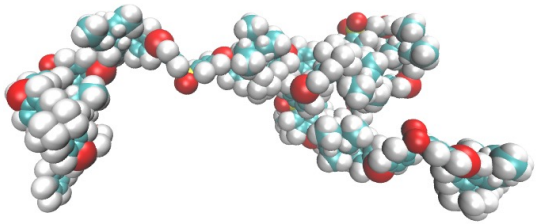
SAND2021-12463D

Simulation of Morphology and Dynamics in Hydroxide-Conducting Polysulfones for Alkaline Batteries

Amalie L. Frischknecht (PI) and Timothy N. Lambert
Sandia National Laboratories

Introduction

Motivation: Alkaline Zn/MnO2 batteries are a priority technology for DOE's grid storage mission to ensure safe, reliable, resilient electricity delivery. A critical issue to improving cycle life and rechargeability is to develop improved separators that have high hydroxide conductivity but prevent the crossover of zincate, $(Zn(OH)_4)^{2-}$, because zincate has undesirable reactions with the cathode. Cationic polysulfone-based separators are promising for this purpose.



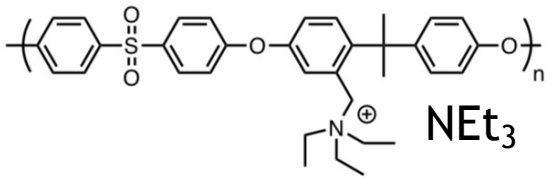
Long-term goal of this work: to develop design rules, such as the preferred polymer blend composition, spacing of functional groups, and identity of functional groups, to create new, optimal separators with high conductivity and low zinc crossover. These separators would enable the use of long cycle-life alkaline Zn/MnO2 batteries for grid storage applications.

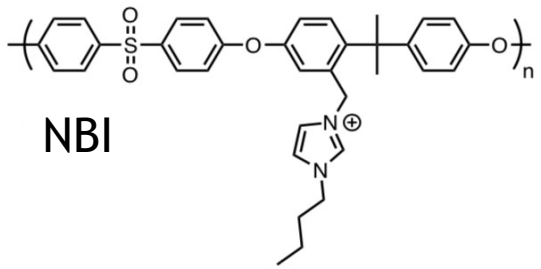
Current work: We used molecular simulations to understand the local morphology of hydrated cationic-functionalized polysulfones and to correlate that morphology with hydroxide diffusion.

Acknowledgments: This work was generously supported by Dr. Imre Gyuk through the Energy Storage Program in the U.S. Department of Energy's Office of Electricity.

Methods

Simulations of 2 different cationic polysulfones in water:





- atomistic molecular dynamics (MD) simulations, OPLS force field
- two water contents: 55% and 74% water uptake
- build 5 configurations of each system so can average properties
  - 8 repeat units/chain
  - 1 OH^- per cationic functional group
  - 50 chains in simulation box
  - box size: ≈ 8 nm per side
- anneal at high temperature, pressure
- final densities of ≈ 1.15 g/cm^3 at 27 °C

water content:
λ = # waters/cationic group

here λ = 15 or 23

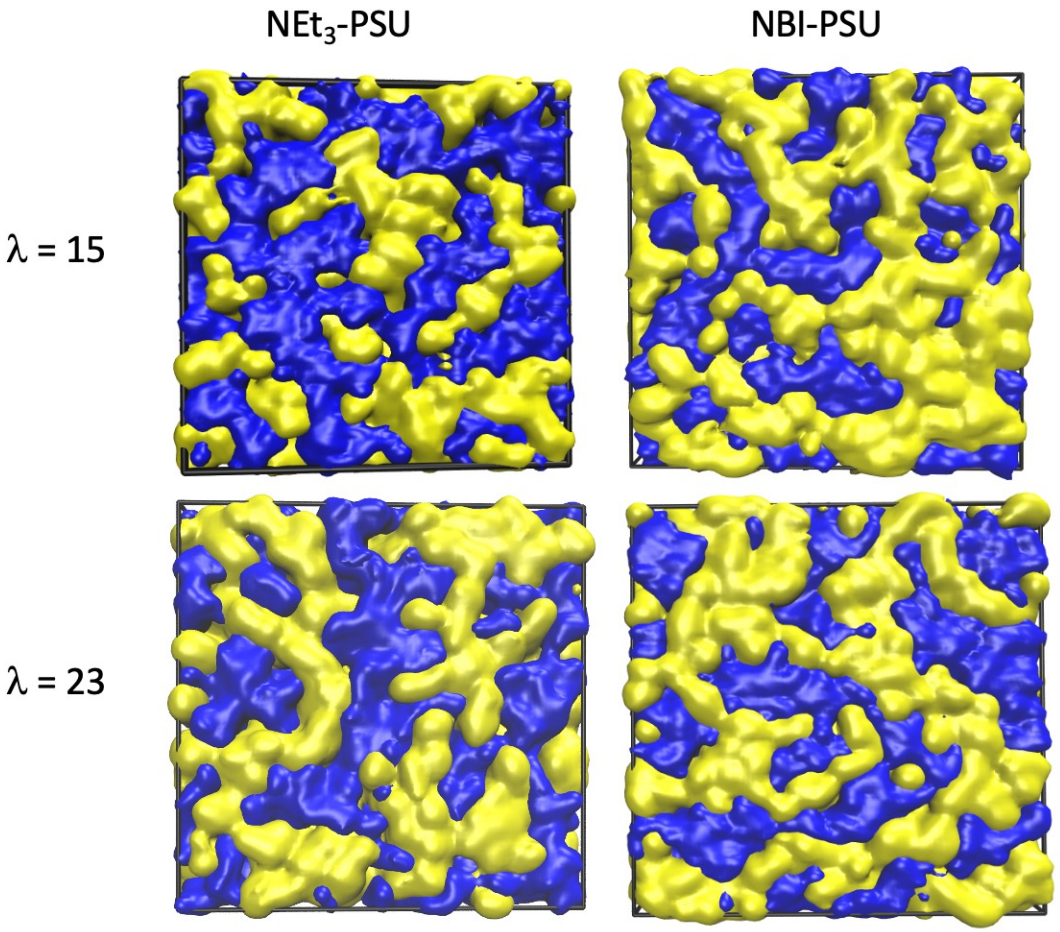
<u>Previous work</u>

- no previous simulations of these particular polymers
- a few simulations of similar polysulfones in water (Zhang et al, J Mat Chem A, 2019; Di Salvo et al, J. Membr. Sci., 2020)
  - focused on use in anion exchange membranes for fuel cells

Nanoscale Morphology

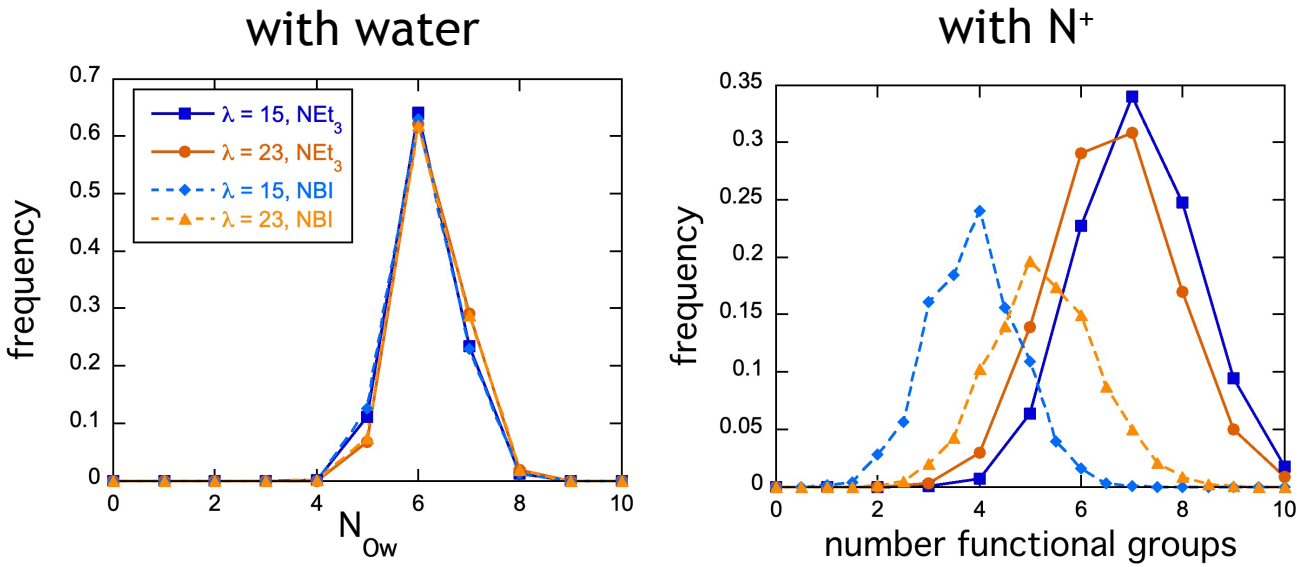
Isodensities from MD simulations

blue = water and hydroxide ions
yellow = polymer backbone



there are nanoscale water domains percolated through the polymers

local coordination of OH- ions

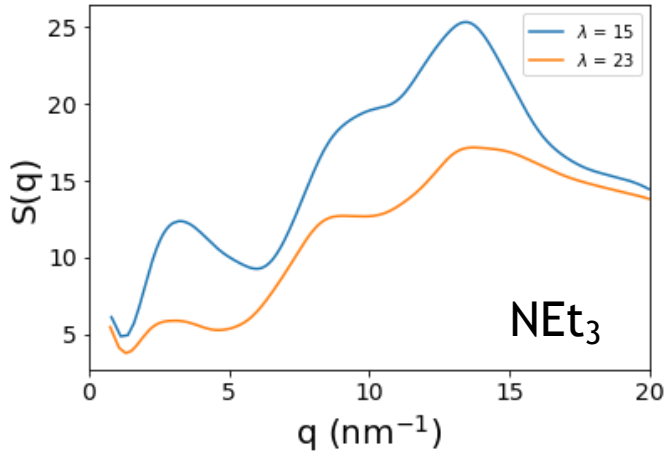


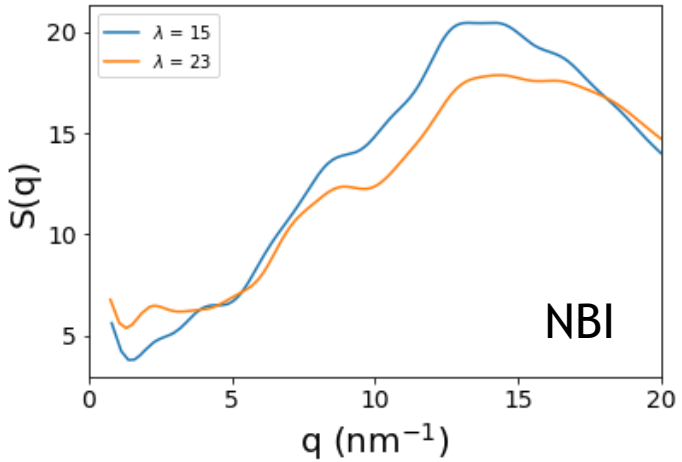
- OH^- prefers to coordinate with 6 waters
- OH^- coordinates with more functional groups in NEt_3 polymers than in NBI polymers

X-ray Scattering Profiles

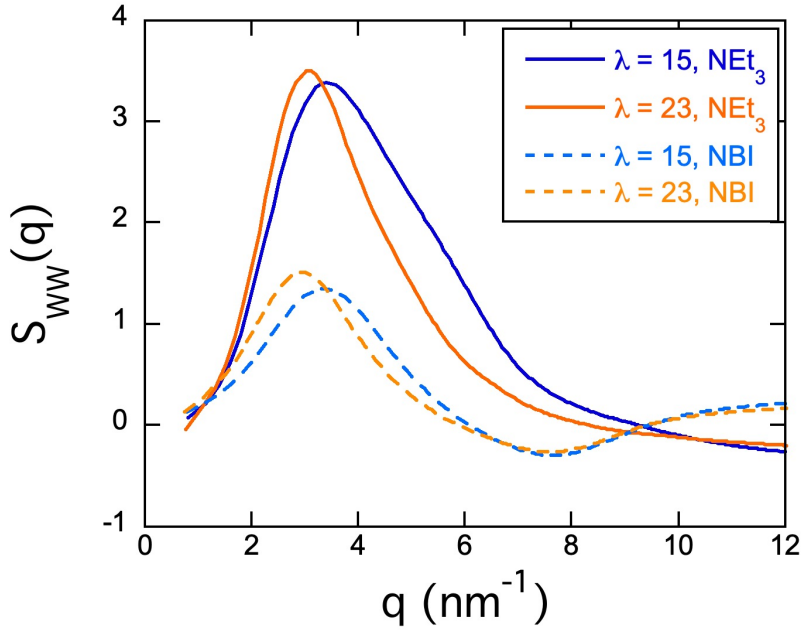
total scattering profiles

- "ionomer" peak at low q indicative of nanophase separation
- not obviously present in NBI polymers





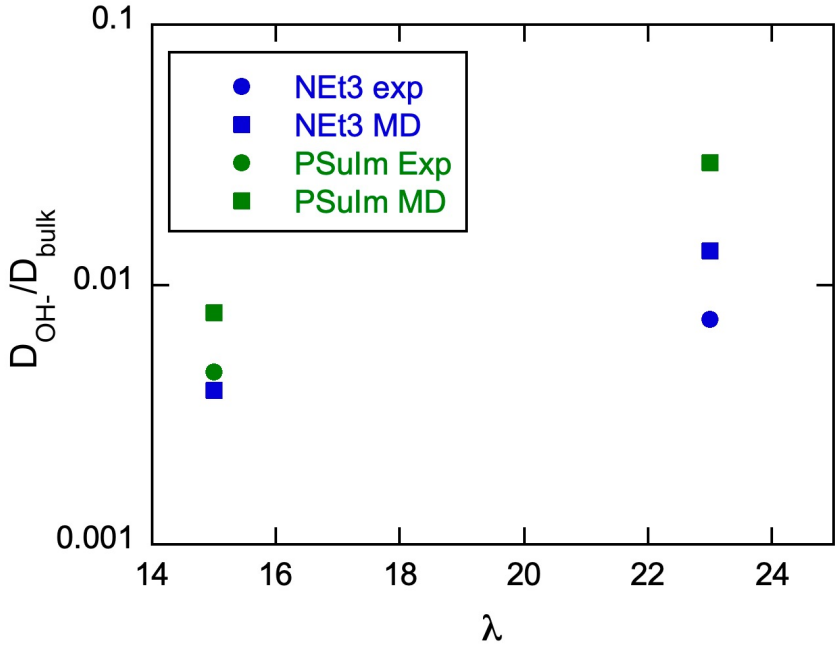
partial scattering functions for water



- clear peaks in water-water scattering
  - indicate water domain sizes of ≈ 1.8 and 2.1 nm
  - water domains larger at larger λ (peak at lower *q*)
- "loss" of ionomer peak due to lack of contrast in scattering
  - system is still nanophase separated
  - seen previously in simulations of SDAPP (Sorte et al, *Macromolecules* 52, 857 (2019))

Diffusion Constants and Conclusions

OH^- diffusion constants relative to bulk values



- simulation values similar to experiment
  - experiments in KOH solution, not yet included in simulations
- larger D at larger water content
- larger D for NBI than NEt_3 polymers
  - possibly becaues OH- more strongly coordinated to cationic groups in NEt_3 polymers

Kolesnichenko, I. V. et al. *ACS Appl Mater Interfaces* **2020**, 12, 50406-50417
Frischknecht et al, in preparation

Conclusions

- water forms percolated domains that are larger with increasing water content
- loss of ionomer peak in scattering due to lack of contrast, not lack of phase separation
- hydroxide diffusion constant D_{OH-} increases with increasing water content
- D_{OH^-} is smaller than in commercial separators like Celgard
  - water channels about 2 nm
  - average pore size in Celgard: about 60 nm
  - indicates lower conductivity but better prevention of zincate crossover
- development of simulation model allows rapid exploration of modifications (blends, different water content, other functional groups, etc.)

Future Work

- calculate partitioning of KOH into polymers
- simulate zincate crossover
- effects of blending, other functional groups

Contact: Amalie Frischknecht, alfrisc@sandia.gov