Multi-scale Transport , Dynamics, and Morphology in Materials

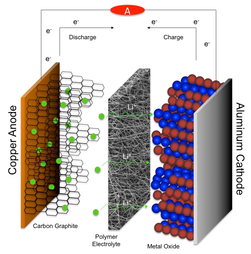
Lou Madsen Group

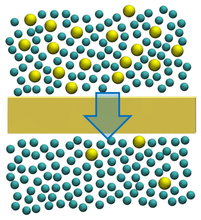
Drew Korovich, Curt Zanelotti, Rui Zhang, Deyang Yu, Shravan Uppala, Nick Pietra, Syeda Anam Bukhari, Alexis McCarthy

DEPARTMENT OF Chemistry VIRGINIA TECH

Macromolecules Innovation Institute — At the intersection of science, engineering, and society

Introduction



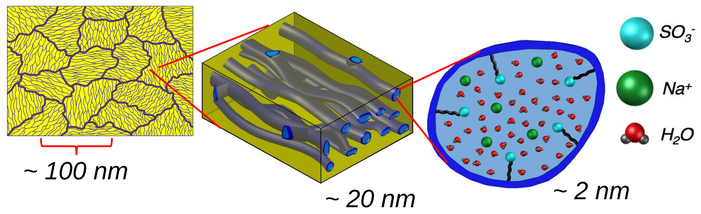


● Water ● Solute (salt, organic molecules, etc.)

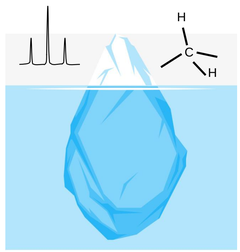
Reverse osmosis membrane

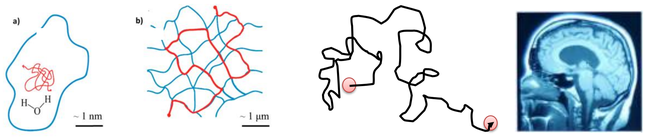
- We measure and build ion conducting and nanostructured materials, specifically involving multi-scale structure and morphology.
- Impacts: Clean energy, water, and nanomedicine applications including batteries, fuel cells, and drug delivery. Determining fundamental mechanisms of ion and water transport.
- Who are we? Physical, analytical, and polymer chemists, materials scientists.

Multi-Modal NMR

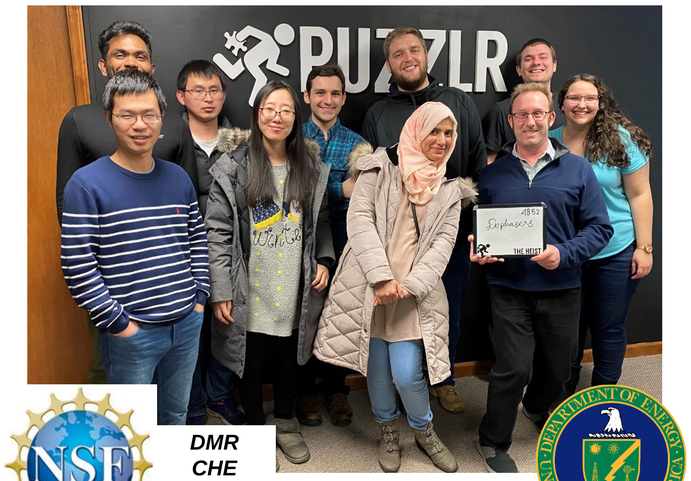


- ***NMR spectroscopy:*** *Molecular structure, internal dynamics, associations, alignment → Å to nm, ps to days*
- ***NMR diffusometry:*** *Species-specific and phase-specific transport, confined motion → 10s of nm to 10s of μm, ms to s*
- ***MicroMRI:*** *Spatial resolution of molecular structure, dynamics, transport → ≥ 10 μm (devices, tissue…), t-resolved*





Group & Funding Sources

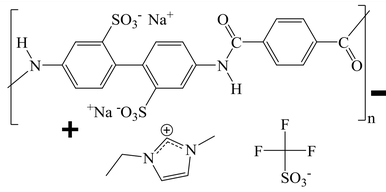


NSF DMR CHE CBET

DEPARTMENT OF ENERGY — UNITED STATES OF AMERICA

Molecular Ionic Composites (MICs)

Combining a Kevlar-like polymer with ionic liquids to enable safer and higher density batteries



Kevlar-like polymer forms double helix! Nature Comm (2019)

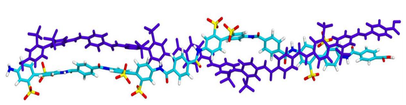
Problem:

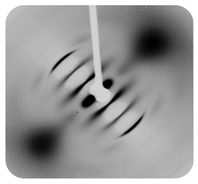
Commercial organic electrolytes
→ safety concerns including flammability, leaking, volatility
→ limited battery energy density

Solution:

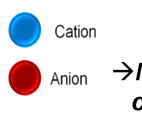
Composite electrolyte of PBDT and ionic liquid ***features***:

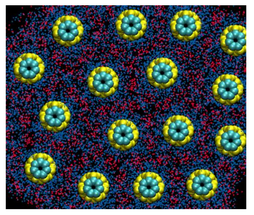
- High ionic conductivity (~1 mS*cm^{-1})
  - Tunable modulus (0.03 – 3 GPa)
  - Thermally stable (up to 300° C)
  - Electrochemical window to 6 V
  - Long cycling Li-metal batteries





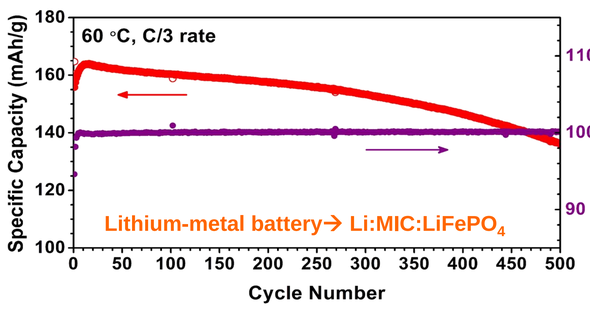
XRD of PBDT aqueous solution

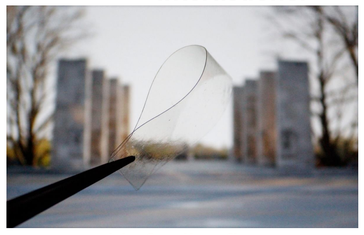




→***MICs held together by collective electrostatic interactions!***

Collaborations with Dingemans (UNC), Colby (PSU), Forsyth (Deakin – Australia), Qiao, Moore, and Lin (VT)



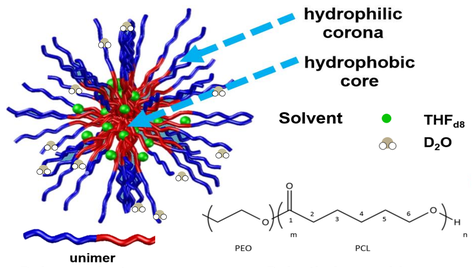


Thin flexible films

Macromolecules (2020) *+5 in prep* ***Langmuir (2017)*** ***Advanced Materials (2016)*** ***ACS Appl. Mater. Interfaces (2019)*** ***J Membrane Sci (2015)*** ***Macromolecules (2014)***

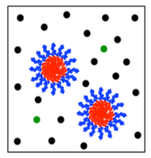
→ *Able to load MICs with Li^+, Na^+, Mg^{2+}, etc.*

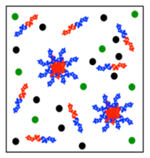
Block Copolymer Micelles



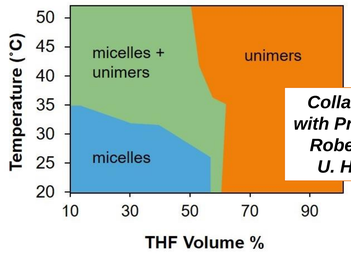
Polycaprolactone (PCL): ***micelles***

Polyethylene oxide (PEO) ***coexistence region***





10 – 50 vol% THF_{d8} *60 vol% THF_{d8}*



Collaboration with Prof. Megan Robertson at U. Houston

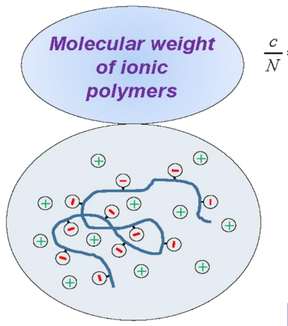
Macromolecules (2017 x2, 2018, 3 in prep)

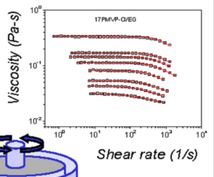
Polyelectrolyte Molecular Weight Determination

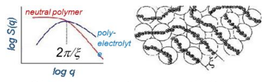
Molecular weight of ionic polymers

$$\frac{c}{N} = \frac{G}{kT} \cong \frac{1}{\eta_{sp}\xi^3} \cong \sqrt{\frac{\eta_{sp}}{\pi\xi^3 kT}} \cong \frac{\eta_s D}{\xi^2 kT}$$

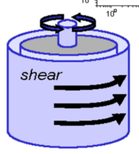
Rouse model and scaling predictions and development



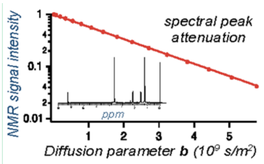


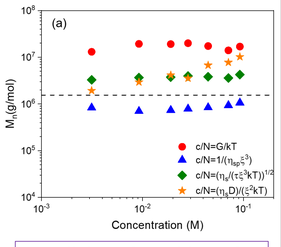


Chain correlation length (ξ) → X-ray scattering



Terminal modulus (G), relaxation time (τ), specific viscosity (η_{sp}) → Rheology

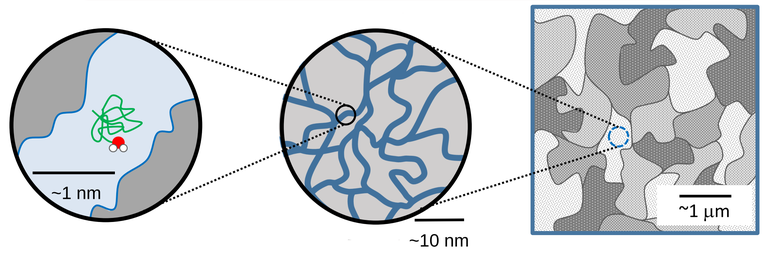




Polymer chain diffusion (D) → NMR diffusometry

Collaboration with Prof. Ralph Colby at Penn State

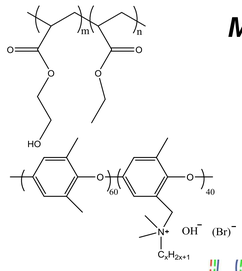
Molecular Transport In Polymer Membranes



Random copolymer membranes

→ μm-scale heterogeneity observed!
→ Change in diffusion behavior on different length scales

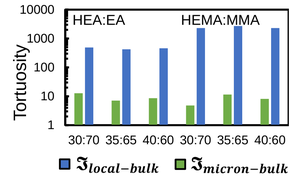
Collaborations with Hickner (PSU), Geise (UVA), Moore (VT)…



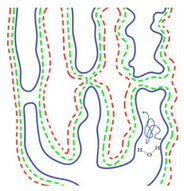
Mechanisms of ion and water transport

$$\mathfrak{I}_{L-B} = \frac{D_{loc}}{D_\infty}$$

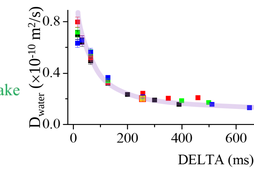
$$\mathfrak{I}_{\mu-B} = \frac{D_0}{D_\infty}$$



Macromolecules (2019) ***Macromolecules (2018)*** ***J Membrane Sci (2013)*** ***Nature Materials (2011)*** ***Macromolecules (2011)*** ***Macromolecules (2010)*** ***Macromolecules (2009)*** *+ 2 in prep*



Low water uptake
Medium water uptake
High water uptake



Hydration modulated tortuosity!

Nanoconfined Transport

Arrhenius Equation

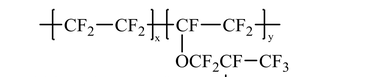
$$D = D_0 e^{-E_a/RT}$$

Macromolecules (2015), JPCB (2014) Chem. Comm. (2013), +2 in prep In review Macromolecules (2020)

- *Diffusion coefficients measured from NMR probes structure/environment on micrometer lengthscale*
- *Activation energy probes local molecular interactions and structure*

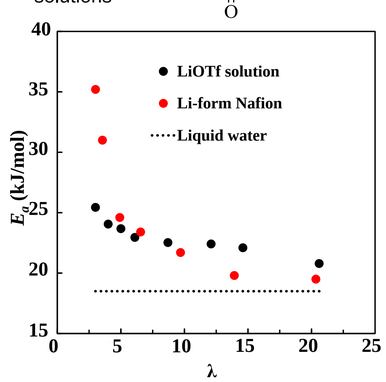
NMR diffusometry

- *Similar molecular/ionic environment*
- *Physically confined environment vs. bulk*

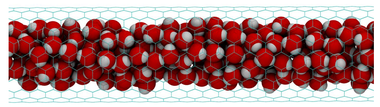


Lithium form Nafion

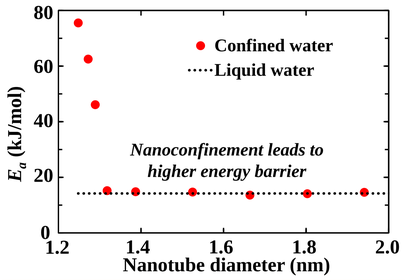
Lithium triflate solutions $F_3C-\overset{O}{\overset{\|}{S}}(=O)-OLi$



Molecular dynamics simulations



Water confined in carbon nanotube



Collaboration with Prof. Diego Troya at VT