Molecular Modeling of Gas and Ion Transport in Alkaline Battery Electrolytes

Amalie L. Frischknecht

Center for Integrated Nanotechnologies

Sandia National Labs

DOE-OE Peer Review, Bellevue, Washington

August 7, 2024

Presentation ID #1004

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

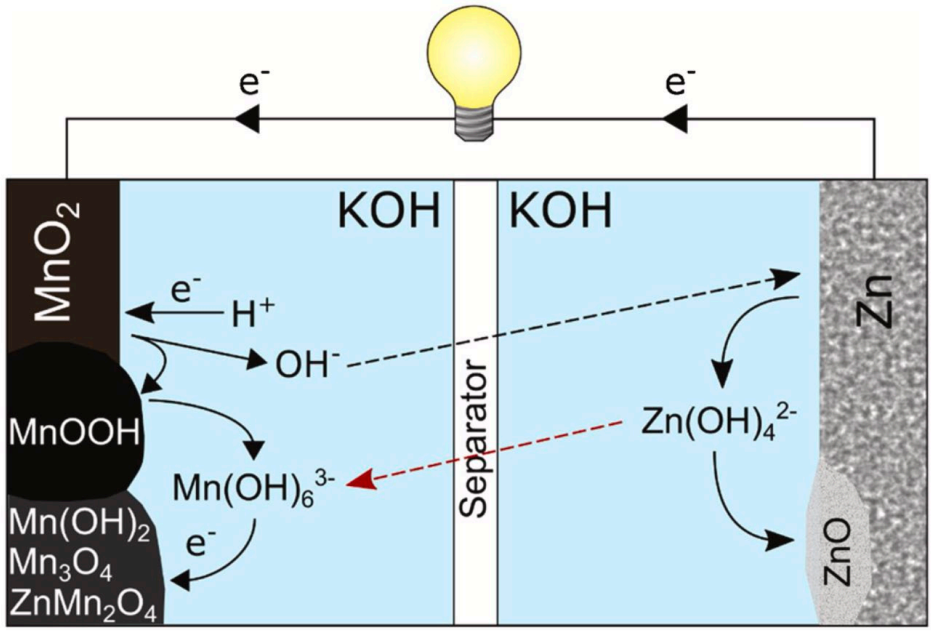
SAND2024-09894C

Zn/MnO_2 batteries are promising

- high energy density in zinc
- cheap
- good supply chain
- safe

Electrolyte and/or separator needs to:

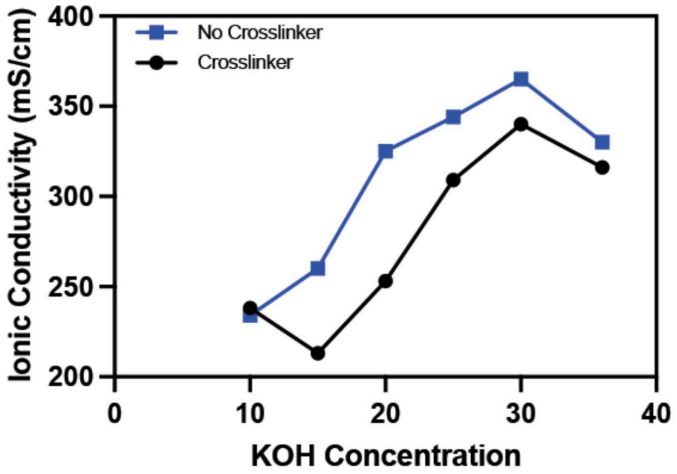
- conduct OH^- well
- prevent crossover of zincate, $Zn(OH)_4^{2-}$

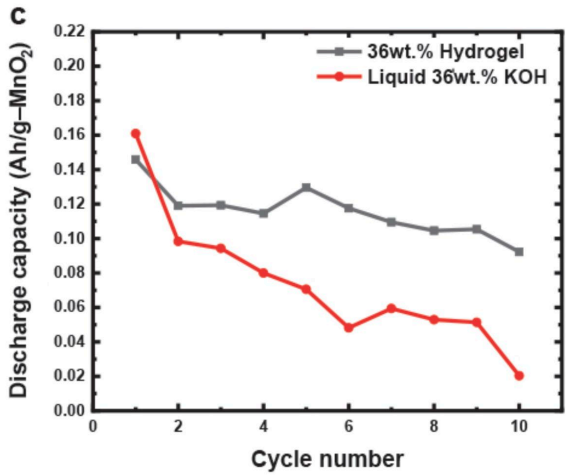


Lim, M. B., Lambert, T. N. & Chalamala, B. R. *Materials Science and Engineering: R: Reports* **2021**, 143, 100593.

What would be a good electrolyte? Do we need a separator?

Polymers and polymer gels as the electrolyte





- good conductivity
- reduces zincate transport/crossover
- improves capacity retention
- minimizes shape change at the Zn anode
- non-spillable

Cho, J., Banerjee, S. et al. *Polymers (Basel)* **2022**, 14, 417
Cho, J., Banerjee, S. et al. *Polymers (Basel)* **2024**, 16, 658.

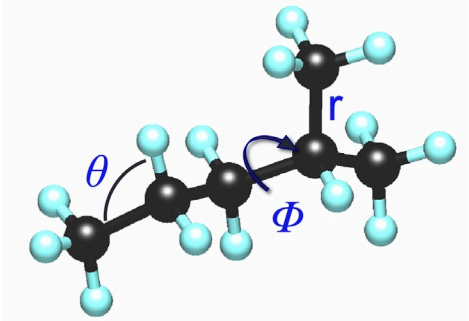
What molecular mechanisms contribute to these properties?

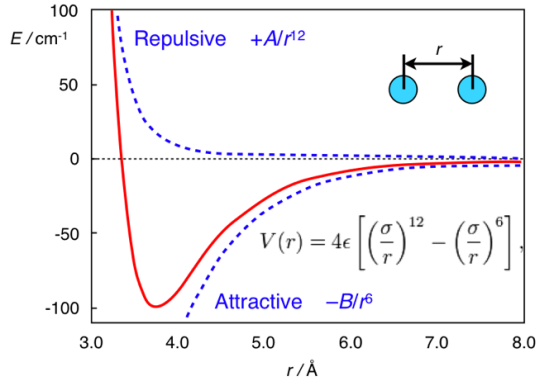
Molecular simulations can provide insight

Classical molecular dynamics (MD) simulations

Needed ingredients:

- force fields (interaction parameters)
  - bonded: bonds, angles, dihedrals
  - nonbond: van der Waals, electrostatics
- equilibration method
  - easy in melts, harder in glasses



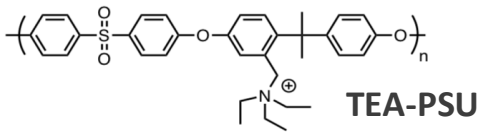


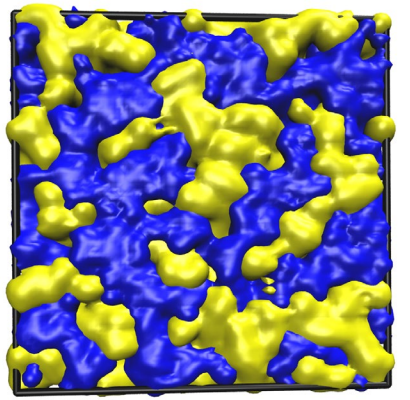
Scope:

- from < ps to 1 μs simulation time
- box sizes: 5-10 nm

Outcomes

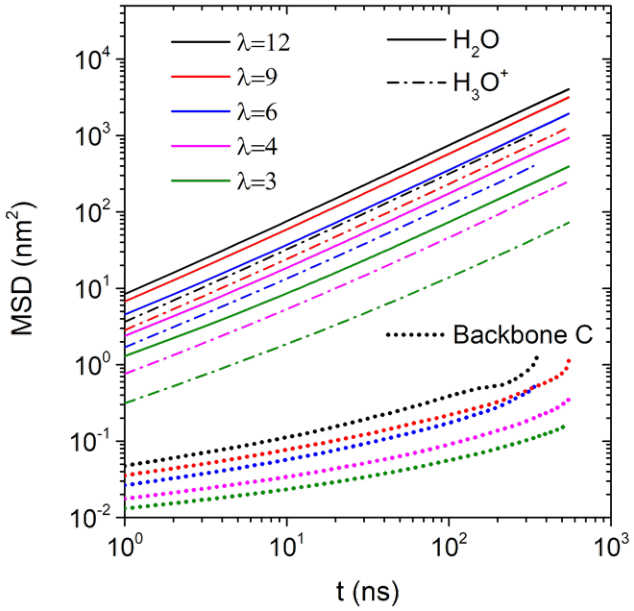
- structure





- dynamics

diffusion from MSD



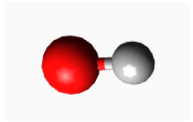
Frischknecht, A. L., in 't Veld, P. J., Kolesnichenko, I. V., Arnot, D. J. & Lambert, T. N. *ACS Appl. Polym. Mater.* **2022**, 4, 2470-2480.

Simulations of ions

Need good interaction parameters to get accurate dynamics

Hydroxide ion OH^-

q_O = -1.3e, q_H = 0.3e



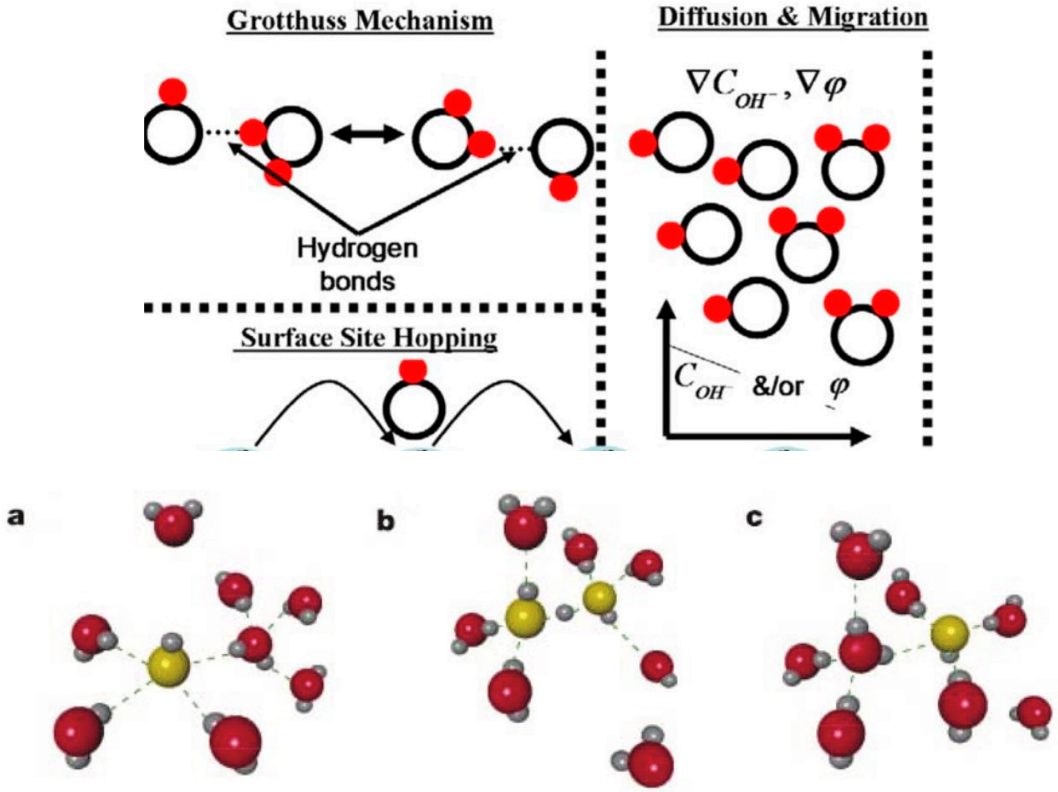
Scale charges to account for electronic polarizability

$$q_i^{\text{eff}} = \frac{q_i}{\sqrt{\epsilon_{\text{el}}}} \approx 0.75\, q_i$$

Leontyev, I. & Stuchebrukhov, A. *Phys Chem Chem Phys* **2011**, 13, 2613-2614.

Hydroxide ions in water can move by:

- vehicular diffusion
- the Grotthuss mechanism—not in classical MD
- surface hopping



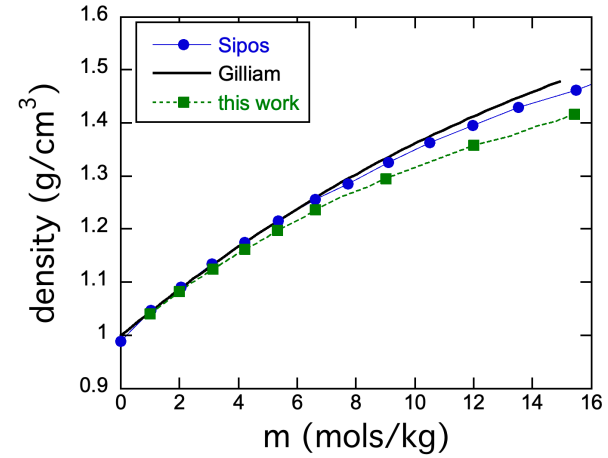
Grew, K. N. & Chiu, W. K. S. *J Electrochem Soc* **2010**, 157, B327.

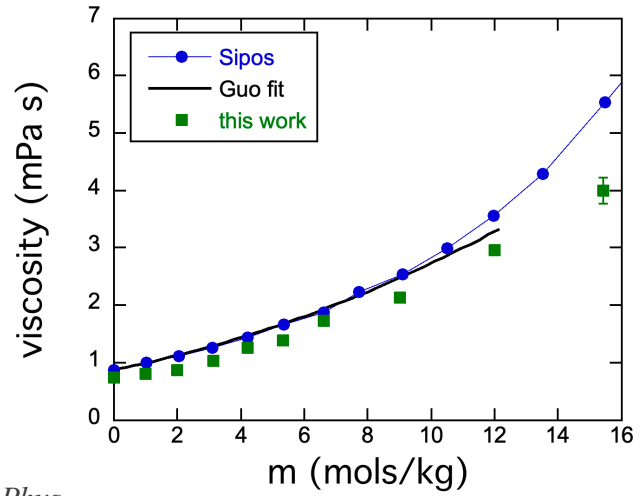
Tuckerman, M. E., Marx, D. & Parrinello, M. *Nature* **2002**, 417, 925-929.

Molecular simulations of KOH solutions

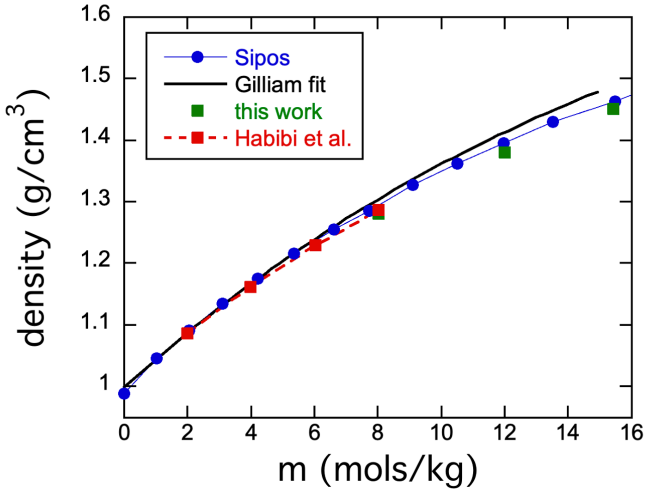
Developed two sets of parameters for KOH valid at high concentrations
Good agreement with experiment

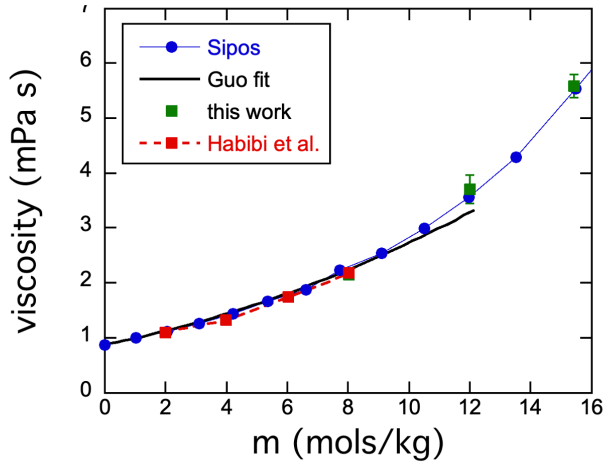
"FNB" parameters; q = 0.8





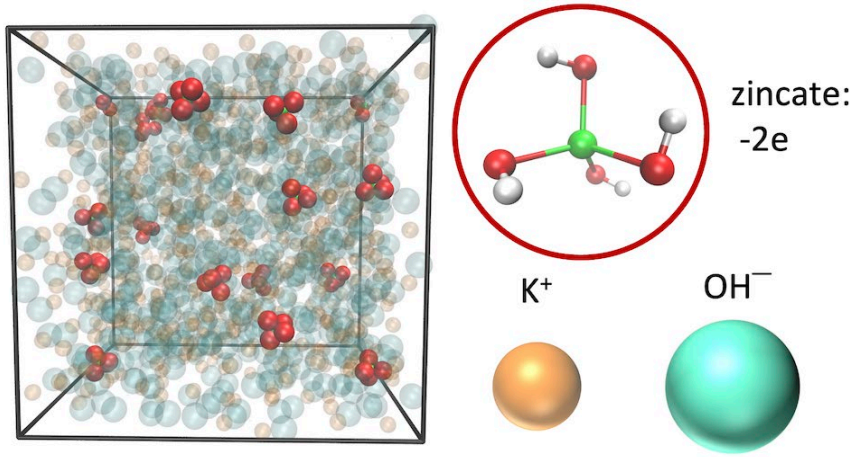
"FHM" parameters; q = 0.75

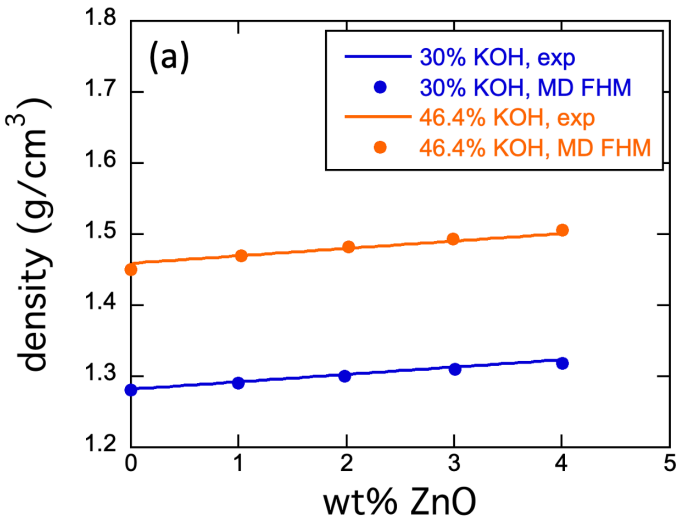


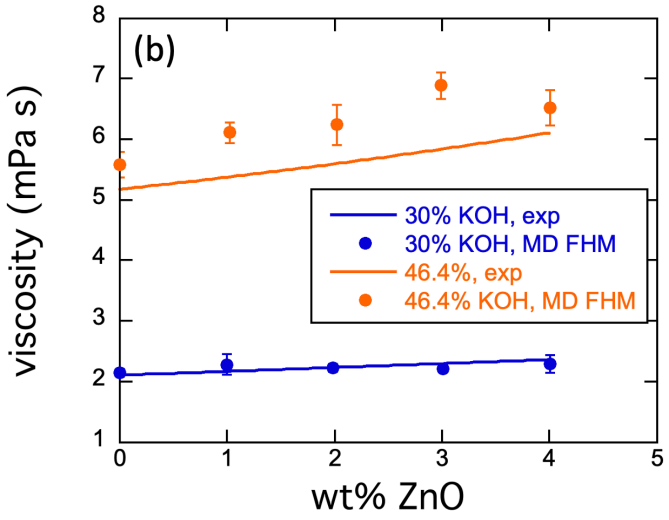


Frischknecht, A. L. & Stevens, M. J. *J. Phys. Chem. B* **2024**, 128, 3475-3484.

Molecular parameters for zincate in KOH solution

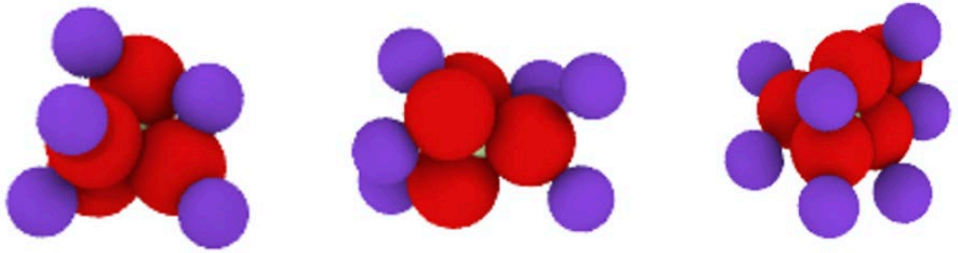






- ab initio calculation to get charges on zincate
- test with force field for aqueous KOH
- use same parameters for OH on zincate
- good agreement with experiment

zincate associates with 5-7 K+ ions

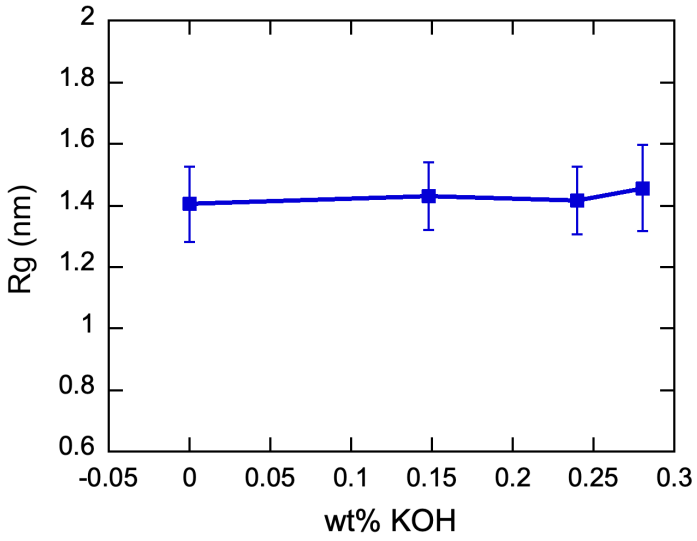


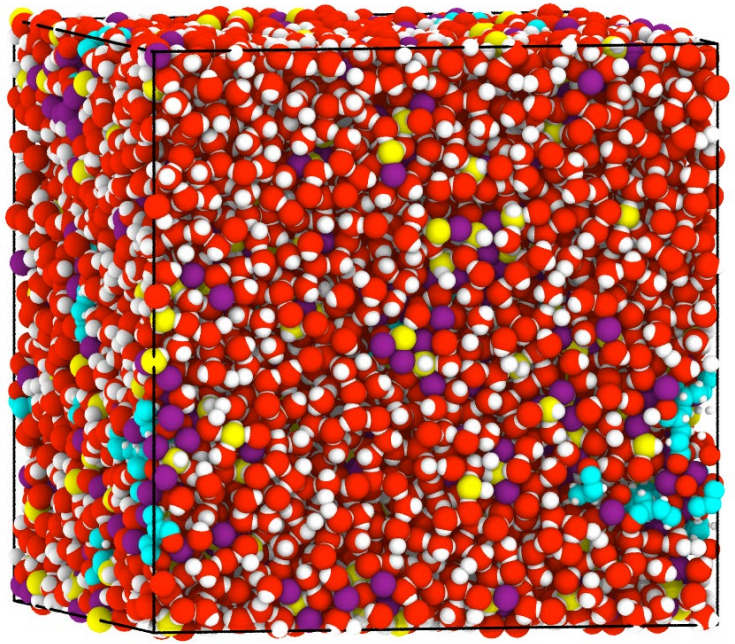
Frischknecht, A. L. & Stevens, M. J. Force Fields for High Concentration Aqueous KOH Solutions and Zincate Ions. *J. Phys. Chem. B* **2024**, 128, 3475-3484.

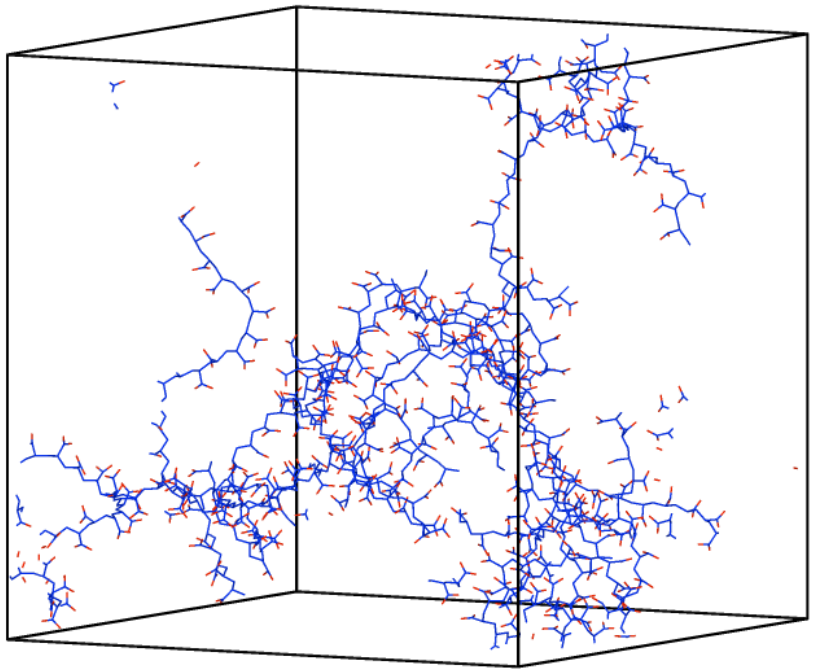
Poly(potassium acrylate)

PAAK chains in aqueous KOH solution

- N = 30 monomers/chain
- 12 chains in the box
- 5 replicas
- final wt% KOH = 15, 24, 28
- use “FHM” parameters for KOH, zincate



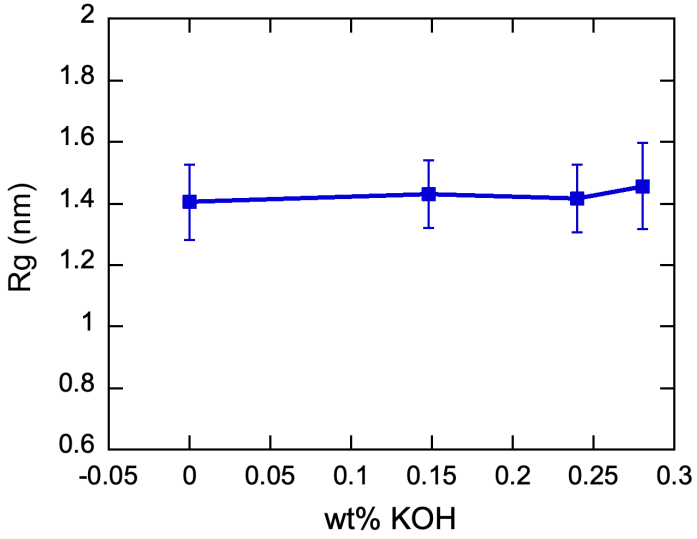


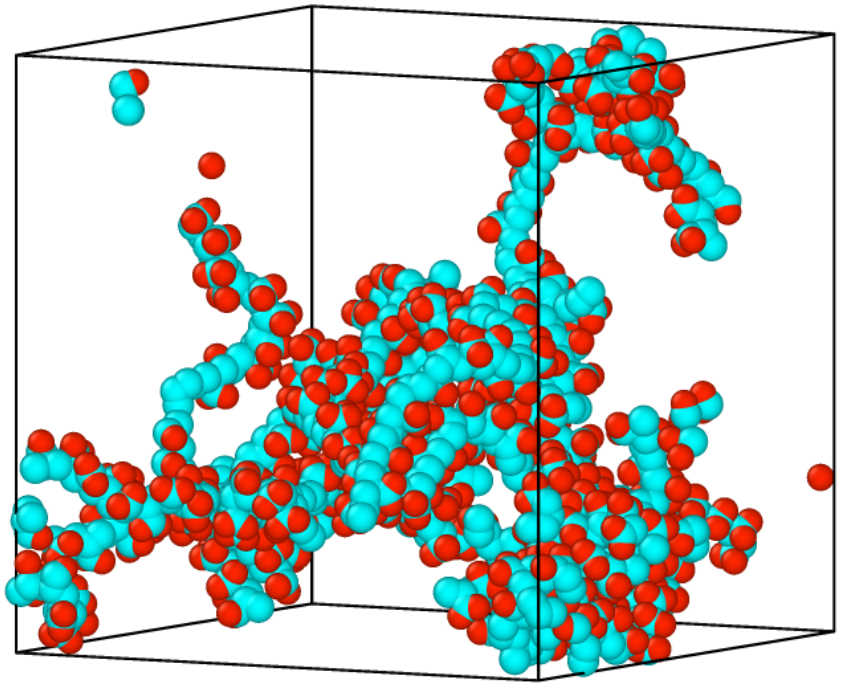


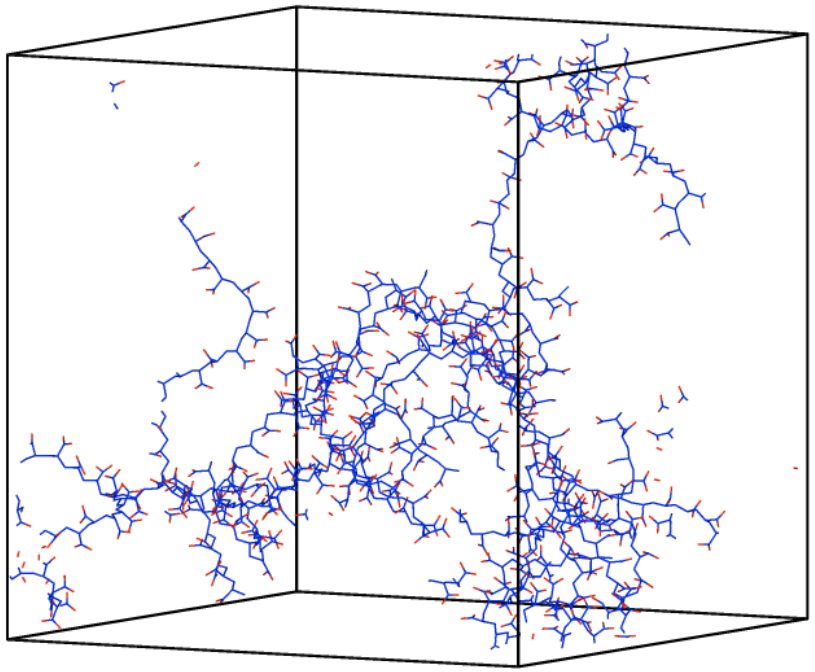
Poly(potassium acrylate)

PAAK chains in aqueous KOH solution

- N = 30 monomers/chain
- 12 chains in the box
- 5 replicas
- final wt% KOH = 15, 24, 28
- use “FHM” parameters for KOH, zincate



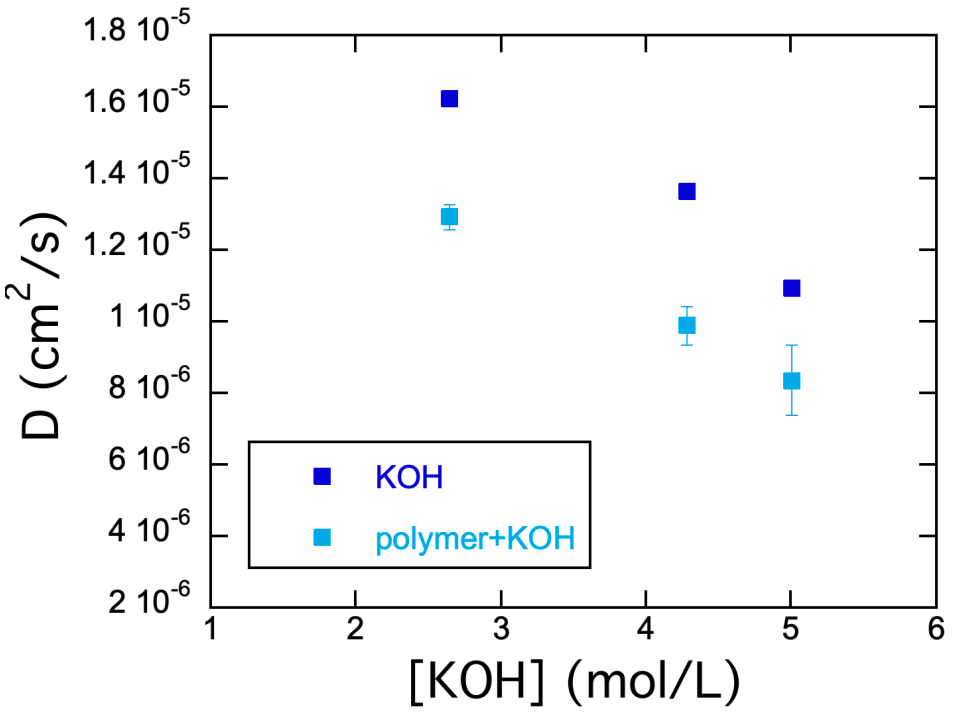




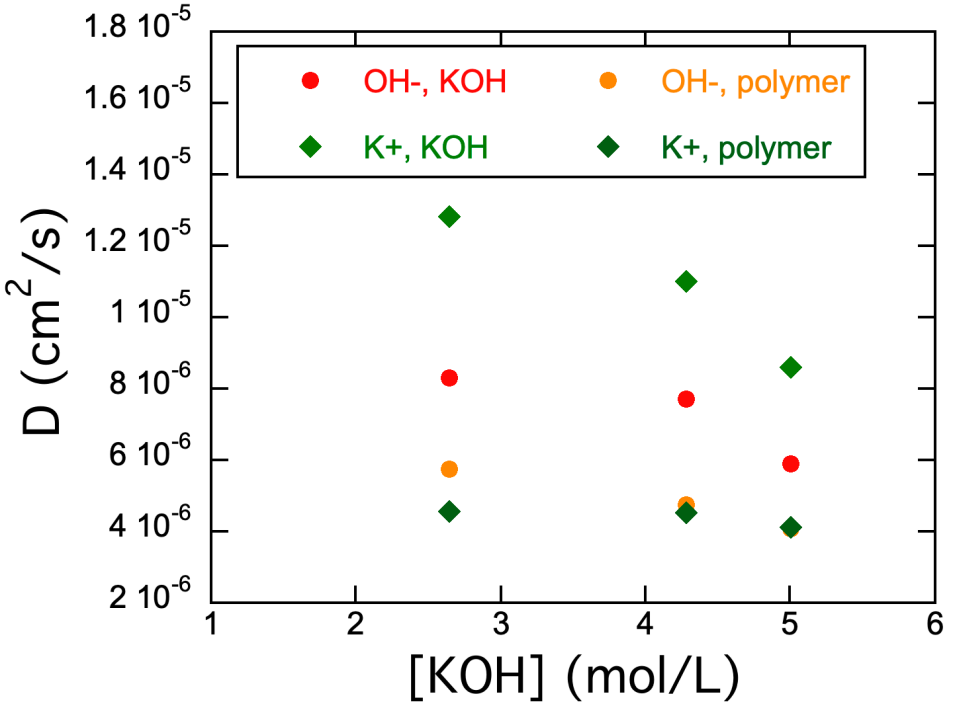
Diffusion in polymer solutions

Polymers are viscous—slows diffusion
ion diffusion is relatively independent of KOH concentration in polymer

water diffusion

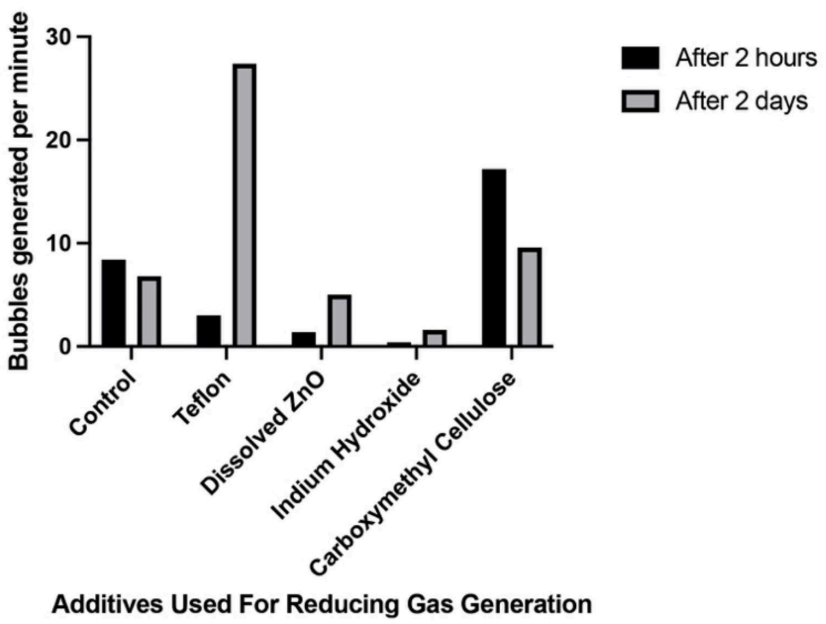


ion diffusion

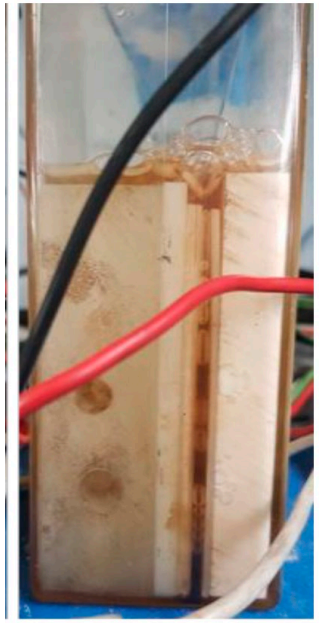


H_2 gas can be a safety issue

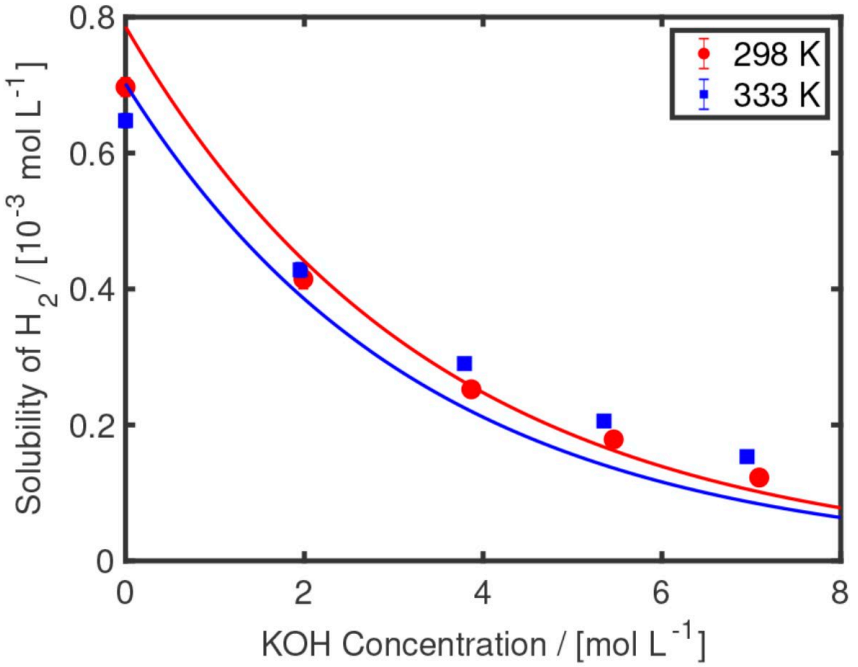
- H_2 evolves from the Zn anode
- H_2 can form bubbles
  - needs to diffuse out safely
  - if can't diffuse, bubbles expand and cause problems



Cho, J., G., Banerjee, S. et al. *Polymers (Basel)* **2022**, 14, 417.



H_2 has low solubility in KOH

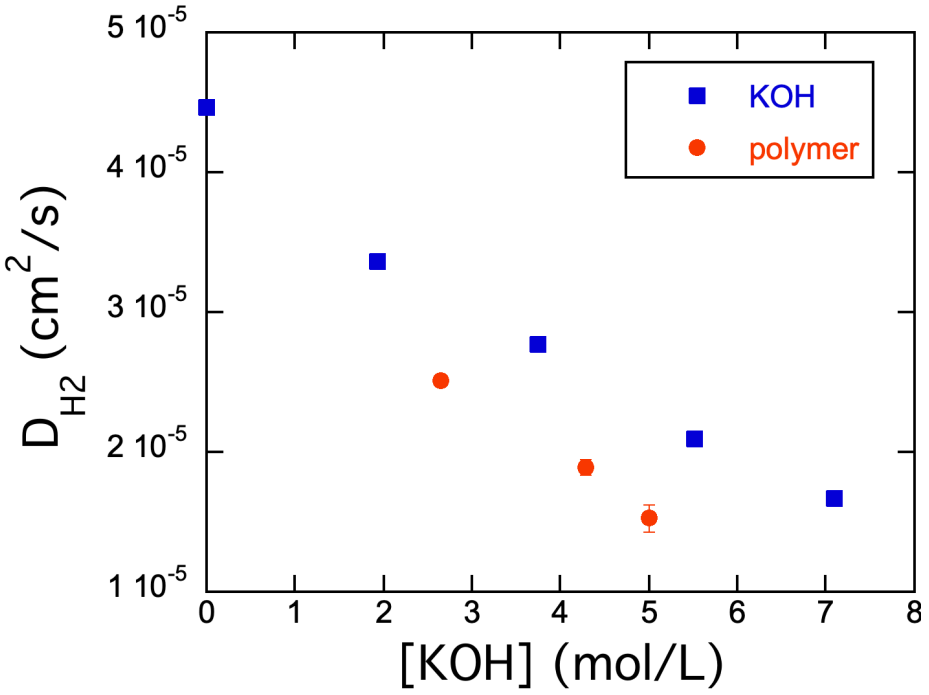


Habibi, P., Rahbari, A., Blazquez, S., Vega, C., Dey, P., Vlugt, T. J. H. & Moultos, O. A. *J. Phys. Chem. B* **2022**, 126, 9376-9387.

Additives can reduce bubble formation, but how does H_2 move through the electrolyte?

H_2 gas moves more slowly in polymers

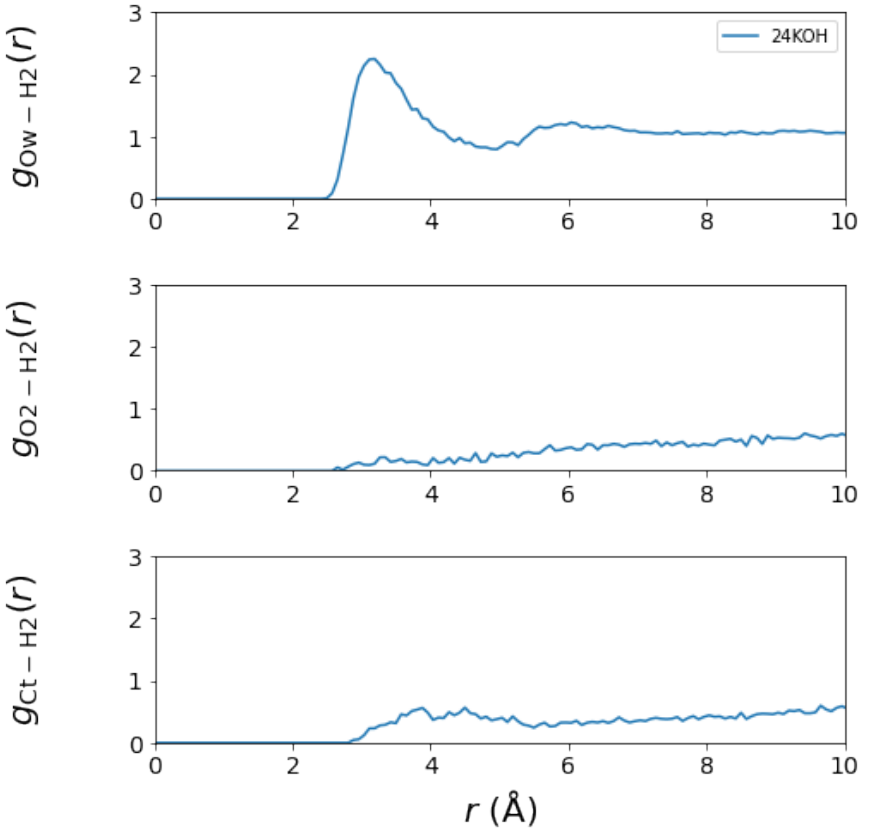
H_2 diffusion decreases in polymer



Slower diffusion could lead to bubble formation

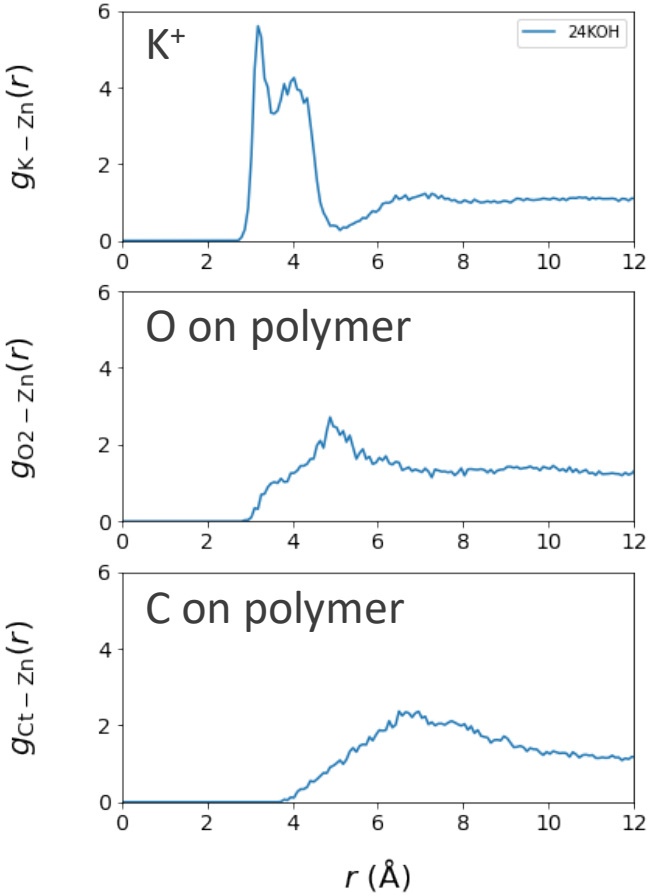
H_2 doesn't interact much with polymer

probability that an atom type is near an H_2 molecule
g(r) < 1: means that H_2 is not near that atom type

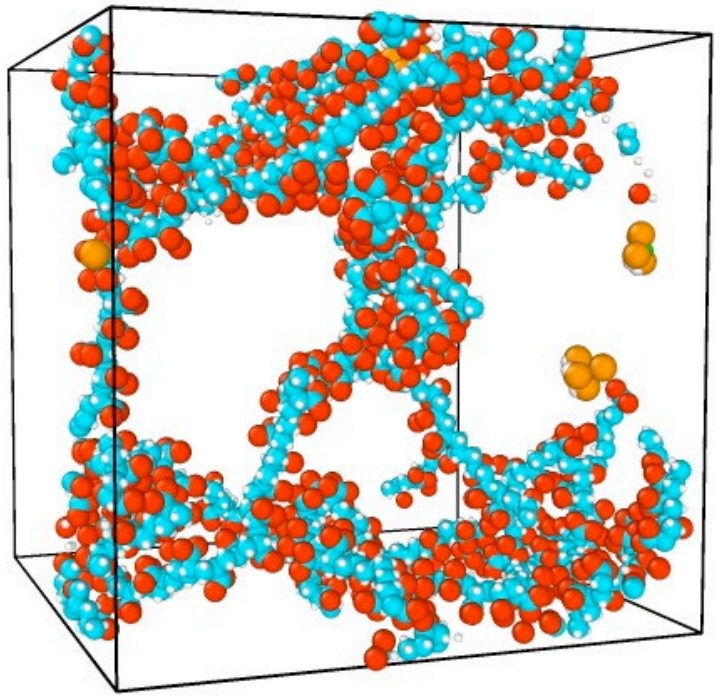


Zincate ions in polymers

zincate mostly associates with K+ ions
associates some with COO^- groups

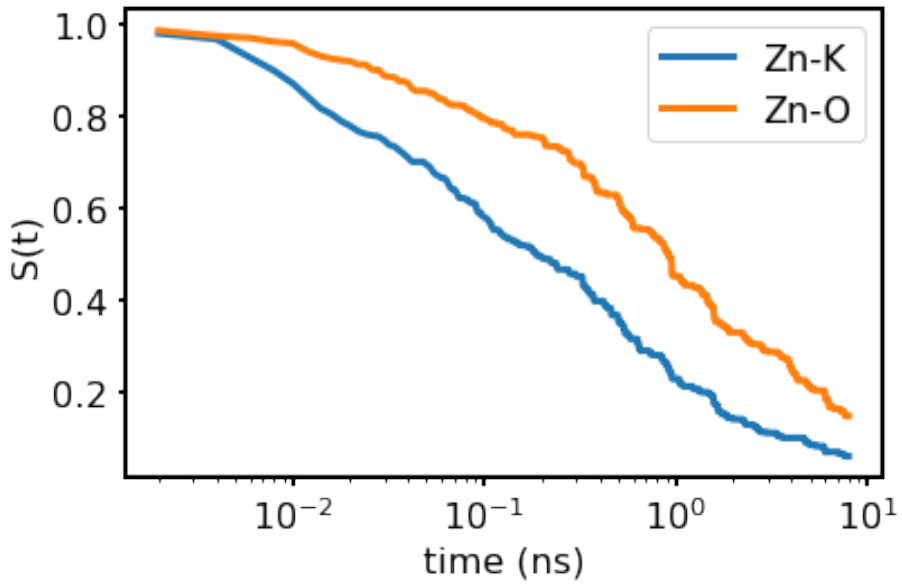


polymer appears to slow zincate diffusion



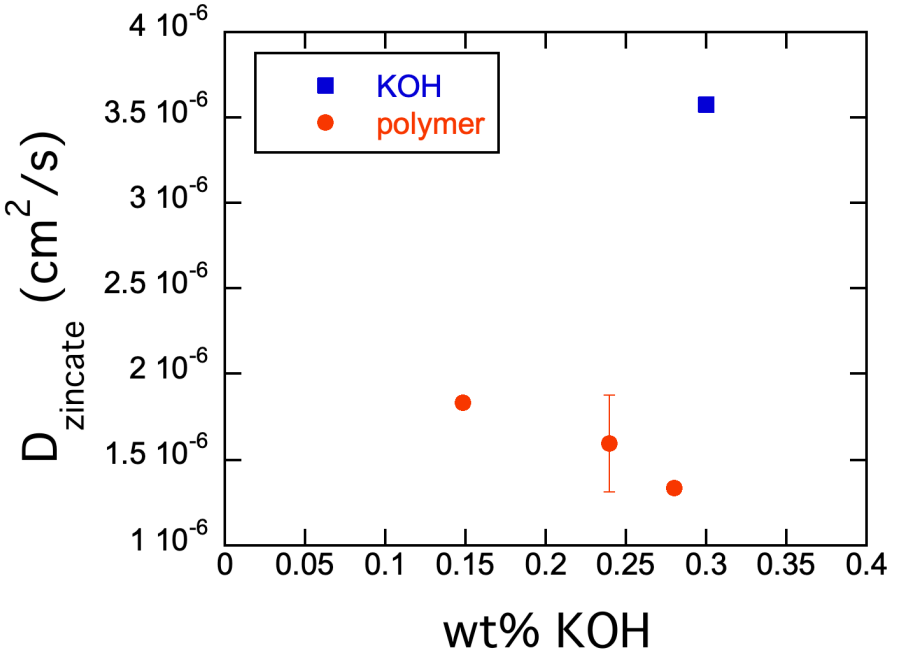
Zincate association times and diffusion

Calculate how long a given zincate ion is associated with a K+ ion or a COO- group on polymer



zincate associated longer with the polymer!

zincate diffusion



zincate diffuses more slowly in polymer

reduction in zincate diffusion can help prevent crossover, unwanted reactions

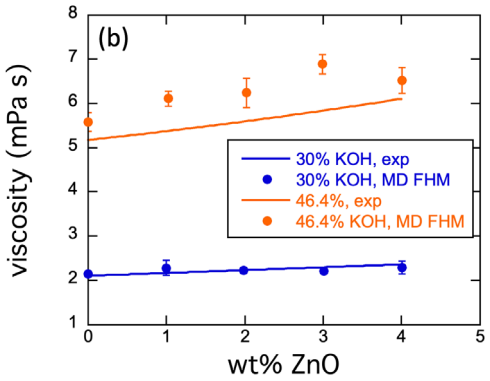
Conclusions

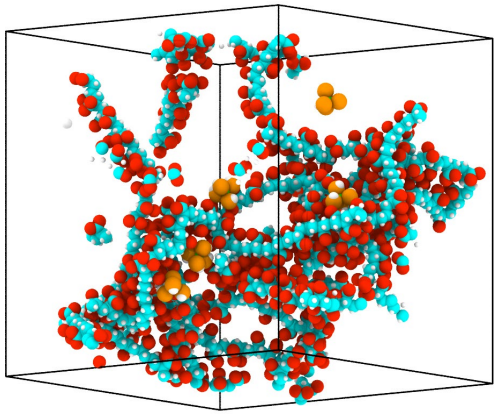
- MD simulations provide molecular-level insight into transport in electrolytes

- trends in physical properties agree with experiment

- H_2 gas diffuses more slowly in polymer electrolyte
  - surprising since H_2 gas doesn't interact much
  - problem if gas gets trapped

- zincate diffuses more slowly in polymer electrolyte
  - despite having same charge as polymer, gets trapped by the polymer

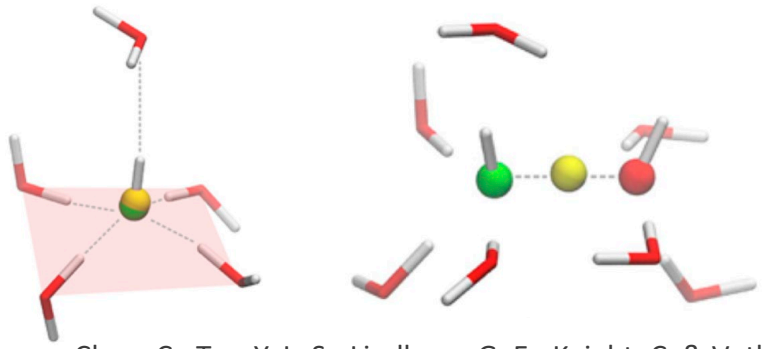




Publication: Frischknecht, A. L. & Stevens, M. J. Force Fields for High Concentration Aqueous KOH Solutions and Zincate Ions. *J. Phys. Chem. B* **2024**, 128, 3475-3484.

Future Work

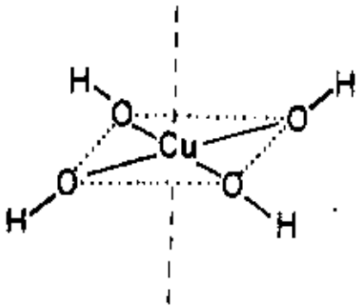
- calculation of polymer solution viscosity
  - is slower transport only due to viscosity changes? or specific interactions?



Chen, C., Tse, Y.-L. S., Lindberg, G. E., Knight, C. & Voth, G. A. *J. Amer. Chem. Soc.* **2016**, 138, 991-1000.

- simulations that include the Grotthuss mechanism for OH^-
  - will enable accurate calculation of conductivity

- *ab initio* MD of zincate, cuprate
  - will allow bonds to form/break
  - more accurate view of complex ions in KOH solution



Chao, Y.-Y. H. & Kearns, D. R. *J Phys Chem*, 1977, 81, 666-668

Acknowledgments

Sandia Team

Cody Bezik

Mark Stevens

Timothy Lambert

This material is based upon work supported by the U.S. Department of Energy, Office of Electricity (OE), Energy Storage Division.

OFFICE OF ELECTRICITY
ENERGY STORAGE PROGRAM

Center for Integrated Nanotechnologies