

Molecular Dynamics Simulations of Liquid and Polymer Electrolytes for Energy Storage Devices



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Summary

At NASA, we are researching new battery technologies to enable **electric airplanes**. A key focus is the design of electrolytes with improved stability.

Molecular dynamics (MD) simulations are an invaluable tool for studying electrolytes. They can:

Dimethoxyethane

DME-based electrolytes with Li[TFSI] and Na[TFSI] salts are widely used in Li-O₂ and Na-O₂ batteries due to relatively high cyclability. We are using polarizable MD simulations to explore their solvation structures.

Polyanions

Polyanions yield unity lithium transference numbers, but low ionic conductivities. Our bead-spring MD simulations investigate the effects of the polymer chain architecture on the ionic aggregation and cation dynamics.

- Evaluate structural, thermodynamic, and transport properties with qualitative or quantitative accuracy;
- Provide important molecular-level details often inaccessible to experimental techniques;
- Couple with other computational tools, such as quantum chemistry calculations and multiphysics models, for a more complete multi-scale description.

We illustrate several relevant examples from studies performed by the **computational materials group** at the NASA Ames Research Center.

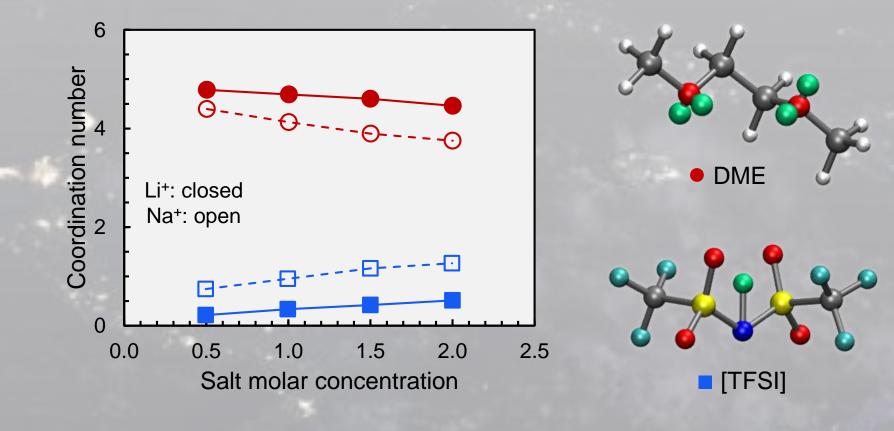
Ionic Liquids

Based on our computational studies of two ionic liquids, [pyr14][TFSI] and [EMIM][BF₄], we propose [pyr13][FSI] for improved performance with Li metal anodes.

Electronic stability with Li anode:

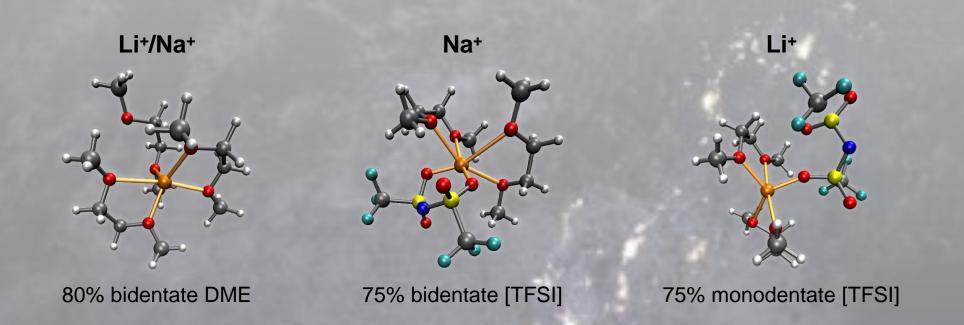
- [pyr14][TFSI] cycles longer due to conductive SEI.
- Ab initio MD simulations show vastly different behavior

- Coordination numbers:
- Both Li⁺ and Na⁺ are primarily coordinated by DME due to favorable interactions with the solvent.
- Cation binding energies are stronger for Li⁺ than Na⁺.

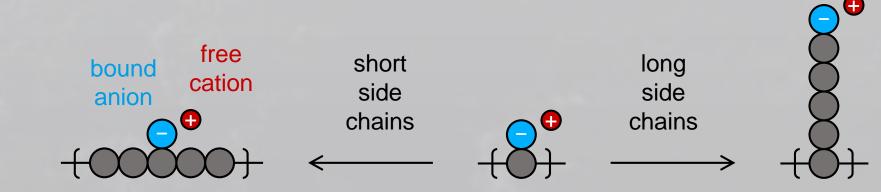


Oxygen coordination denticity:

- Bidentate DME are more common for both Li⁺ and Na⁺.
- Bidentate [TFSI] are more stable for Na⁺ than Li⁺, due to the larger solvation shell of Na⁺.



Bead-spring models:

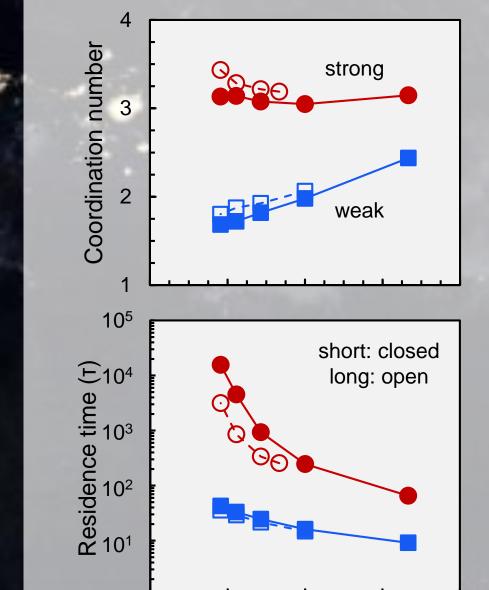


Longer side chains yield:

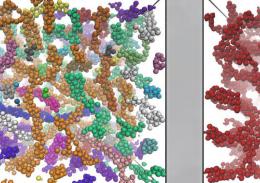
- Greater ionic aggregation (percolated aggregates);
- Faster cation dynamics along percolated ionic pathways.

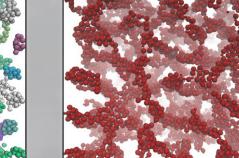
Stronger ionic interactions yield:

- Greater coordination and aggregation of ions;
- Slower cation dynamics due to longer ion residence times.



Strong ionic interactions:

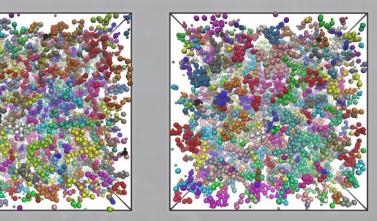




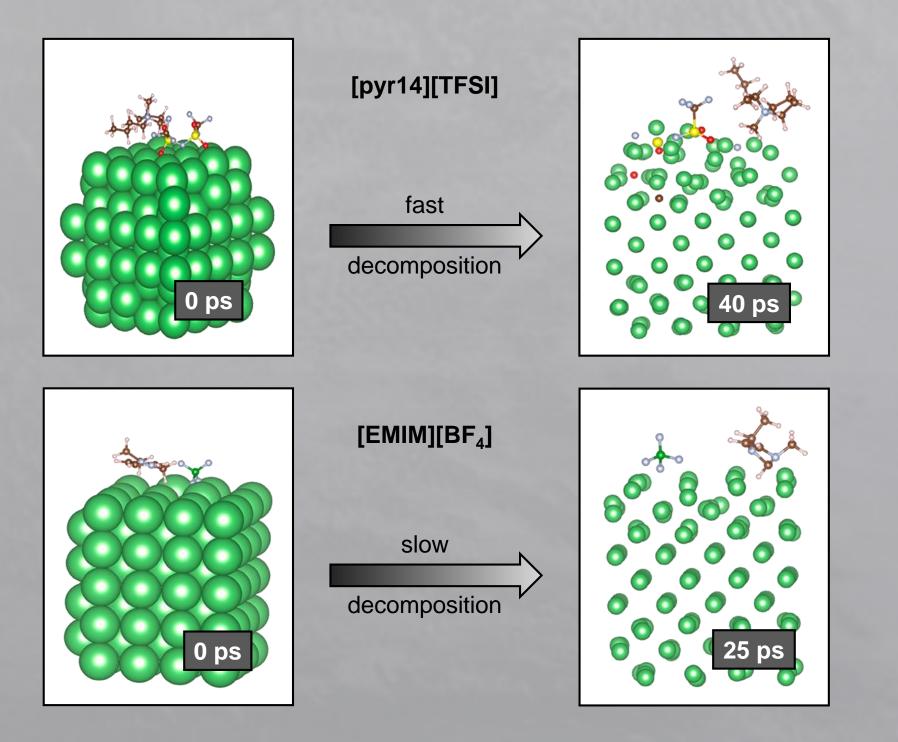
O lona

short

Weak ionic interactions:



of the ionic liquids at the Li surface.⁶



Ionic conductivities:

- Although more stable to the Li anode, [pyr14][TFSI] has low ionic conductivities.
- Polarizable MD simulations indicate that ion mobility is improved by reducing the ion solvation size.¹
- [pyr13][FSI] balances high mobility with stability.

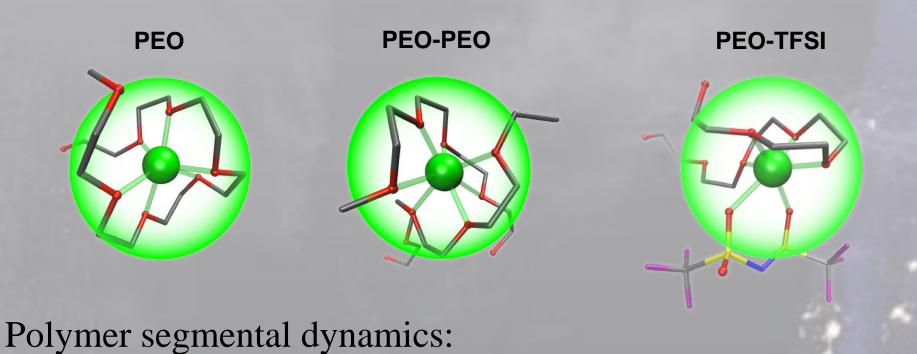
[1] T. P. Liyana-Arachchi, J. B. Haskins, C. M. Burke, K. M. Diederichsen, B. D. McCloskey, and J. W. Lawson, *in review*.

Polyethylene Oxide

PEO/Li-salt mixtures have been extensively investigated as electrolytes, but their ionic conductivities tend to be low at room temperature. Using polarizable MD simulations, we are elucidating the dynamics in PEO/Li[TFSI].

Li⁺ solvation:

- PEO forms helical structures that highly coordinate and tightly bind Li⁺ with consecutive oxygen atoms.
- Li⁺ transport is governed by polymer segmental motion.



 10° 0.0 0.2 0.4 0.6 0.

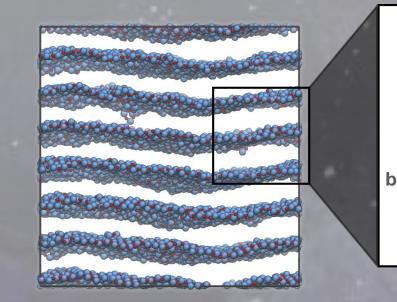
Ion fraction

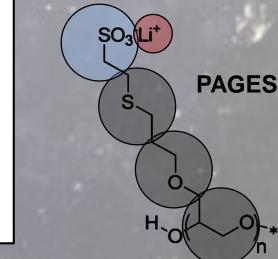
short long

*systems with ion fraction = 0.29, only ions shown, colored by aggregate

Layered ionic structures:

Formed for two long-side-chain bead-spring models.
Polymer backbone layers are formed between ionic layers.
Consistent with experimental X-ray scattering for PAGES.



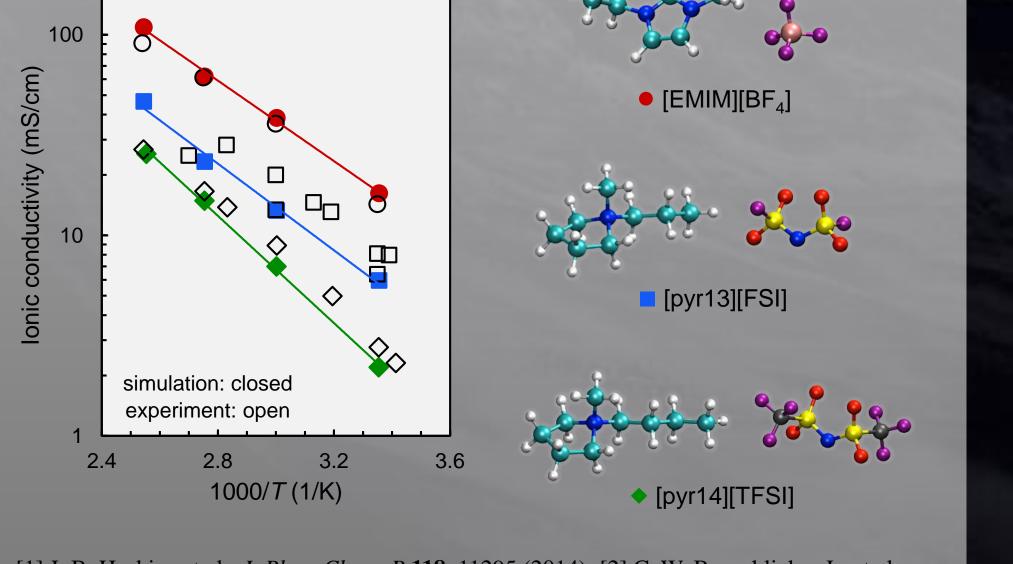


[1] L. J. Abbott and J. W. Lawson, *in preparation*; [2] L. J. Abbott, H. G. Buss, B. D. McCloskey, and J. W. Lawson, *in preparation*.

Methods

Ab initio MD simulations:

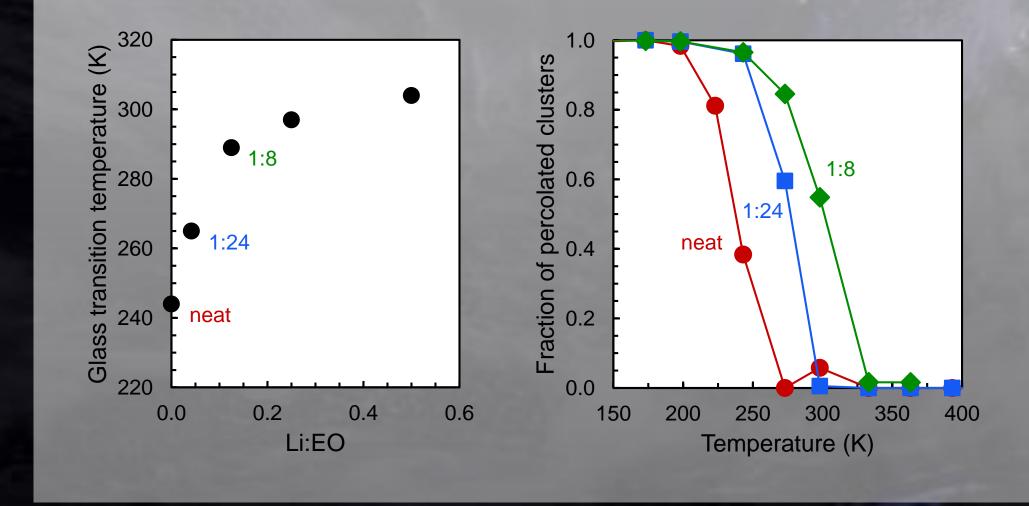
• Energetics are described based on density functional theory (DFT),



[1] J. B. Haskins et al., *J. Phys. Chem. B* 118, 11295 (2014); [2] C. W. Bauschlicher Jr. et al., *J. Phys. Chem. B* 118, 10785 (2014); [3] J. B. Haskins et al., *J. Phys. Chem. B* 119, 14705 (2015); [4] J. B. Haskins and J. W. Lawson, *J. Chem. Phys.* 144, 184707 (2016); [5] J. B. Haskins et al., *J. Phys. Chem. C* 120, 11993 (2016); [6] H. Yildirim et al., *J. Phys. Chem. C* 121, 28214 (2017); [7] J. B. Haskins et al., J. Phys. Chem. C 121, 28235 (2017).

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- The glass transition temperature increases with salt concentration; systems are glassy for Li:EO \geq 0.3.
- The glass transition corresponds with the onset of percolated clusters of temporarily immobile monomers.



where electron densities are taken into account.

- These high fidelity models allow bond breaking and formation, but are limited to smaller system sizes and simulation times.
- Simulations were performed in VASP.

Polarizable MD simulations:

- Energetics are described using a classical force field that includes atomic polarizability with induced dipoles (APPLE&P).
- This type of force field provides more accurate dynamics.Simulations were performed in LAMMPS.

Bead-spring MD simulations:

- Energetics are described using a simple bead-spring model with repulsive and Coulombic nonbonded interactions.
- This model significantly reduces the degrees of freedom, allowing larger system sizes and simulation times to be accessed.
- Simulations were performed in LAMMPS.

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