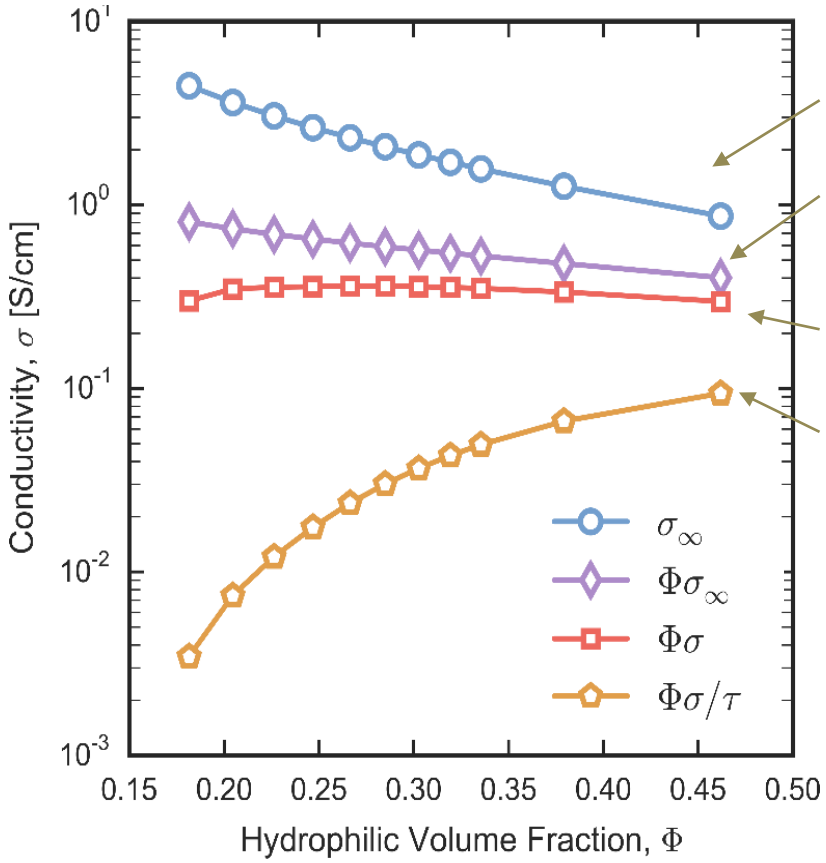


Lithium-form



Macroscale Resistances

- Mesoscale effects such as the network tortuosity and the hydrophilic volume fraction are key sources of resistance for macroscale conductivity
- Identified areas of how to improve membrane conductivity through material design and maximum expected values



Ideal conductivity limit

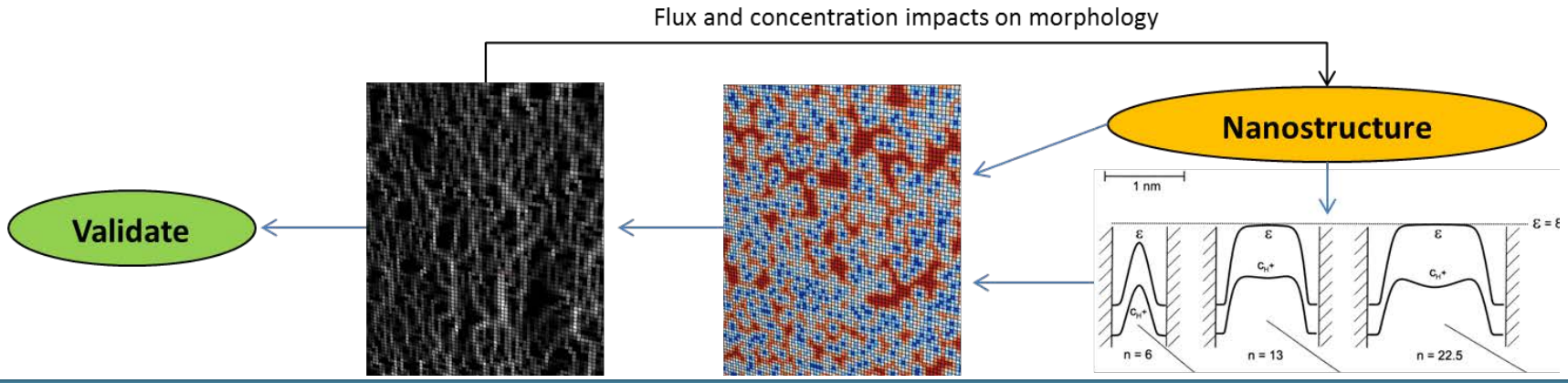
Including hydrophilic volume fraction

Including domain-scale resistances

Including tortuosity

Future Work

- Utilize measured network
  - Predict its changes for domain sizes with water content and gradient
- Expand model to include solvent uptake and transport
  - Changing of the domains with water content and water-content gradients
    - Good uptake model with mechanical/chemical forces
- Make the model dynamic
  - Feedback between morphology, concentration, and flux
- Measure solvent transport for validation
- Couple solvent and proton transport using concentrated solution theory
  - Expand model to include transport of impurities and contaminates



Summary

- Relevance/Objective:
  - Help optimize and explore design criteria for transport in ion-conducting membranes across length scales in various environments
- Approach/Collaborations:
  - Use novel multiscale modeling methodology to examine and detail controlling interactions for ion and solvent transport
- Technical Accomplishments:
  - Modeled transport within the ionomer mesoscale network using a resistor-network approach
    - Informed from experiments
    - Quantified impact of different conduction zones in different geometries
  - Developed energy-balance framework for the electrochemical potential of cations based on atomistic simulations
    - Isolated individual energetic components

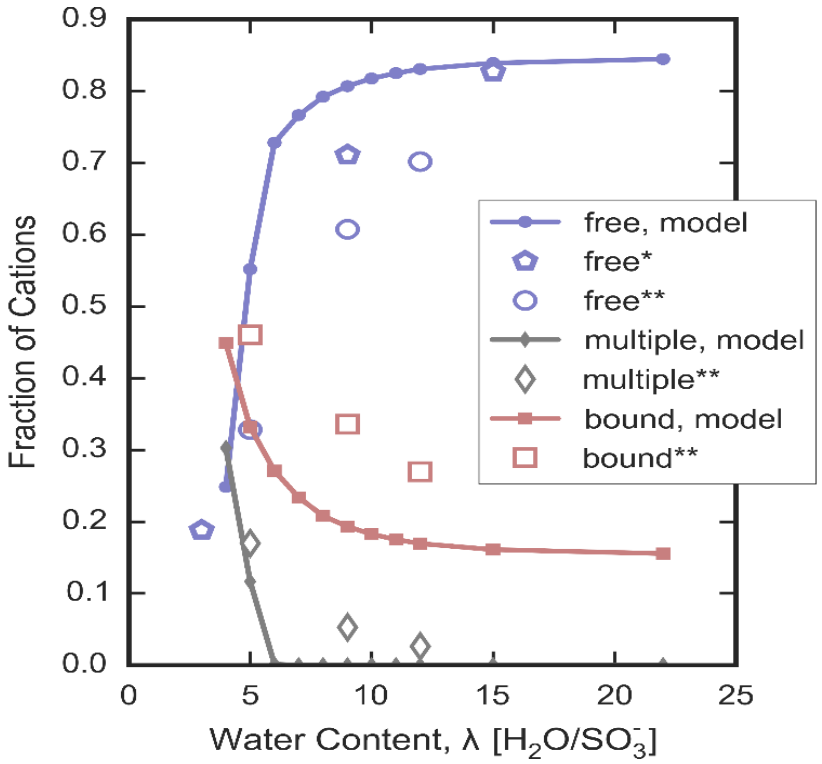
      Solvation and electrostatic interplay

      Cations do not share solvation shells between two sulfonate groups
    - Increasing negative charge delocalization on the side chain increases conductivity because of increased cation dissociation
  - Initially validated model using experimental measurements *and* atomistic simulations
    - Proton transport is very rapid and explained by bulk-like transport at the domain-scale
    - Tortuosity has large impact on conductivity
- Future Work:
  - Enhance model by examining solvent-cation and multi-cation interactions and integrating a sorption model
  - Develop design guidelines for membrane developers and optimize membrane transport and durability

Technical Back-Up Slides

Nanodomain Validation

- **Model shows good agreement with molecular dynamics simulations without fitting parameters**



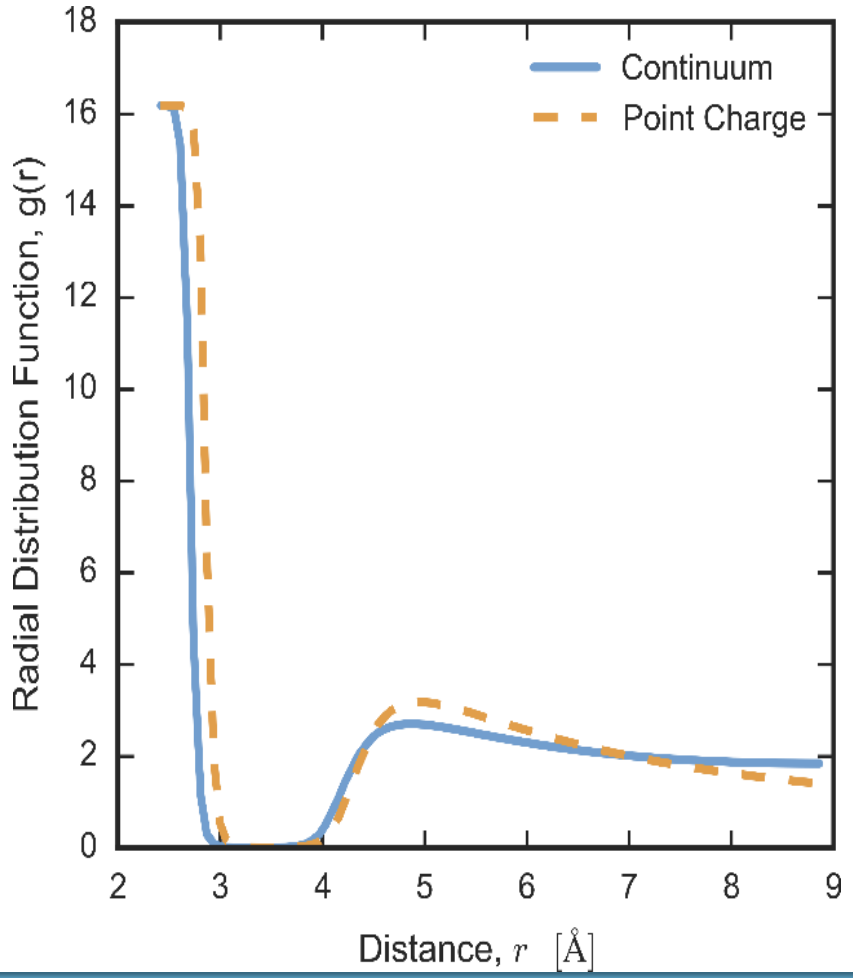
	H^+	Li^+	Na^+
r_+ [Å]*	1.38	0.780	1.02
r_{hyd}^{∞} [Å]**	3.8	4.2	4.0
ΔG_{vac}^{b} [kJ mol^{-1}]***	-401	-510	-411
ΔG_{vac}^{s} [kJ mol^{-1}]‡	-227	-387	-296
ς_{∞} [S cm^2 mol^{-1}]†	349.8	38.6	50.1

*Ab initio MD from Devanthan et al. 2013

** MD from Savage et al. 2014

Test of Mean Field Approximation

- **Comparison of the mean-field approximation with the exact point-charge case showed close agreement for a simplified system of two cations in solution**



Energy Terms and Dielectric Saturation

- **Solvation chemical potential based on a modified Born solvation cycle**

$$\mu_{solv} = A\left(\frac{1}{\varepsilon(\bar{r})} - \frac{1}{\varepsilon_b}\right)$$

- **Finite size effects based on a lattice gas argument**

$$\mu_{fs} = \ln\left(1 - a(\bar{r})^3 \sum_i c_i(\bar{r})\right)$$

- **Dielectric saturation from Booth's Equation with Langevin dipoles**

$$\varepsilon(\bar{r}) = \eta^2 + \frac{3(\varepsilon_{base}(\bar{r}) - \eta^2)}{\beta|\nabla\Phi(\bar{r})|} L(\beta|\nabla\Phi(\bar{r})|)$$

↳ where ε_{base} accounts for confinement effects

Remaining Challenges and Barriers

- Membrane performance in fuel-cell linked to both solvent and proton transport
  - Solvent transport impacts proton transport through electroosmosis
- Solvent content impacts polymer morphology
- To develop avenues to improve overall membrane performance, solvent transport and uptake must be also considered for these reasons
  - Need dynamic model with integrated feedback between concentrations and morphology