Simulation of Li\textsuperscript{+} in Ionic Liquids

*Structure, Transport, and Electrochemical Windows*

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Efficient Aircraft: NASA LEAPTech

UAVs: NASA “Greased-Lightning”

Solar-Battery Hybrid: NASA “Pathfinder”

Battery-Gas Hybrid: Boeing “SUGAR Volt”
Battery Energy Density Limitations on Green Aviation

Major requirement is: High Energy Density

Other requirements are rechargeable, safety, power, recharge time, cost, etc.
Li-air battery chemistry: The reaction pathway is shown with lithium metal (Li metal) and oxygen (O₂) reacting to form lithium superoxide (Li₂O₂). The electrolyte is indicated by arrows and ions (Li⁺) and electrons (e⁻) are depicted. 

Electrolytes for Li-metal: An SEM image shows the morphology of the electrode material with lithium deposits visible. 

Structural electrolytes: A molecular structure is shown with atoms and bonds indicating the chemical composition. 

Hybrid battery/supercapacitors: A graph plots power (W) against energy (Wh) comparing hybrid, ultracapacitor, and battery technologies.
Ionic Liquid Electrolytes for Li-metal Electrodes

Chosen for suppression of dendrites on Li\(^+\) metal anodes

Computational Study of Electrolytes

- Quantum simulations for structure:
  - small systems
  - Li/Anion cluster structure/energetics
  - Li-salt in liquid MD simulation
  - validation of classical approaches

- Classical Polarizable-MD (APPLE&P) simulation for transport:
  - large systems
  - diffusion and ionic conductivity
  - influence of Li-networks
  - transport mechanisms

Simulations provide insight into solvation and transport of Li-salts (difficult to assess from experiment)

Stable Solvation Shells of Li[TFSI] (Quantum)

Many potential 2, 3, and 4 anion Li$^+$ solvation shells

Raman Analysis of Li[TFSI] (Quantum)

2 and 3 [TFSI] coordination are shifted

Li Solvation Shell Stability (Quantum)

Highly unfavorable configurations exchange anions within 20 ps

Li[FSI]_2

Li[FSI]_3

20-100 ps; 12-16 pairs; T = 363 K

Stable Solvation Shells of Li[TFSI] (Quantum)

2-anion  3-anion  4-anion

2, 3 anion Li⁺ solvation shells for Li[TFSI]

Electrochemical Window (Quantum)

Electrochemical Window of Liquids with Pure and Hybrid Functional Bounds Experiment

High Accuracy Comparison (Quantum/Classical)

Figure 2: Radial distribution function (g(r)) as obtained by PFF-MD and DFT-MD simulation at \( T = 363 \) K for \( \text{Li}^+ \) with the ionic liquid anions (a) \([\text{TFSI}]^-\), (b) \([\text{FSI}]^-\), and (c) \([\text{BF}_4^-]\) as well as with the (d) O atoms in \([\text{TFSI}]^-\), O atoms in \([\text{FSI}]^-\), and F atoms in \([\text{BF}_4^-]\). The radial distributions are averaged over a 100 ps DFT-MD trajectory and a 6 ns PFF-MD trajectory, with one \( \text{Li}^+ \) in ionic liquid systems having 8, 10, and 12 pairs for \([\text{pyr14}]\)[TFSI], \([\text{pyr13}]\)[FSI], and \([\text{EMIM}]\)[BF\(_4^-\)], respectively.

Classical radial distributions in good agreement with DFT-MD

8-12 pairs; \( T = 363 \) K

Classical radial distributions in good agreement with DFT-MD

Diffusion (Classical)

[pyr14][TFSI]

[EMIM][BF₄]

[pyr13][FSI]

Measures within 10% of experiment

Figure 12: Diffusion coefficients for [pyr14][TFSI] in both (a) the neat form and (b) that having x\text{Li}^{+}=0.10, [EMIM][BF₄] in both (c) the neat form and (d) that having x\text{Li}^{+}=0.10, and [pyr13][FSI] in both (e) the neat form and (f) that having x\text{Li}^{+}=0.10 as a function of T. MD simulation results (solid symbols) are compared with available experiments (outlined symbols).
Ionic Conductivity (Classical)

Li-doping suppresses conductivity of all systems

Room-T Li Transport (Classical)

Li⁺ contribution to conduction plateaus at high salt doping

Li\textsuperscript{+} ... Li\textsuperscript{+} networks (PFF-MD)

Network Li\textsuperscript{+} share bridging anions

Conclusions

• Computational study of Li-doped ILs with experimental validation

• Solvation structure identification through complimentary simulation approaches

• Influence of networks on experimental anion solvation number

• Bulk transport and electrochemical properties in good agreement with experiment