

Lauren J. Abbott,<sup>1</sup> Justin B. Haskins,<sup>1</sup> Thilanga P. Liyana-Arachchi,<sup>1</sup> Charles W. Bauschlicher, Jr.,<sup>2</sup> and John W. Lawson<sup>2</sup>

<sup>1</sup>AMA Inc. and <sup>2</sup>NASA Ames Research Center, Moffett Field, California

## 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:

- 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.

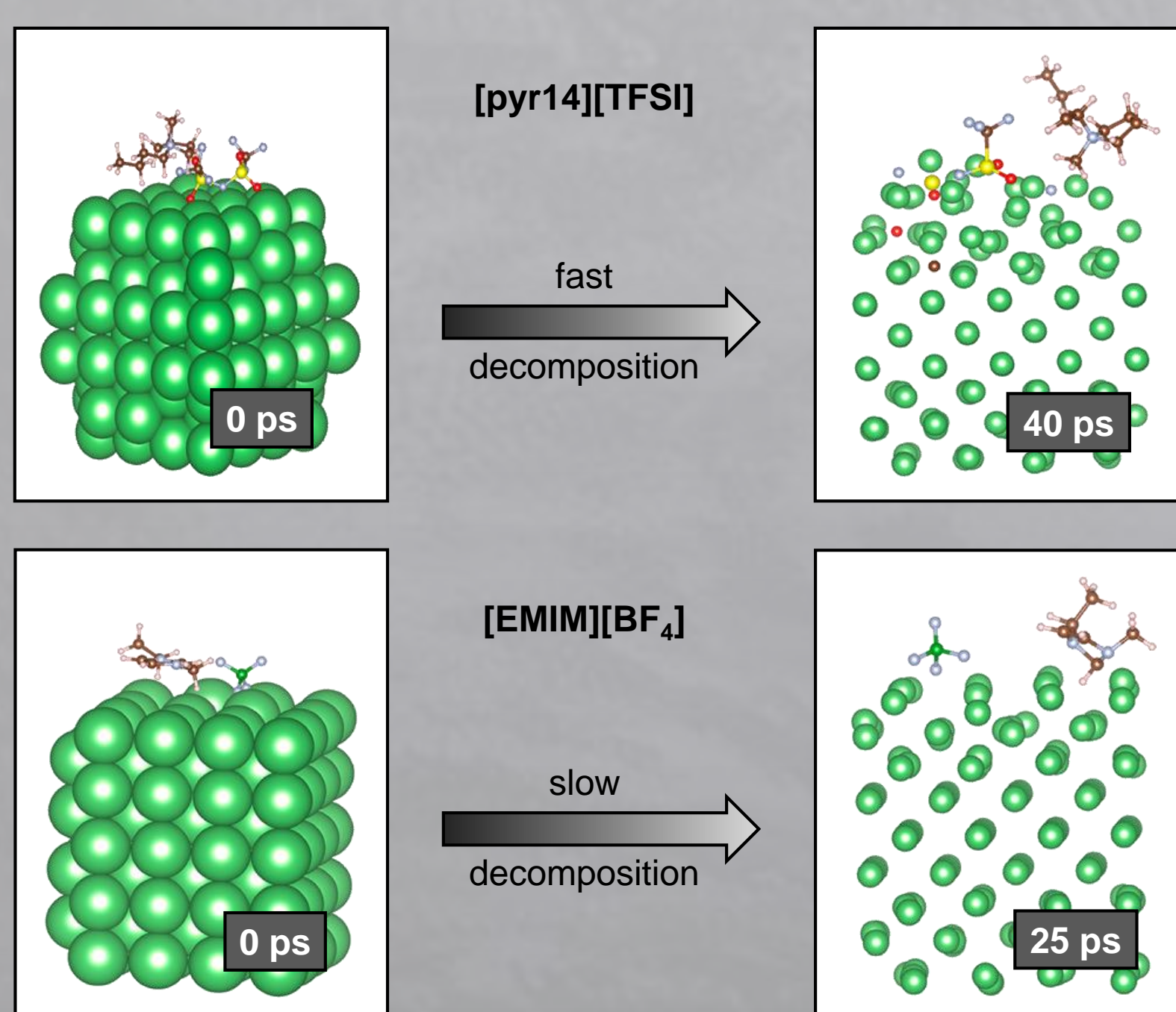
We illustrate several relevant examples from studies performed by the **computational materials group** at the NASA Ames Research Center.

## Ionic Liquids

Based on our computational studies of two ionic liquids, [pyr14][TFSI] and [EMIM][BF<sub>4</sub>], we propose [pyr13][FSI] for improved performance with Li metal anodes.

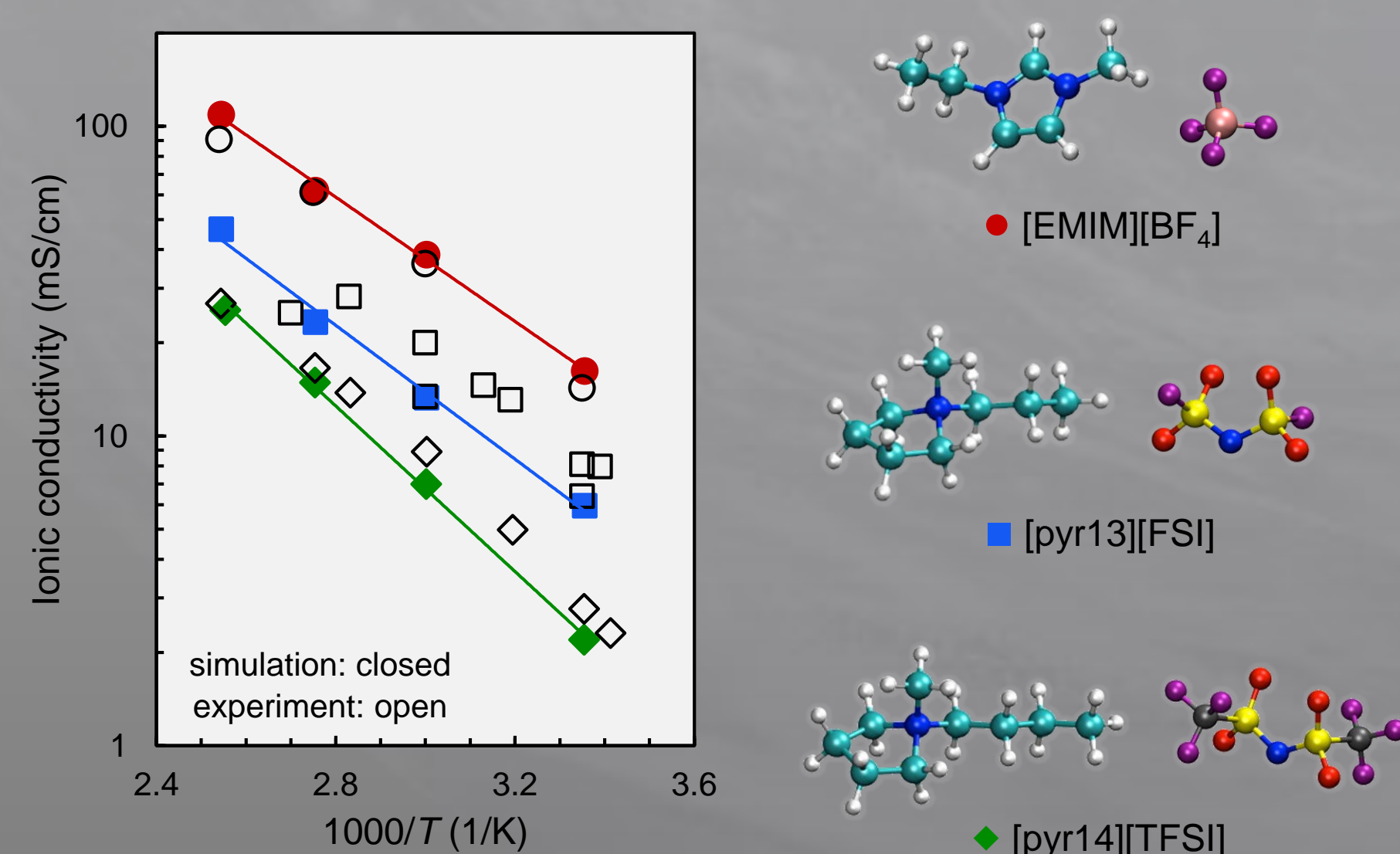
Electronic stability with Li anode:

- [pyr14][TFSI] cycles longer due to conductive SEI.
- Ab initio MD simulations show vastly different behavior of the ionic liquids at the Li surface.<sup>6</sup>



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.<sup>1</sup>
- [pyr13][FSI] balances high mobility with stability.



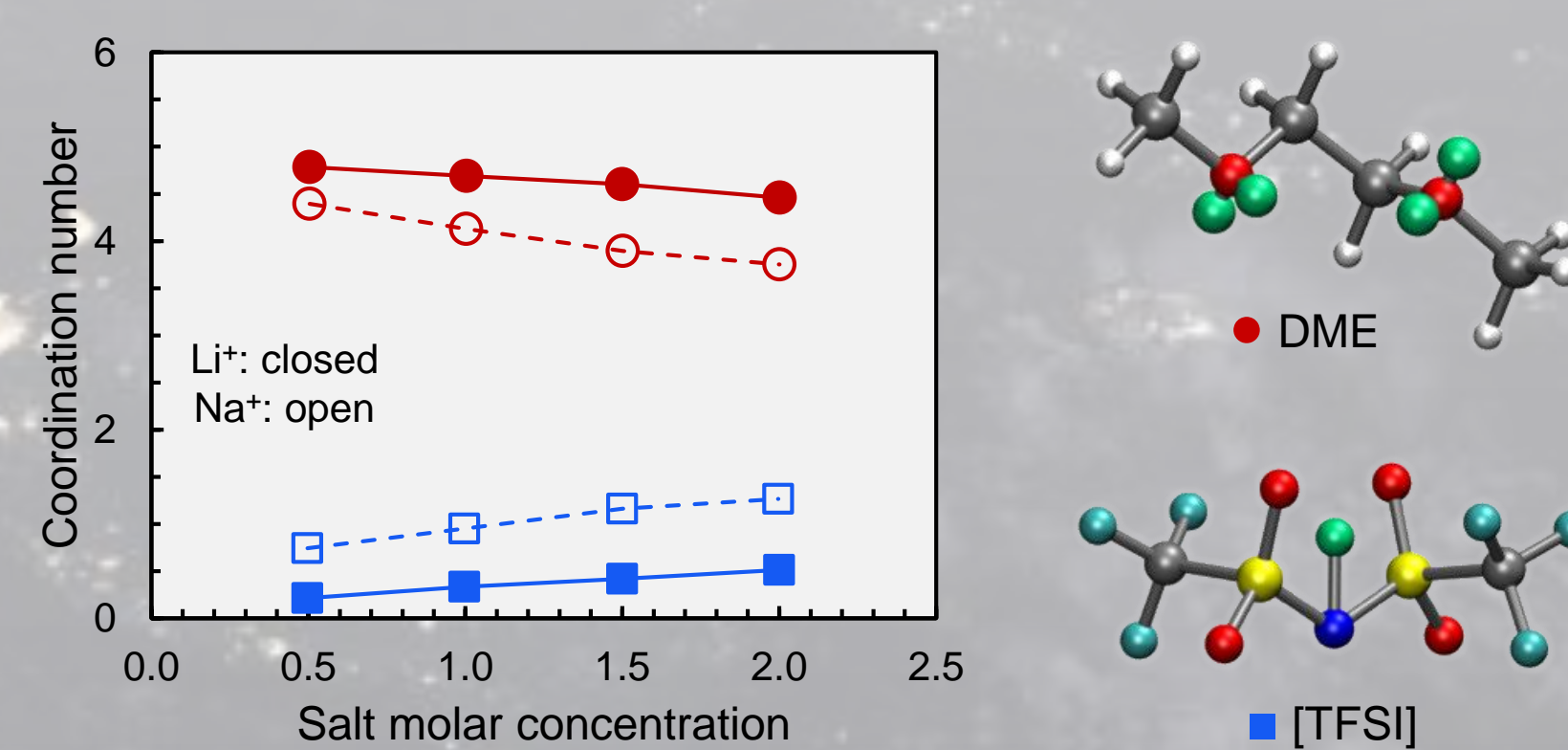
[1] J. B. Haskins et al., *J. Phys. Chem. B* **118**, 11295 (2014); [2] C. W. Bauschlicher Jr. et al., *J. Phys. Chem. B* **118**, 10785 (2014); [3] J. B. Haskins et al., *J. Phys. Chem. B* **119**, 14705 (2015); [4] J. B. Haskins and J. W. Lawson, *J. Chem. Phys.* **144**, 184707 (2016); [5] J. B. Haskins 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).

## Dimethoxyethane

DME-based electrolytes with Li[TFSI] and Na[TFSI] salts are widely used in Li-O<sub>2</sub> and Na-O<sub>2</sub> batteries due to relatively high cyclability. We are using polarizable MD simulations to explore their solvation structures.

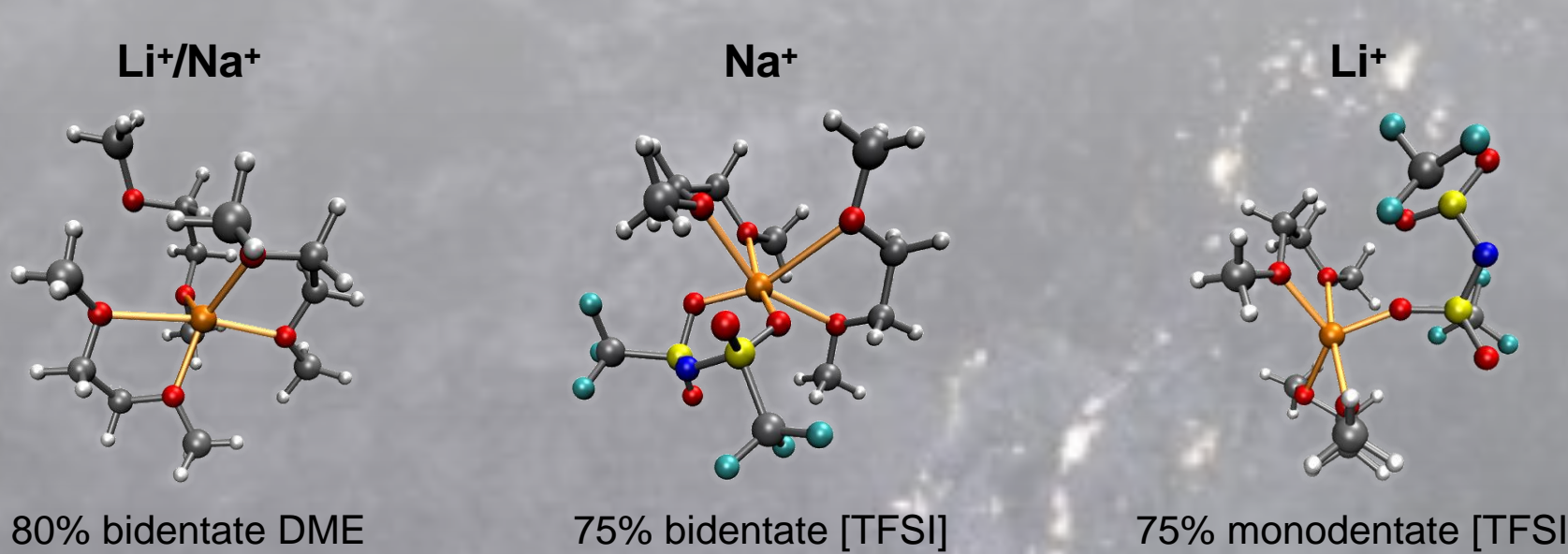
Coordination numbers:

- Both Li<sup>+</sup> and Na<sup>+</sup> are primarily coordinated by DME due to favorable interactions with the solvent.
- Cation binding energies are stronger for Li<sup>+</sup> than Na<sup>+</sup>.



Oxygen coordination denticity:

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



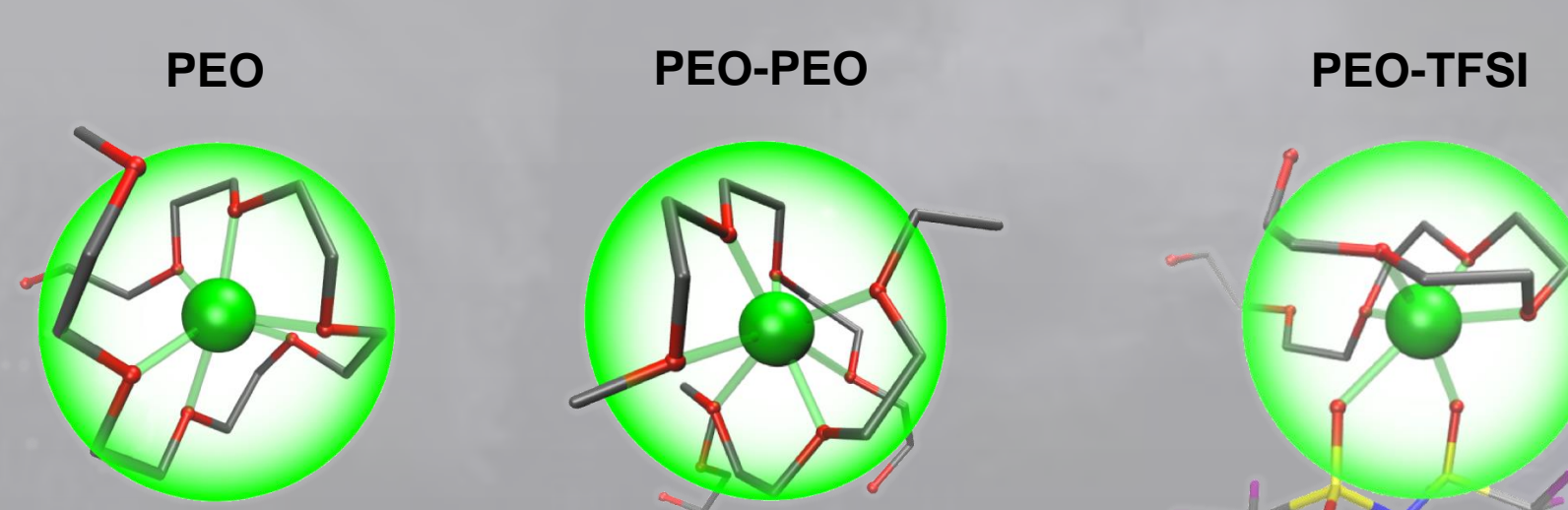
[1] T. P. Liyana-Arachchi, J. B. Haskins, C. M. Burke, K. M. Diederichsen, B. D. McCloskey, and J. W. Lawson, *in review*.

## 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].

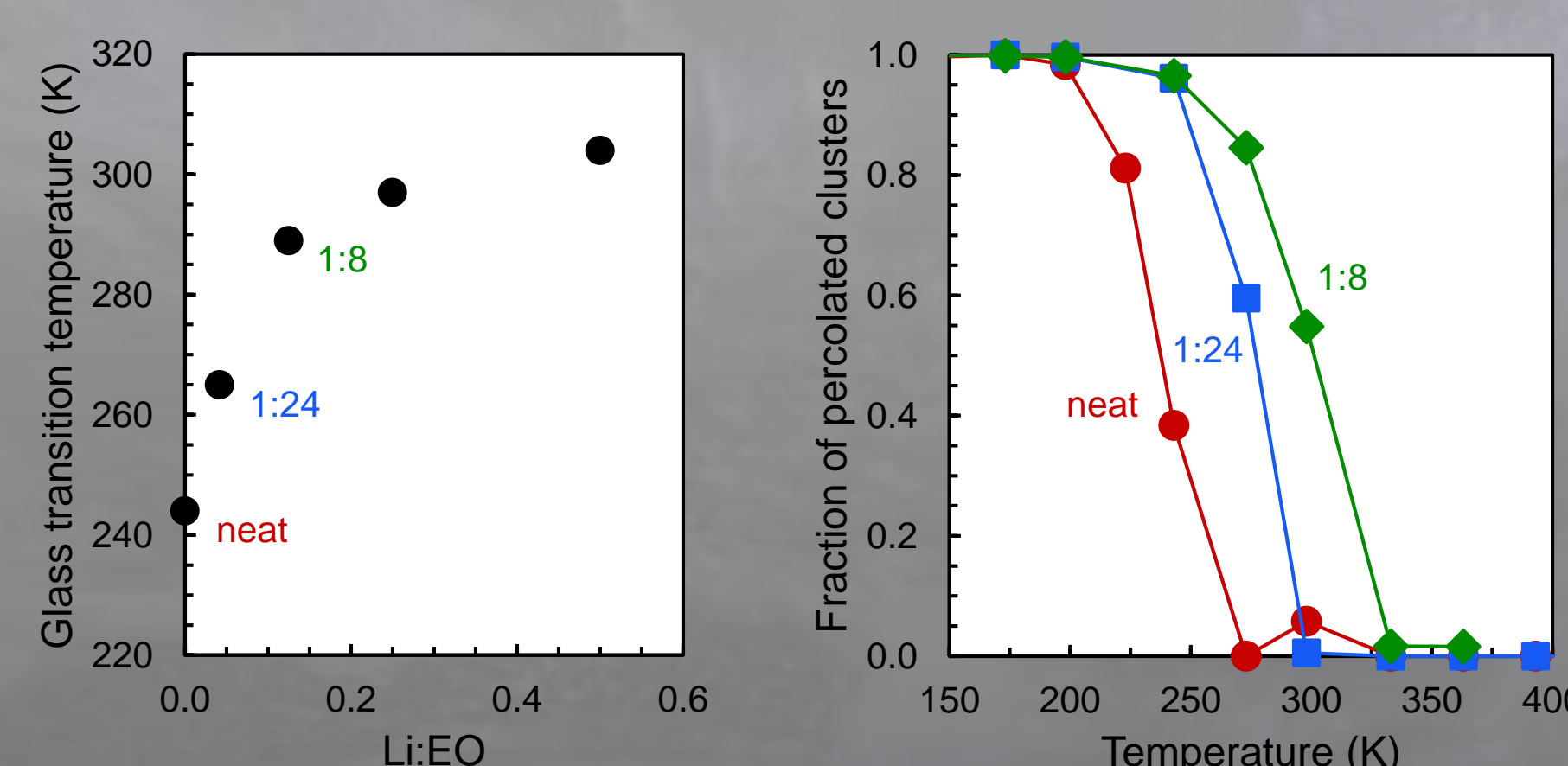
Li<sup>+</sup> solvation:

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



Polymer segmental dynamics:

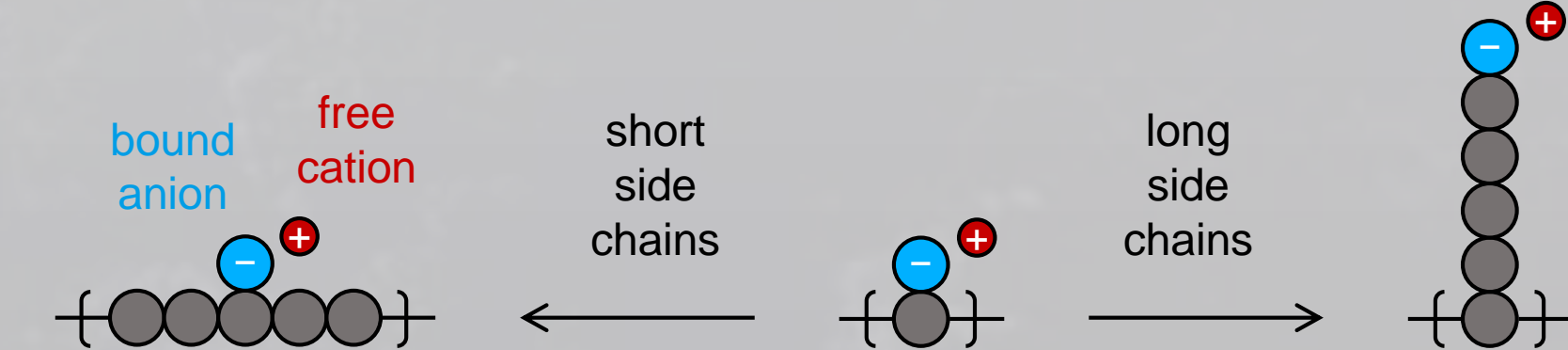
- The glass transition temperature increases with salt concentration; systems are glassy for Li:EO ≥ 0.3.
- The glass transition corresponds with the onset of percolated clusters of temporarily immobile monomers.



## 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.

Bead-spring models:

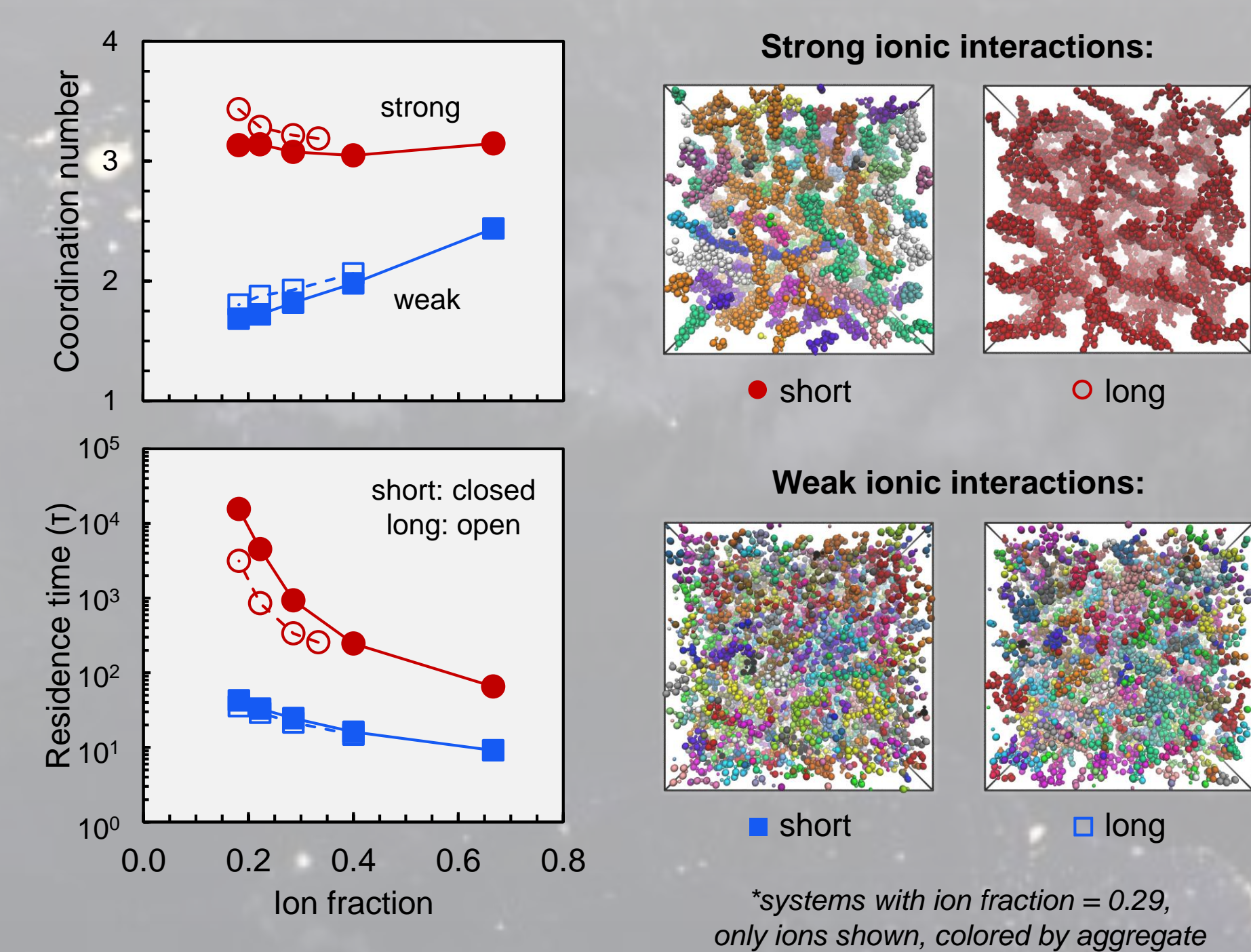


Longer side chains yield:

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

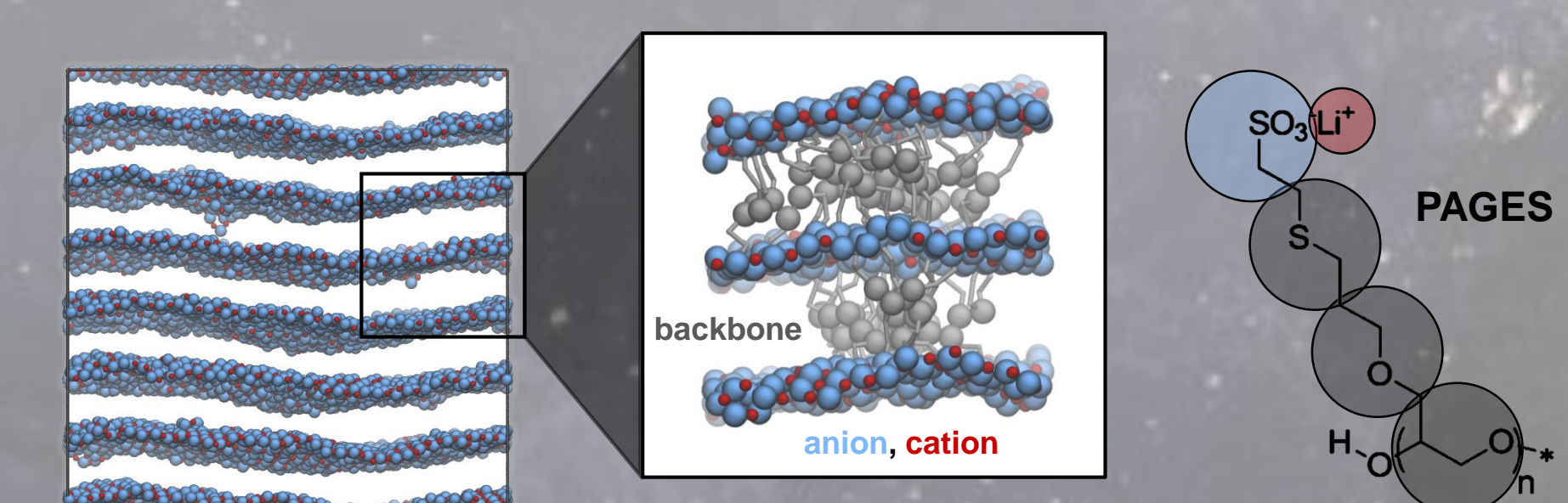
Stronger ionic interactions yield:

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



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), 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.