Atomistic Simulations of Sulfone-based Polymer Electrolytes for Alkaline Batteries

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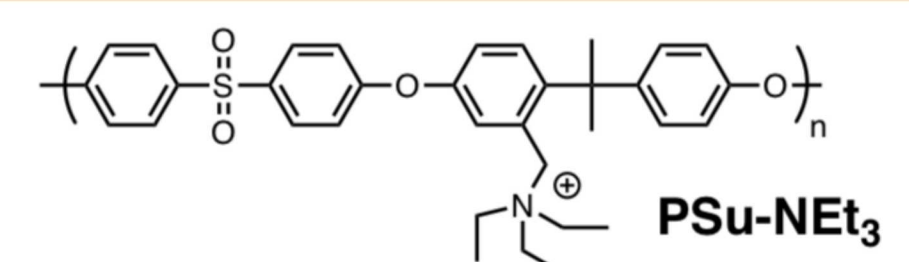
Introduction

<u>Motivation</u>: Alkaline Zn/MnO_2 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.

<u>Long-term goal of this work</u>: 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/MnO_2 batteries for grid storage applications.
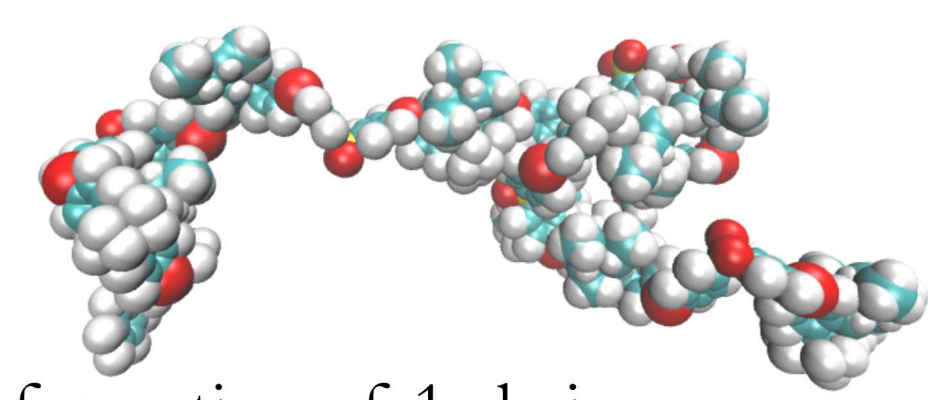
<u>Current work</u>: We use molecular simulations to understand the local morphology of hydrated cationic-functionalized polysulfones and to correlate that morphology with hydroxide diffusion.

Methods

- atomistic molecular dynamics (MD) simulations of $PSu-NEt_3$
- 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 1.24 g/cm^3 at 27 °C

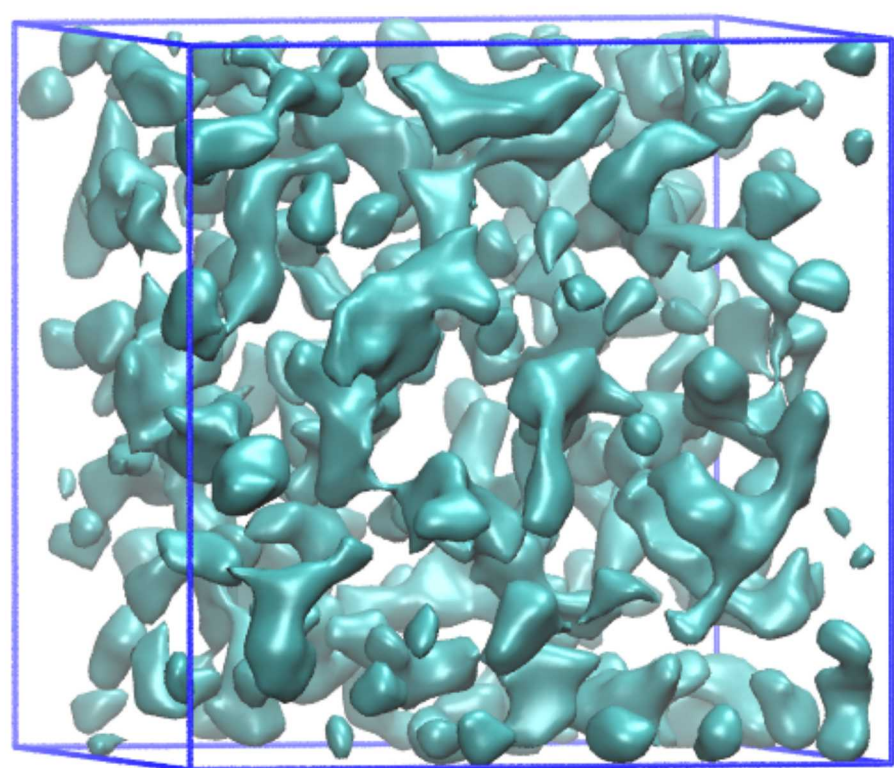polymer is glassy; water and OH^- move

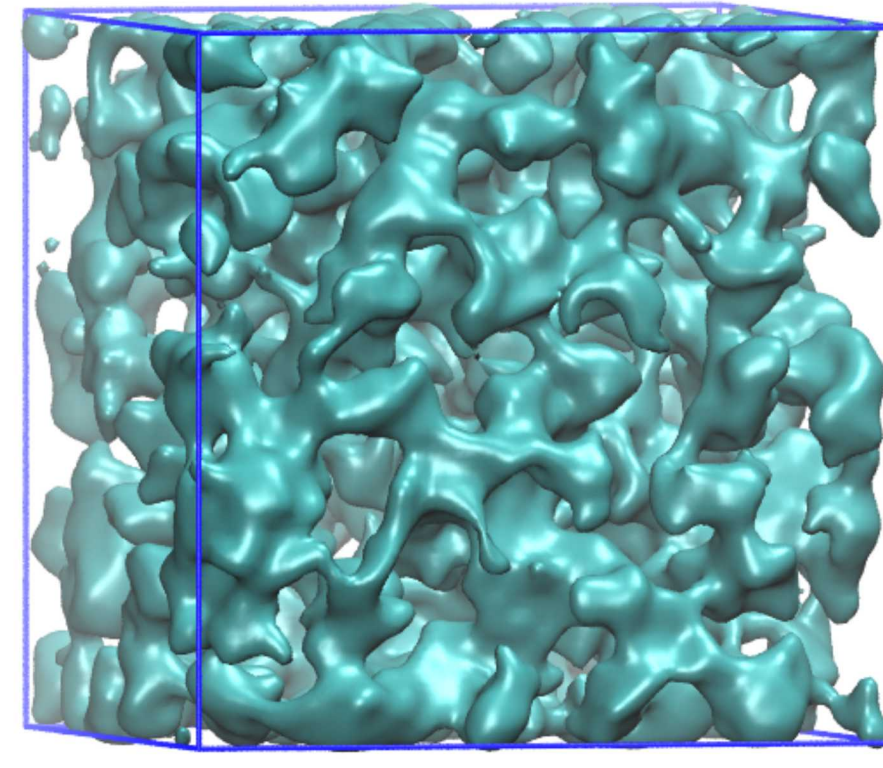**PSu-NEt3**

<u>Previous work</u>
- no previous simulations of these polymers
- a few simulations of similar polysulfones in water (Zhang et al, J Mat Chem A, 2019)
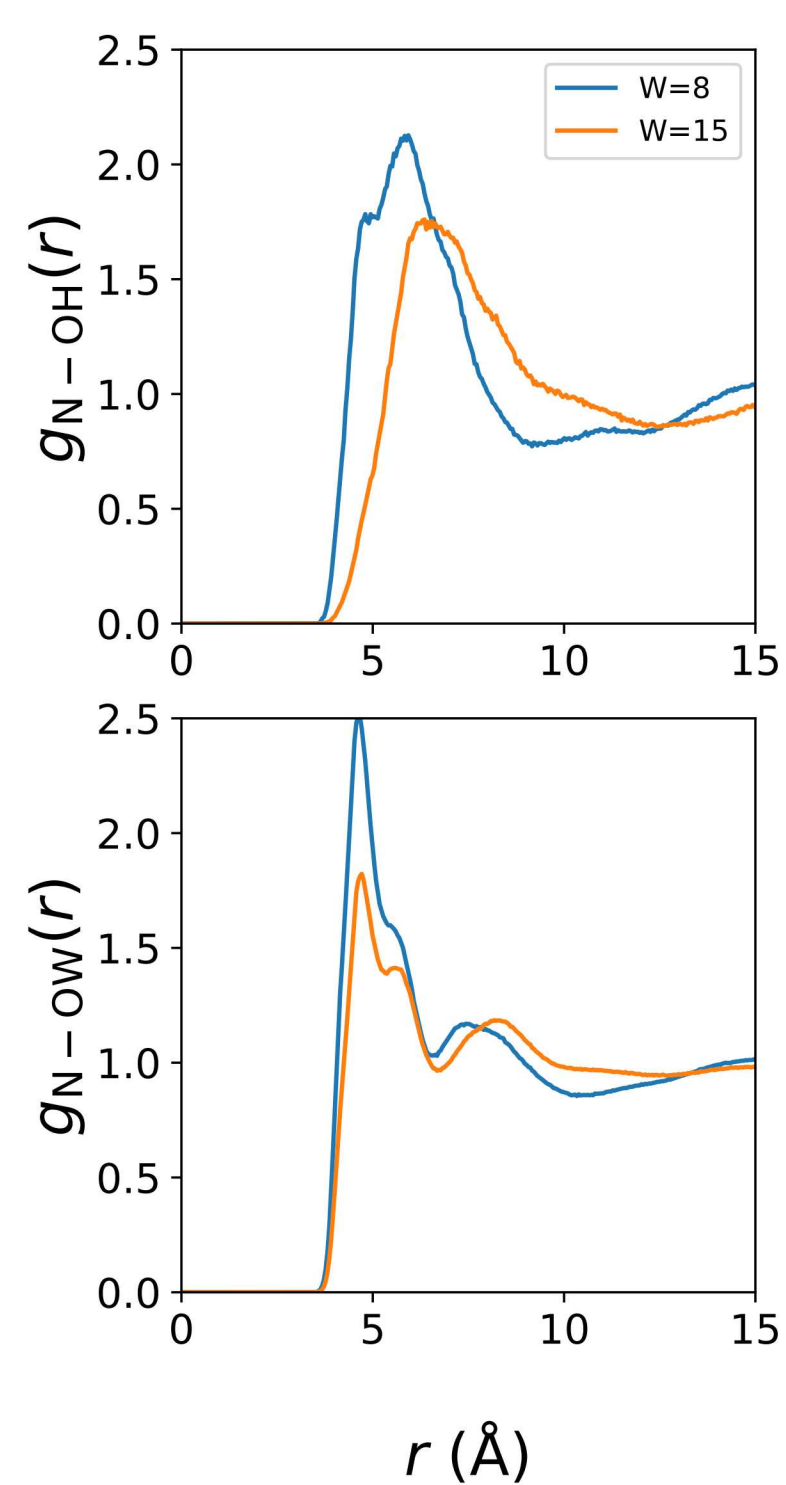- no work in the literature on zincate

conformation of 1 chain

Local Morphology

25% water, W = 8 waters/N^+
isolated water clusters

50% water, W = 15 waters/N^+
percolated water channels

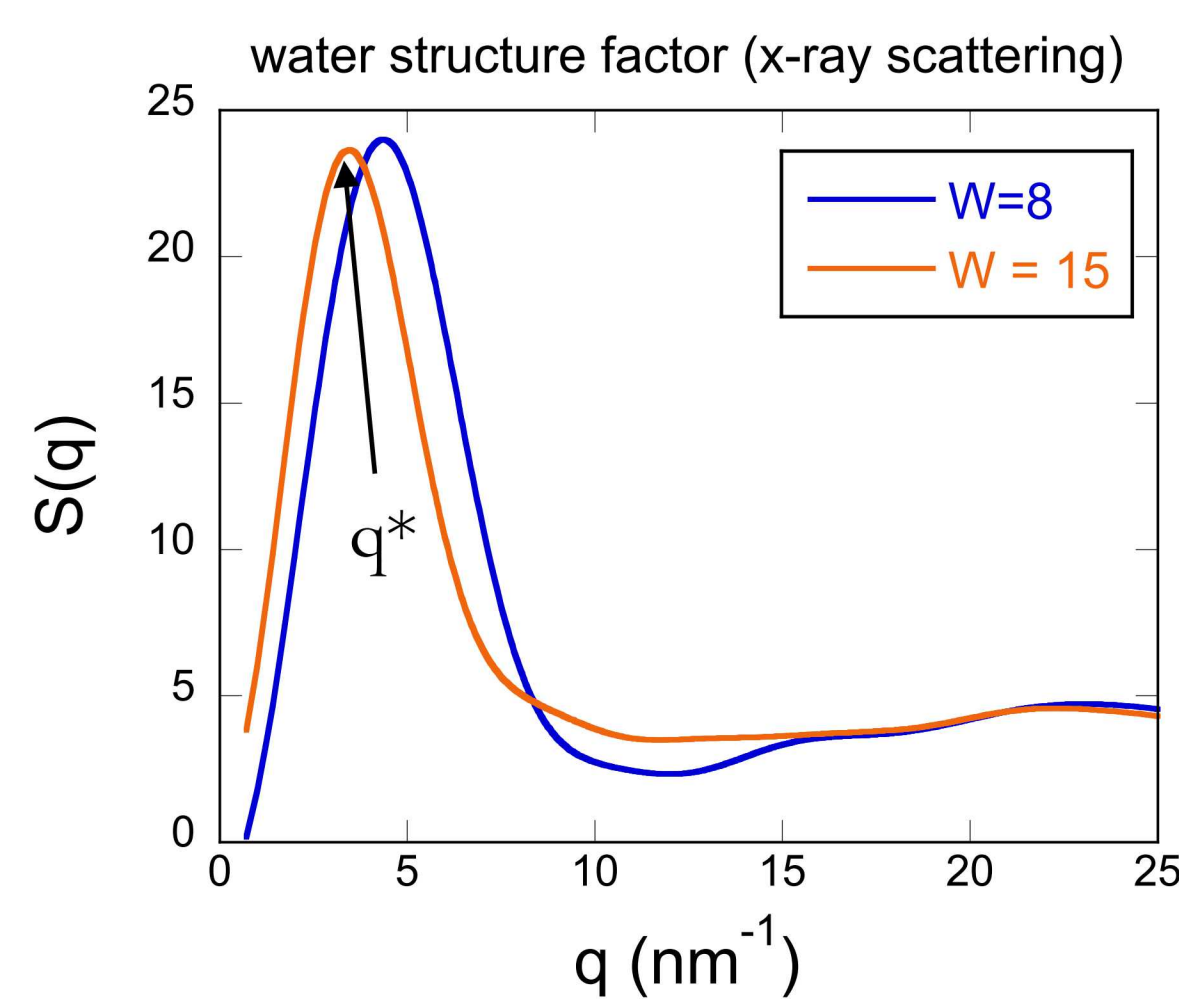snapshots show isodensity surfaces of water and hydroxide ions

$g_{ij}(r)$: probability that atom *j* is distance *r* from atom *i*

- Peaks show more water molecules (OW) are near the ammonium ion than OH^- ions (OH)
- Water and ions are closer to ammonium in system with less total water

This shows OH^- ions are not strongly bound to the cationic group on the polymer, and hence are more free to move
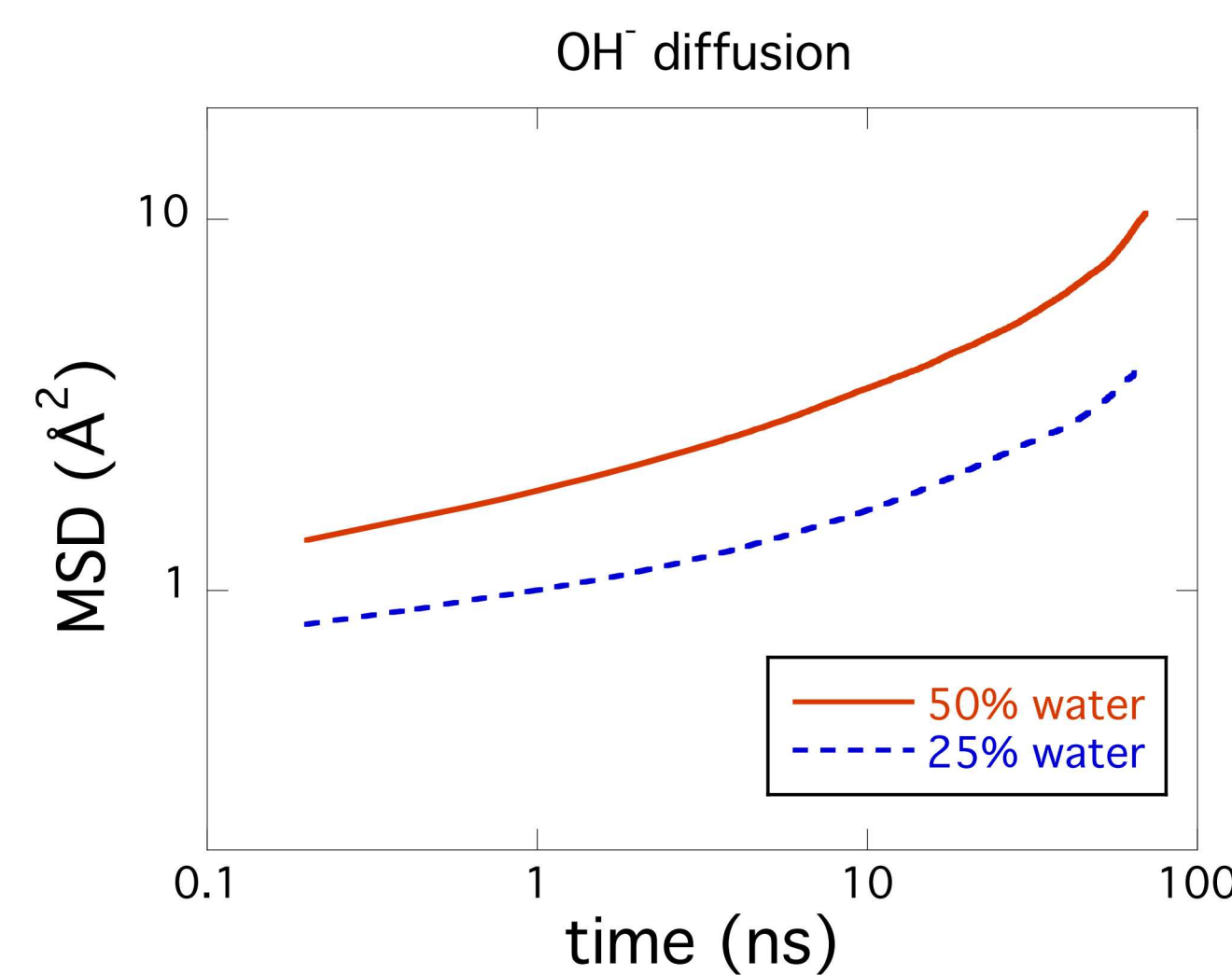
Water Channels

water structure factor (x-ray scattering)

first peak: average distance d* between water domains

$d* = 2\pi/q* =$ 1.4 nm for W = 8
= 1.8 nm for W = 15

- very small water domains compared to commercial separators which have pore sizes of 10s of nm
- small water domains may help prevent crossover of zincate

Hydroxide Transport

diffusion constant D calculated from: MSD = 6Dt
MSD = mean-squared displacement

OH^- diffusion

at 50% water: $D_{OH^-} \approx 1.6*10^{-9}$ cm^2/s

- compare to commercial separator: Celgard: $D_{OH^-} \approx 9.5*10^{-8}$ cm^2/s
- likely means conductivity of PSu-NEt3 is somewhat lower than commercial separators

Conclusions

- water forms percolated channels in polymer with increasing water content
- hydroxide diffusion constant D_{OH^-} increases with increasing water content
- D_{OH^-} is smaller than in commercial laborators
    - water channels in PSu-NEt3: 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

- include KOH solution; need permeability of KOH in polymer
- develop molecular interaction parameters for zincate
- simulations of zincate crossover
    - build KOH/polymer interface
    - calculate probability of zincate entering membrane
- effects of blending, other functional groups

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