Sandia National Laboratories

SIMULATIONS OF COMPLEX ION STRUCTURE IN KOH ELECTROLYTES FOR ZINC BATTERIES

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PROJECT PROFILE

Topic: Zinc & Lead Batteries | Vertical: Materials & Systems Innovation

Strategic Pathway: Grow

Project start and finish: FY24-FY26

PROBLEM

Motivation:

- DOE/OE goal is to develop energy storage technologies that use safe, low-cost, and earth-abundant elements
- The US needs reliable and affordable storage for utilities, industrial facilities, and infrastructure

Problem:

- In zinc batteries, complex ions such as zincate $(Zn(OH)_4)^{2-}$ and cuprate $(Cu(OH)_4)^{2-}$ form and cause unwanted reactions
- There is little understanding of the basic physical chemistry of these ions in the literature

APPROACH AND GAS PHASE RESULTS

Ab initio molecular dynamics (AIMD) simulations

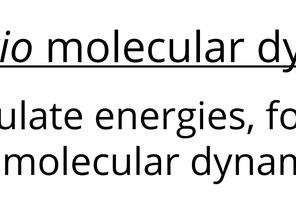
- Calculate energies, forces on the fly from DFT
- Run molecular dynamics simulations

Advantages	Disadvantages
• More accurate than classical MD	• Slower than classical MD
• Allows bond breaking/forming	• Small system sizes, short times
	• Still involves approximations

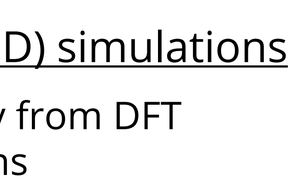
Research questions

- How accurate are MD force fields for ions in KOH?
- What are the structures of zincate and cuprate ions in high concentration KOH solution?

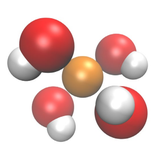
Proposed $Cu(OH_4)^{-2}$ structure[1] (planar)

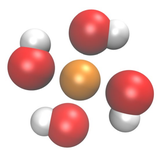


$Zn(OH_4)^{-2}$ structure[2] (tetrahedral)



Geometry optimization confirms planar structure for $Cu(OH_4)^{-2}$

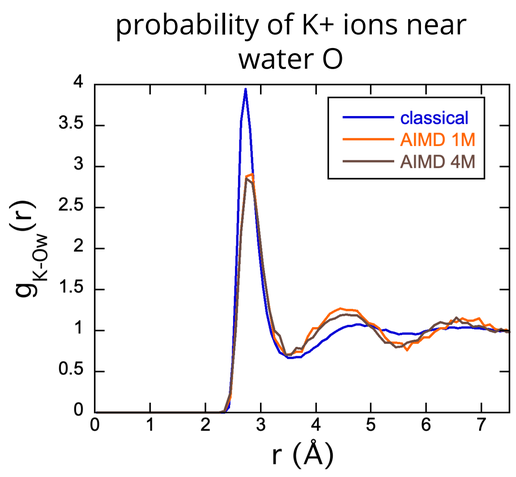


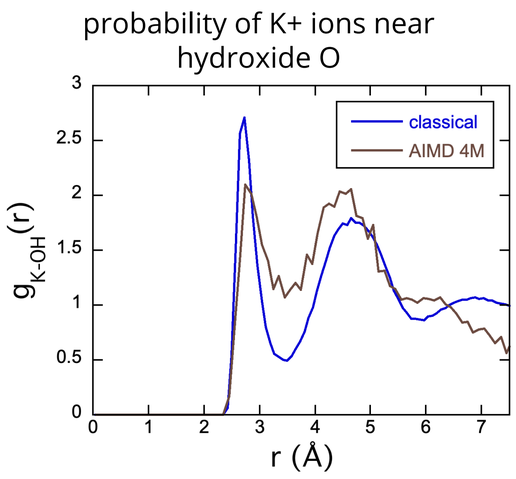


Planar structure has lower energy by ΔE = 11.1 kcal/mol

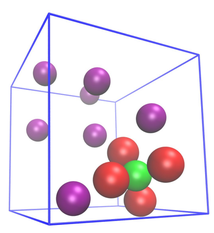
RESULTS IN SOLUTION

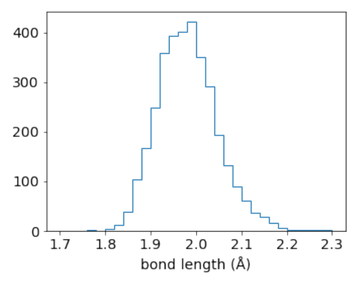
Solvation in KOH: 1M and 4M KOH



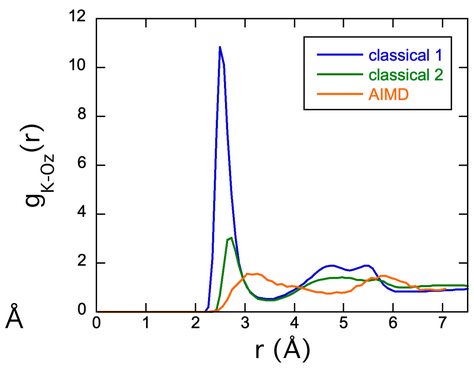


Zincate in KOH





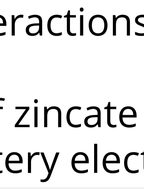
average bond length 1.98 Å



- Classical results might not capture local structure
- Overestimate zincate/K+ clustering

Cuprate in KOH

- Still mostly planar
- Average Cu-O bond length 1.85 Å



CONCLUSIONS & IMPACT

- Classical force fields[2] for KOH agree with *ab initio* results
- Classical force field for zincate[2] overestimates clustering
- Cuprate has planar structure as proposed

Impact

- Results from AIMD will inform better force fields
- Increased accuracy in future simulations of Zn battery electrolytes → better predictions of battery performance

FUTURE DIRECTIONS

- Complete study of structure and interactions in KOH solutions and publish journal article
- Use results to build better models of zincate and cuprate in KOH for future simulations of battery electrolytes

References

[1] Chao, Y.-Y. H. & Kearns, D. R. Electron spin resonance investigation of the soluble blue copper (II) hydroxide complex. J Phys Chem, 1977, 81, 666-668.
[2] 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.

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

SAND2026-23841C