

Molecular Simulations of Gas and Ion Transport in Potassium Polyacrylate Electrolytes

Amalie L. Frischknecht (PI)

Introduction

Motivation:

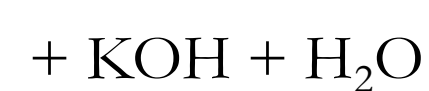
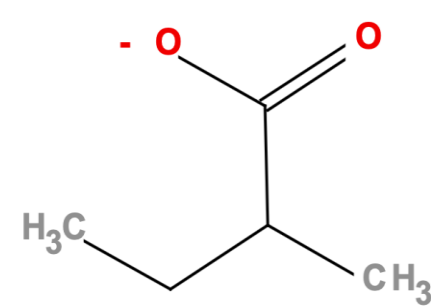
- DOE/OE goal is to modernize the grid using cost-effective solutions
- Alkaline Zn/MnO₂ batteries are a priority technology for DOE's grid storage mission
- Improved separators are needed with high OH⁻ conductivity and low crossover of zincate, (Zn(OH)₄)²⁻

Overall goals:

- use molecular modeling and simulations to understand gas and ion transport mechanisms
- use understanding to develop design rules for improved separators that would enable long cycle-life for grid storage applications

PAAK is promising as an electrolyte/separator

poly(potassium acrylate)

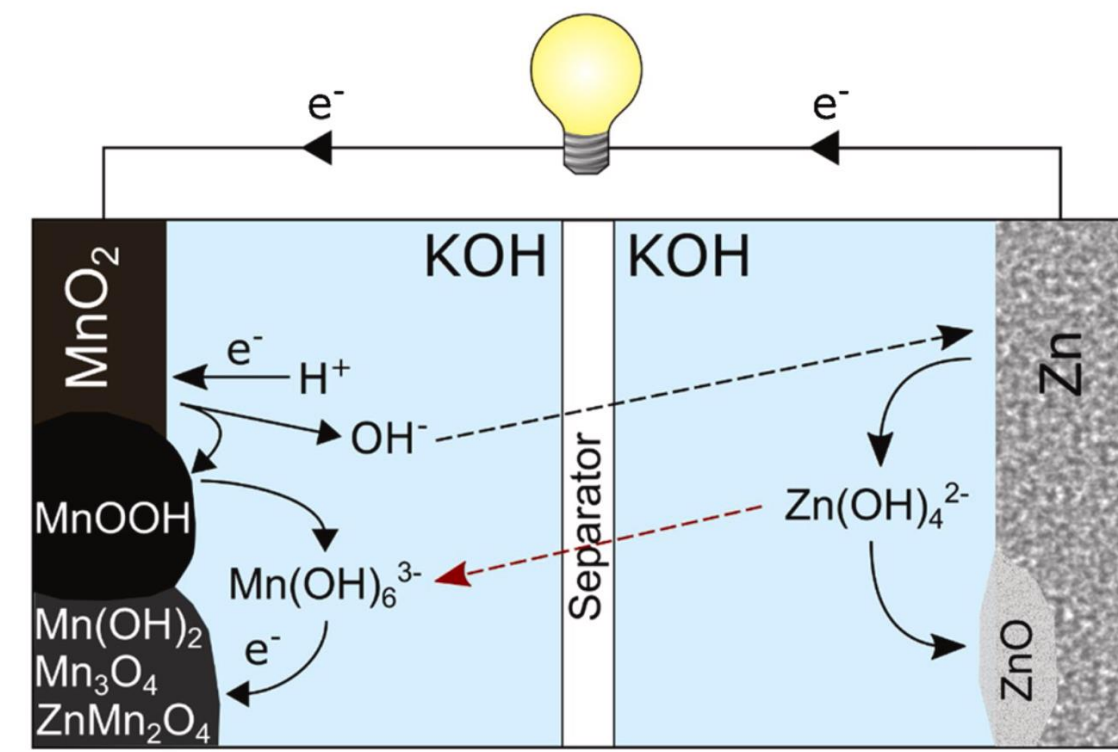


has low zincate diffusion—why?

Cho, J. et al. *Polymers* 2022

Current Work:

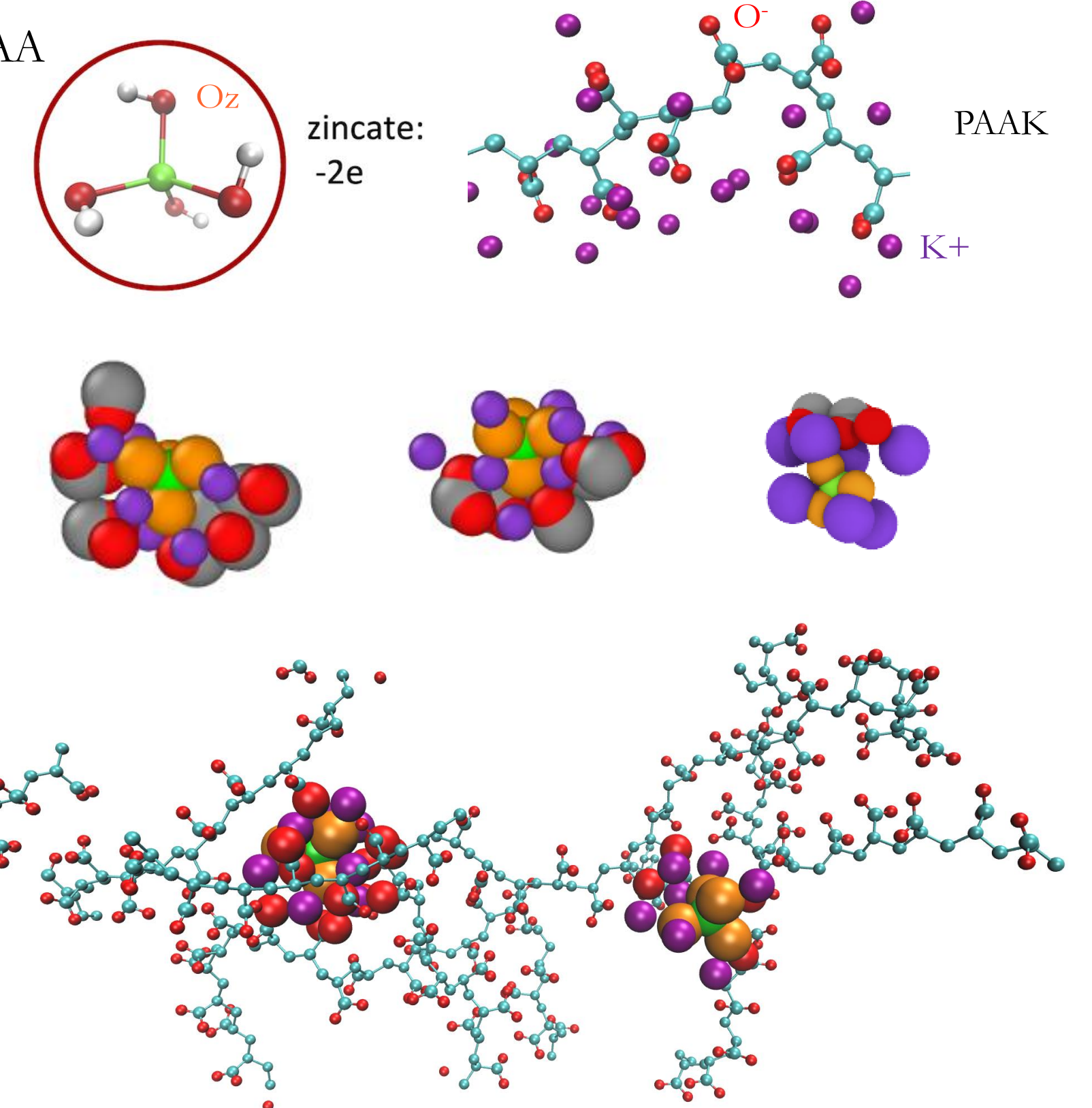
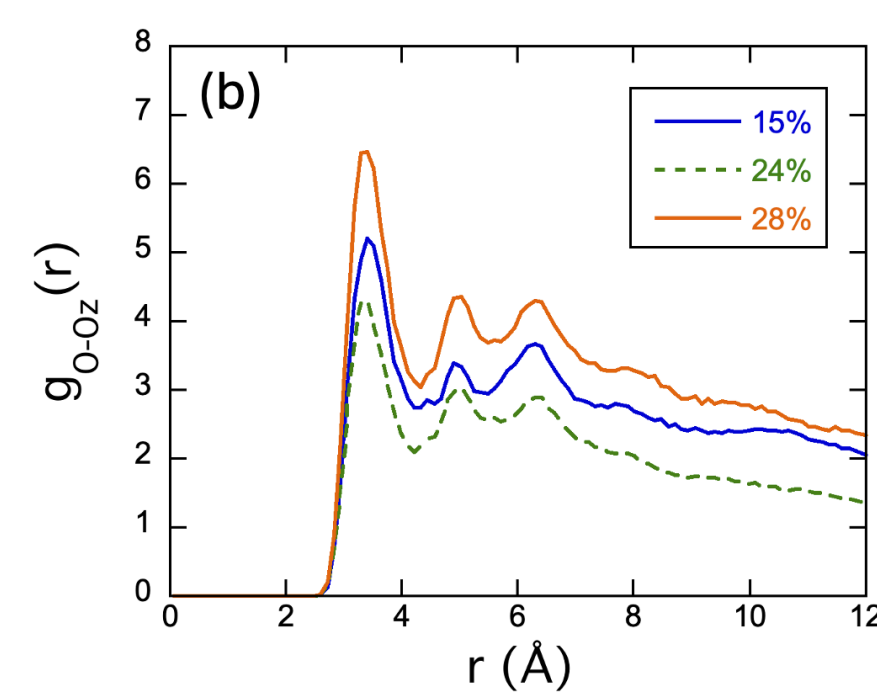
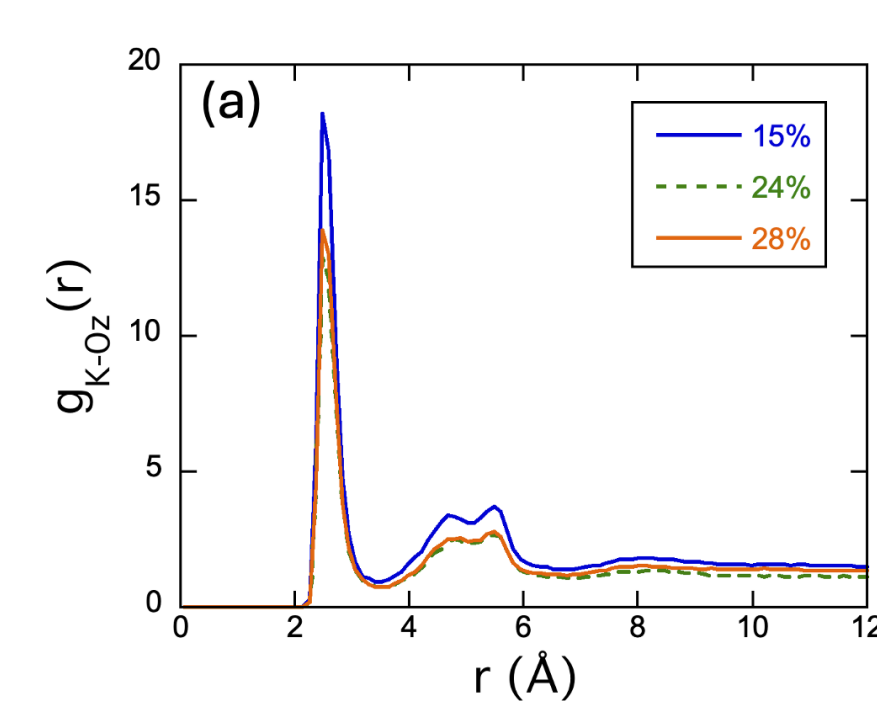
- limited previous work on poly(potassium acrylate) in high concentration KOH
- MD simulations to understand transport



Lim, M. B., Lambert, T. N. & Chalamala, B. R. *Materials Science and Engineering: R: Reports* 2021, 143, 100593.

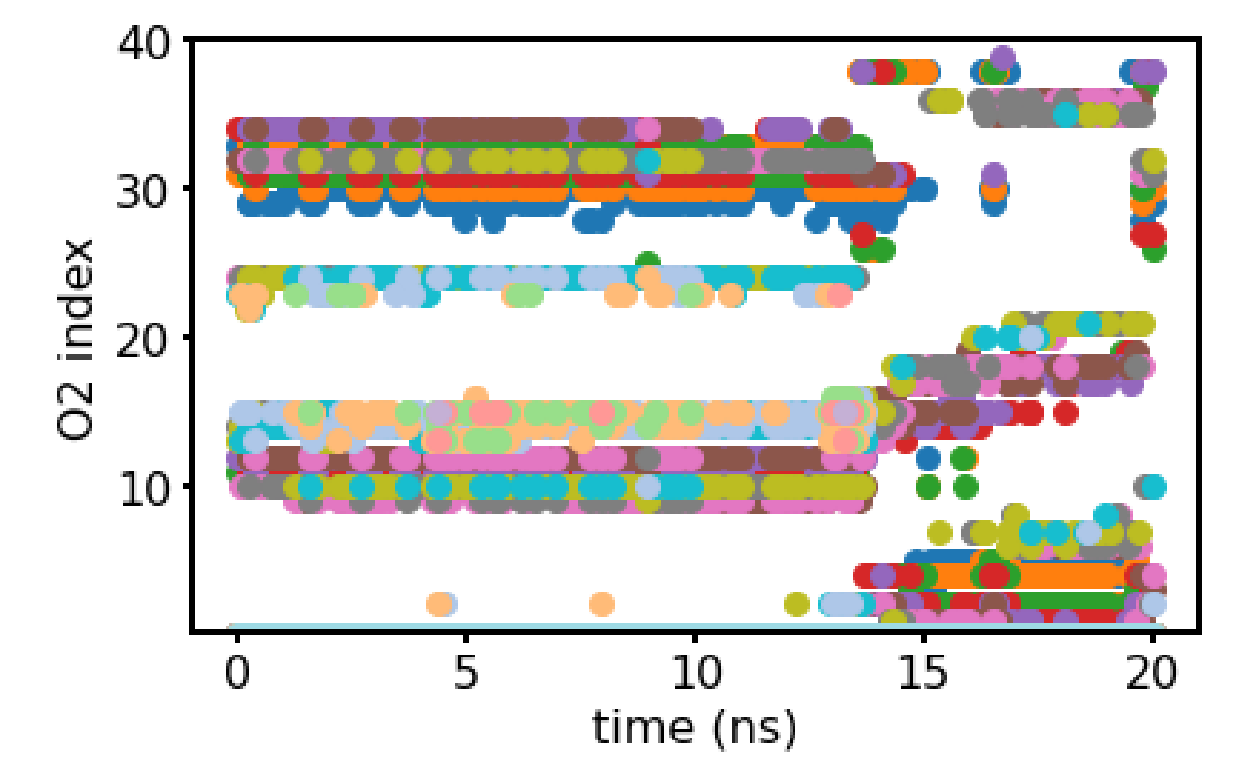
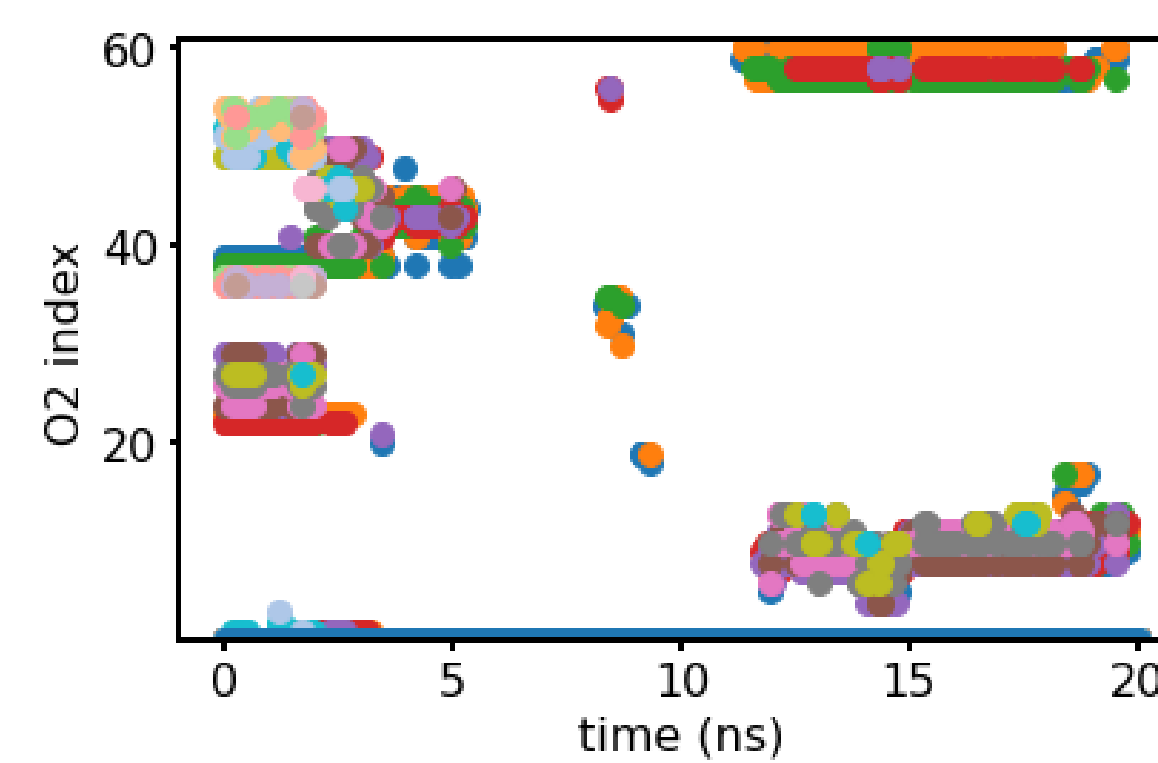
Zincate Clusters with K⁺ and PAA

Oz on zincate: close to K⁺ and O⁻ on PAA



Zincate clusters are long-lived

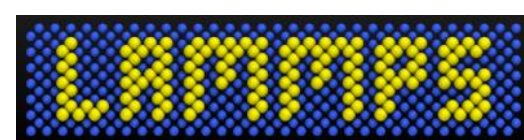
Index of O atoms coordinated to Zn



Methods

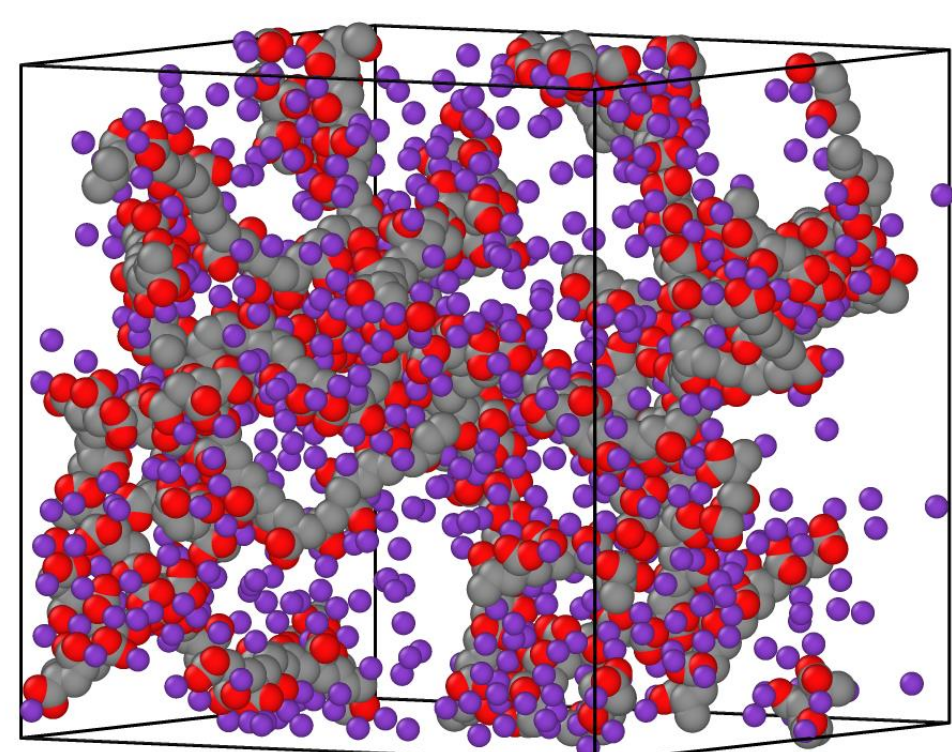
atomistic molecular dynamics (MD) simulations

- OPLS, TIP4P/2005 water
- multiple configurations for better statistics
- Sandia's MD code, LAMMPS
- zincate interactions from previous OE work



- Frischknecht and Stevens, *J Phys Chem B*, 128, 3475 (2024)

Polymer Slows Diffusion

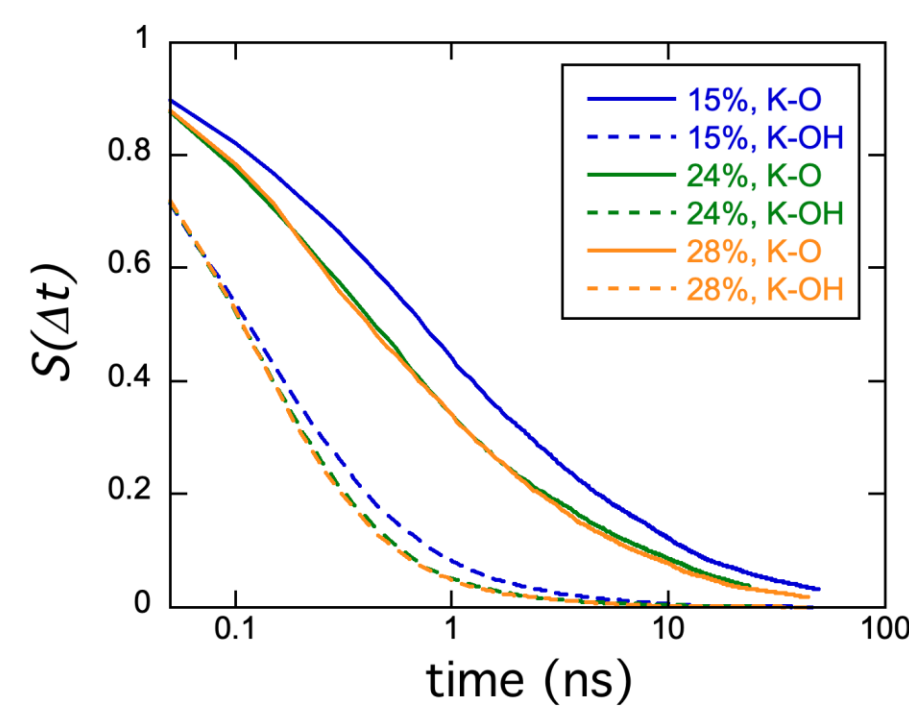


K⁺ ions:

- some condense on PAA chains as expected
- exchange between PAA chains and solution

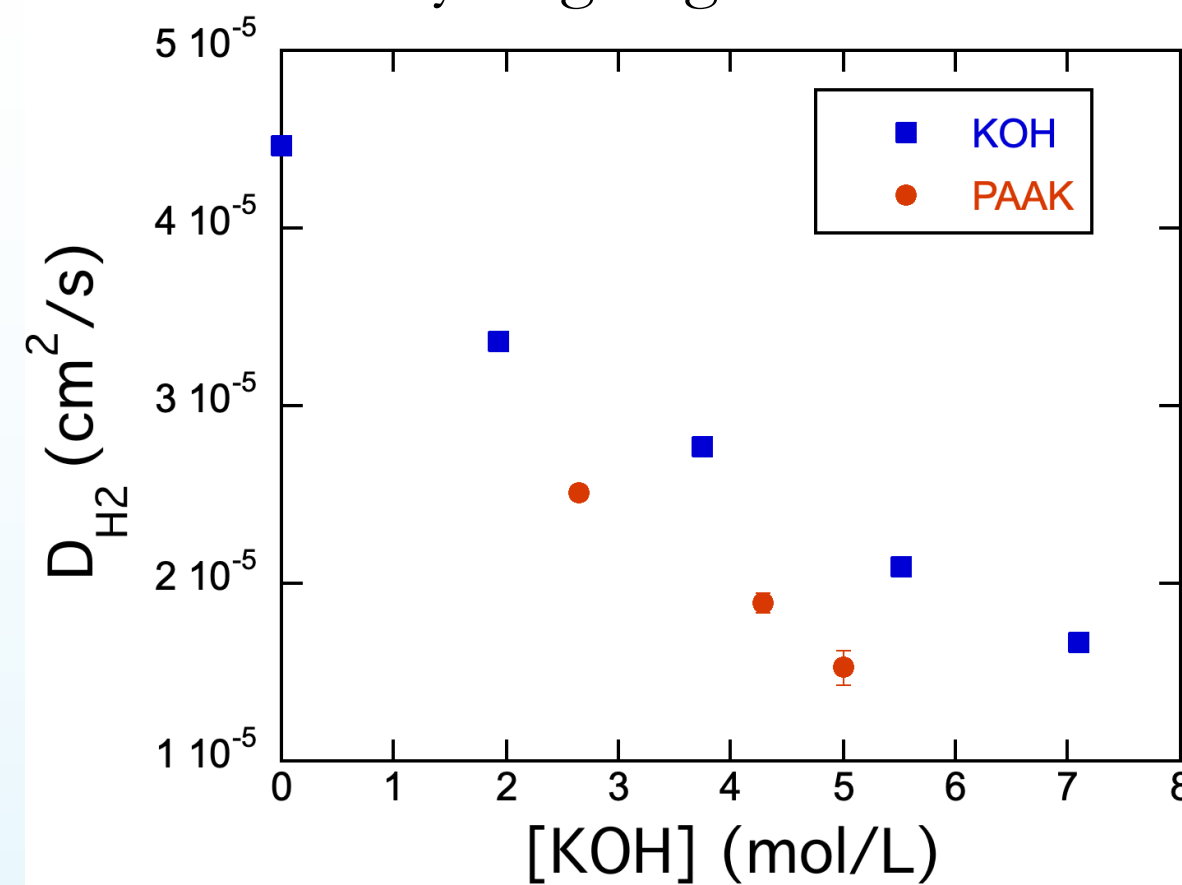
ion association times

K-O on PAA: 3-5 ns
K-OH: 0.3-0.4 ns

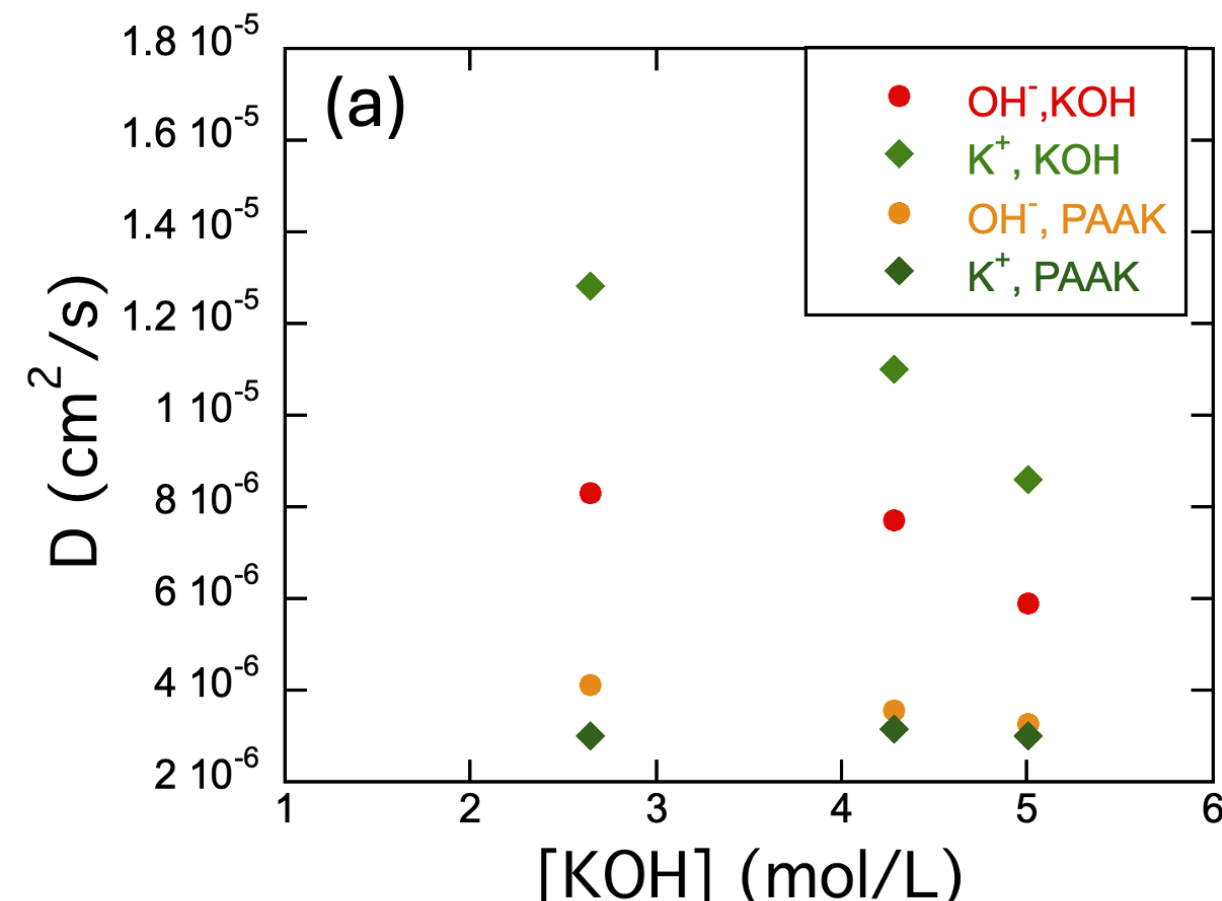


purple: K⁺ ions
red: O atoms on polymer
gray: C atoms on polymer

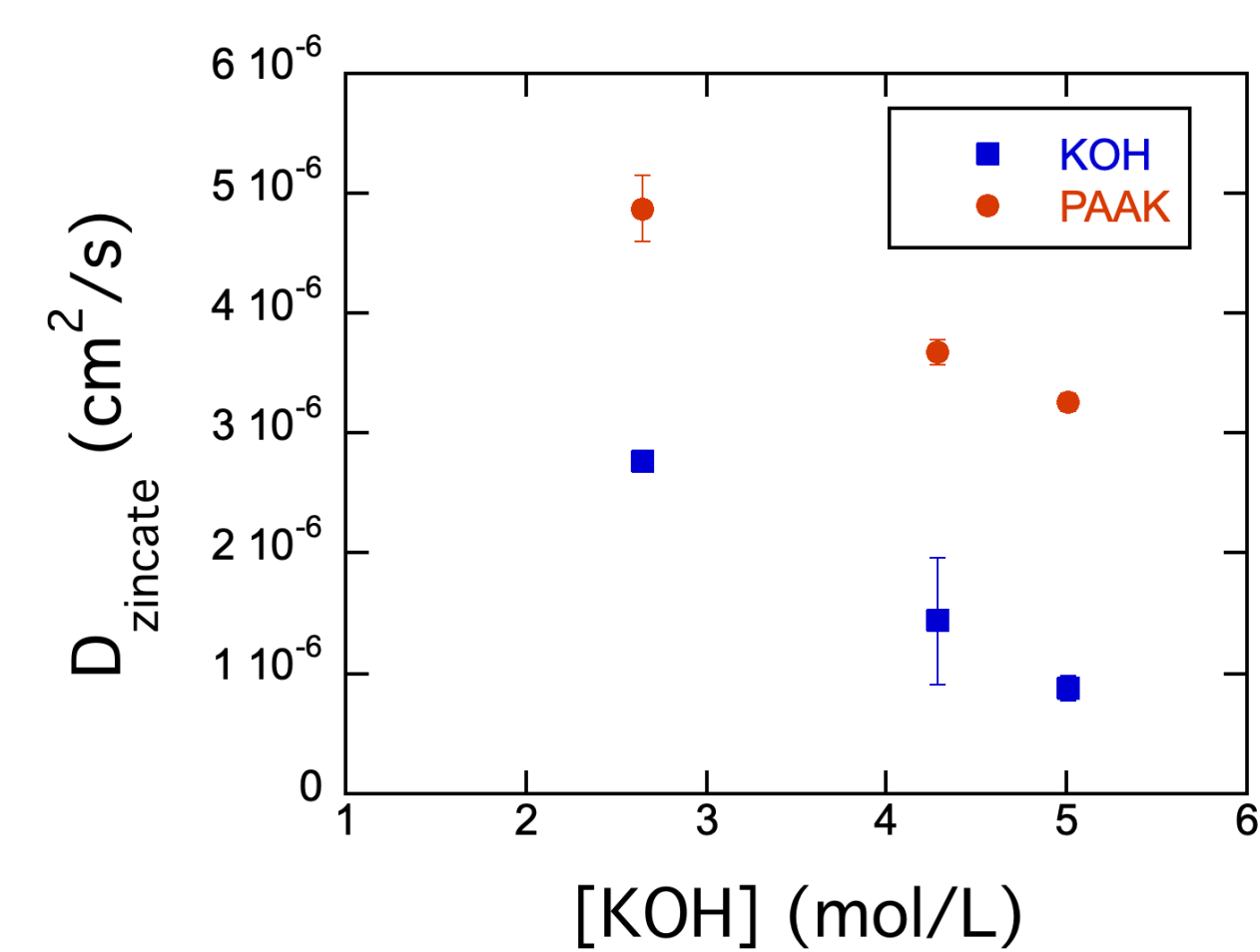
hydrogen gas diffusion



KOH diffusion



Polymer Traps and Slows Zincate



- zincate becomes trapped by polymer over 10s of ns
- significantly slows zincate transport
- mechanism for improved cycling of polymer electrolytes over KOH

A. L. Frischknecht, manuscript in preparation for *ACS Appl Polym Mat*

Future Work

- include proton hopping mechanism to calculate ionic conductivity in alkaline electrolytes from MD simulations
- investigate complex ions in KOH solution
 - need to understand physical chemistry of zincate, cuprate, etc
 - use *ab initio* MD to determine structures, dynamics

Contact: Amalie Frischknecht, alfrisc@sandia.gov