Sandia National Laboratories

Enabling Simulations of Alkaline Electrolytes in Zinc Batteries

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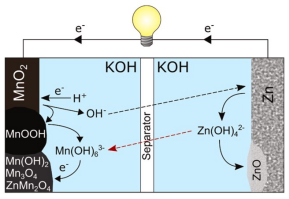
Introduction

Motivation:

- Alkaline Zn/MnO_2 batteries are a priority technology for DOE's grid storage mission
- Improved separators are needed with high OH^- conductivity and low crossover of zincate, $(Zn(OH)_4)^{2-}$



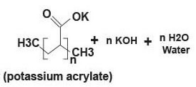
Lim, M. B., Lambert, T. N. & Chalamala, B. R. *Materials Science and Engineering: R: Reports* **2021**, 143, 100593.

Overall goals:

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

Promising Polymeric Separators

gelled poly(potassium acrylate)



Cho, J. et al.. *Polymers* **2022**

Current Work:

- develop accurate models for polymers, electrolytes
- no models in literature for $(Zn(OH)_4)^{2-}$
- limited previous work on poly(potassium acrylate) gels

Methods

LAMMPS

atomistic molecular dynamics (MD) simulations

- OPLS, SPC/E or TIP4P/2005 water
- multiple configurations for better statistics
- Sandia's MD code, LAMMPS

density functional theory for zincate charges

- Gaussian

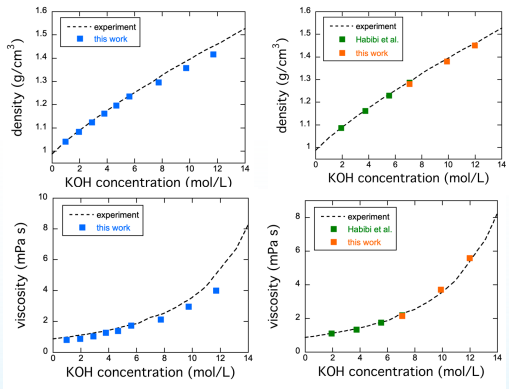
Concentrated KOH Solutions

typical electrolytes: 20-45 wt% KOH (4-12M)

parameters from Netz
OH^- : *J. Chem. Phys.* **2016**, 144, 104503-104511
K^+ : *J Phys Chem B* **2021**, 125, 8581-8587
SPC/E water

parameters from Habibi et al.
J. Phys. Chem. B **2022**, 126, 9376-9387
TIP4P/2005 water

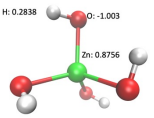
data: Sipos, P. M., Hefter, G. & May, P. M. *Journal of Chemical & Engineering Data* **2000**, 45, 613-617.



- both parameter sets good
- Habibi more accurate at high concentrations

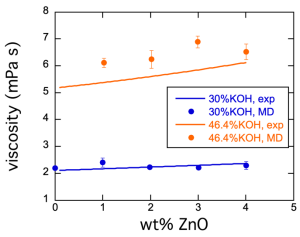
Zincate/KOH Solutions

- use *ab initio* charges
- experimental geometry
- combine parameters with Habibi model

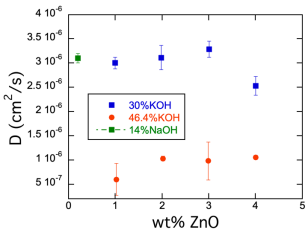


zincate data:
Siu, S. & Evans, J. W. *J Electrochem Soc* **1997**, 144, 1278; Kimura, K. et al. *Anal Chem* **2020**, 92, 9956-9962.

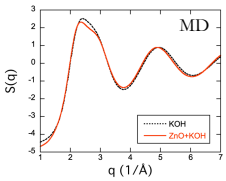
viscosity

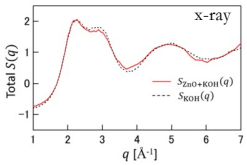


zincate diffusion constant

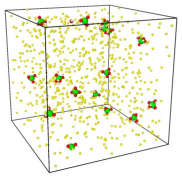


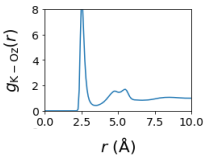
scattering agrees with experiment





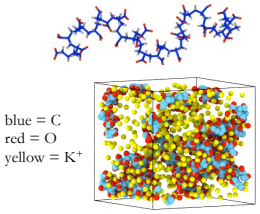
Kimura et al, *Anal Chem* **2020**, 92, 9956-9962.



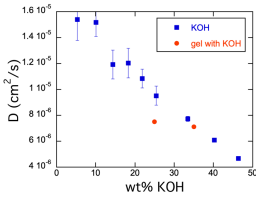


- zincate well distributed (no big clusters)
- 4.66 K+ ions coordinate with each zincate ion

PAAK Gel Electrolytes



Netz parameters



Preliminary findings:

- OH^- diffusion decreases with increasing KOH
- OH^- moves slower in gel than in neat KOH

Future Work

- complete simulations of poly(potassium acrylate) gels in KOH
  - diffusion mechanism of OH^-, zincate
  - diffusion mechanism of H_2 gas in the gel
- determine gel parameters to enhance H_2 diffusion, reduce zincate diffusion

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