Molecular Dynamics Simulations of Electrolyte Solutions for Organic Redox Flow Batteries

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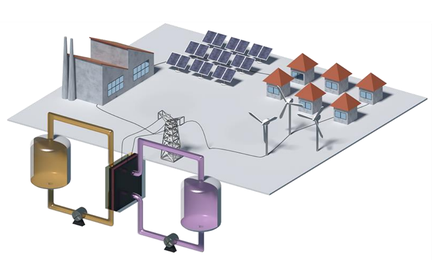
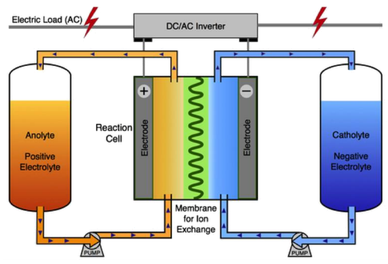
Introduction

Efficient storage of energy is required to meet the goals associated with the large-scale application of the renewable energy resources like wind and solar. Organic redox-flow batteries (ORFBs) are promising since they utilize tunable and eco-friendly organic molecules instead of expensive metals. ORFBs employ liquid electrolytes and have four major elements: electrolyte, electrodes, membranes, and a system through which fluids are circulated.

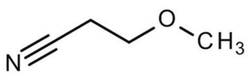




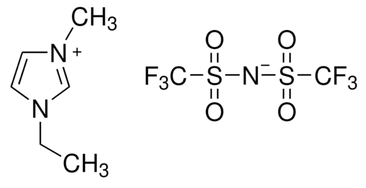
The electrolyte is composed of: 1- redox active species (RAMs), 2- solvent, and 3- support electrolyte.

Acetonitrile

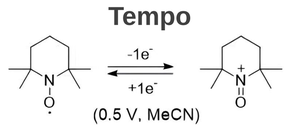
3-methoxypropionitrile



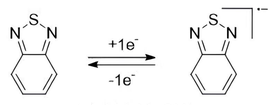
EMIMTFSI



Tempo



Benzothiadazole



The behavior of ORFBs is depends on the way the molecules in the electrolyte interact with each other and with the electrode interfaces. These interactions influence parameters such as how easily the molecules can dissolve, how stable they are, and how would be the motion of ions or molecules. Molecular dynamics (MD) simulations are a potential method to study the interactions effectively, and researchers can learn and improve how the batteries work.

How can MD help us?

Solvation structure
- How solvents surround redox-active molecules and ions.

Diffusion and conductivity
- By tracking how molecules and ions move, MD helps estimate transport properties critical to battery performance.

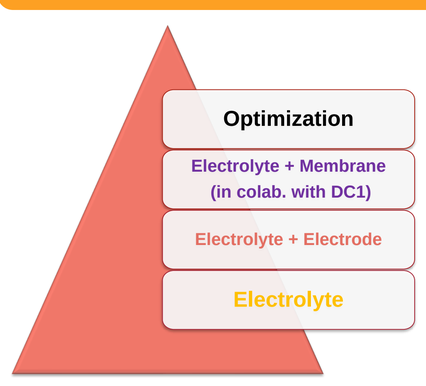
Ion coordination and aggregation
- MD reveals how supporting electrolyte or additives affect molecular arrangement and stability.

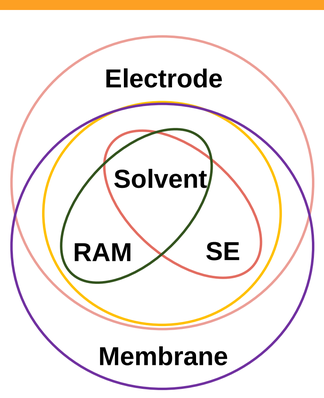
Electrode/electrolyte interface
- MD provides insight into how redox species interact with electrode surfaces, which help to have an understanding of kinetic of electrochemical reactions.

Temperature and concentration effects
- Simulations can explore how operational conditions influence molecular dynamics.

Molecular design
- With MD insights, researchers can test how different molecular structures and solvents might improve performance before synthesizing them.

Methodology





Force Field

Solvent

OPLS-AA [3]

Ionic Liquid

CL&P [4]
(Canongia Lopes & Padua)

LAMMPS · python · OVITO · VMD

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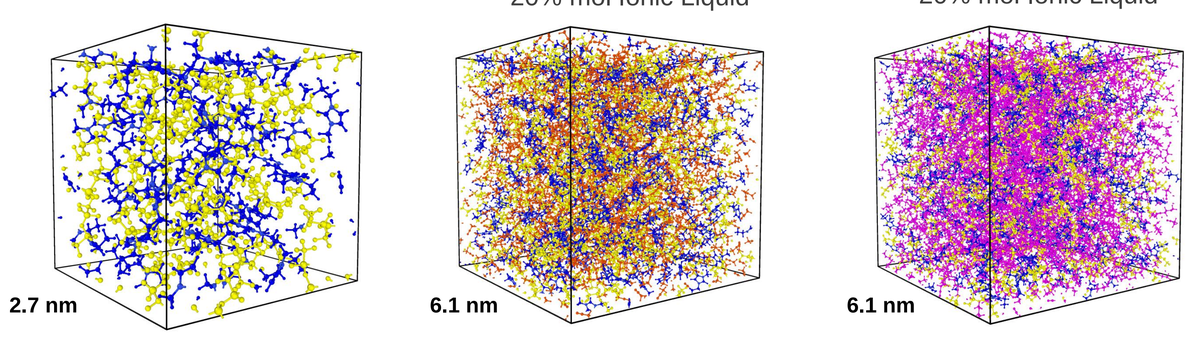
Results

EMIMTFSI

EMIMTFSI + Acetonitrile
20% mol Ionic Liquid

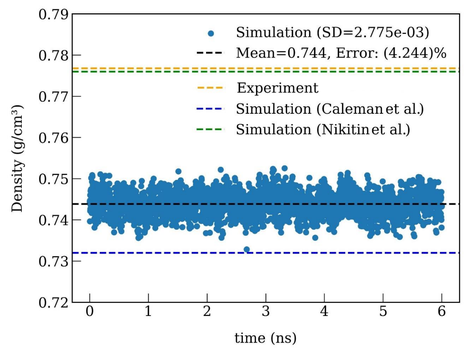
EMIMTFSI + 3MPN
20% mol Ionic Liquid

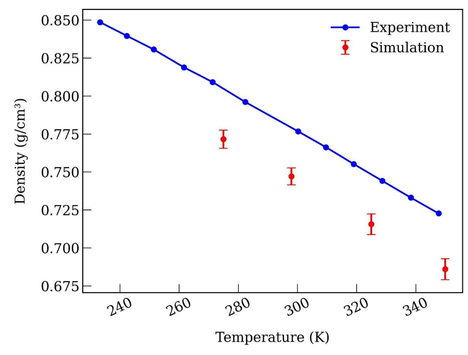


50 ion-pairs

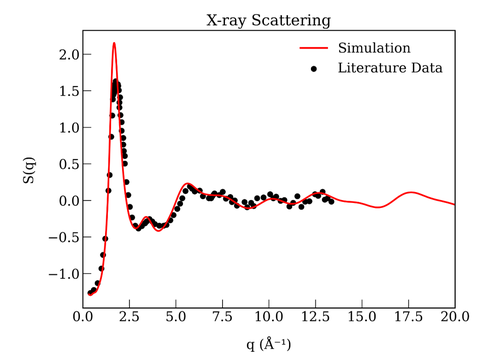
300 ion-pairs + 1200 Solvent Molcules

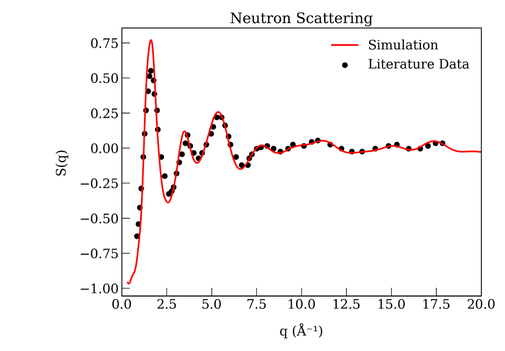
Acetonitrile

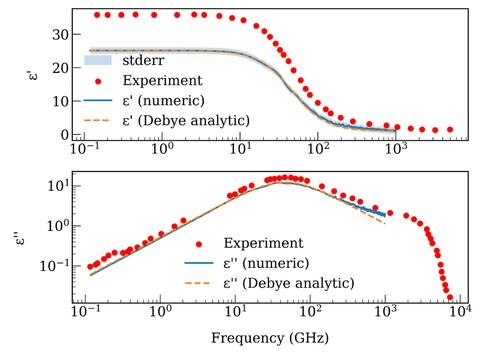


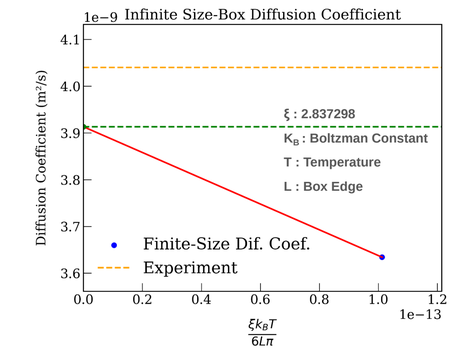


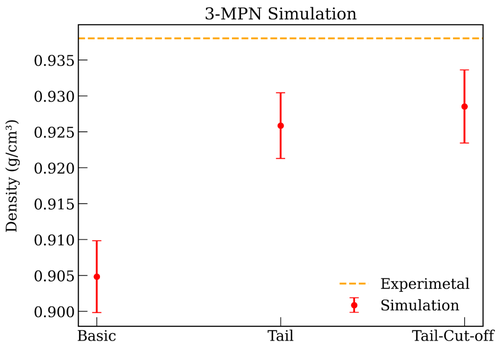
	Evaporation Heat (kJ/mol)	Molecular Dipole (Debye)	Dipole Relaxation (ps)	Viscosity (mPa·s)	Diffusion Coefficient (cm^2/s)
Simulation (this work)	35.88	3.92	3.4	0.375	3.91
Experiment	34.47	3.92	3.3	0.343	4.04
Simulation (Caleman *et al.*)	30.41	-	-	-	-
Simulation (Nikitin *et al.*)	33.66	4.12	-	-	3.45

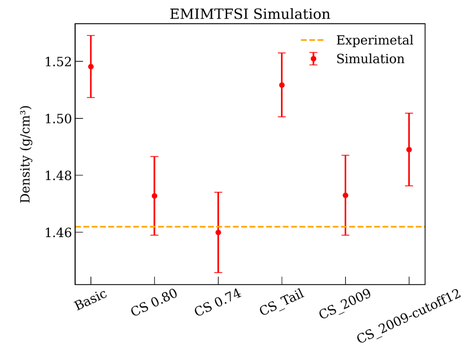












Acknowledgements

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References

[1] Zhao, Z. *et al.* Journal of Energy Chemistry, (2022). 67, 621-639.

[2] Zhao, Ziming, *et al.* Journal of Energy Chemistry (2022) 67 621-639.

[3] Jorgensen *et al.* Journal of the American Chemical Society 118, no. 45 (1996): 11225-11236.

[4] Canongia Lopes *et al.* Theoretical Chemistry Accounts 131, no. 3 (2012): 1129.

[5] Nikitin, Alexei M *et al.* Journal of Computational Chemistry 28, no. 12 (2007): 2020-2026.

[6] Caleman, Carl, *et al.* Journal of Chemical Theory and Computation 8.1 (2012): 61-74.

[7] Pothoczki *et al.* Journal of Molecular Liquids, (2017). 225, 160-166.