

Simulation of Li^+ in Ionic Liquids

Structure, Transport, and Electrochemical Windows

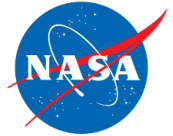


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Collaborators



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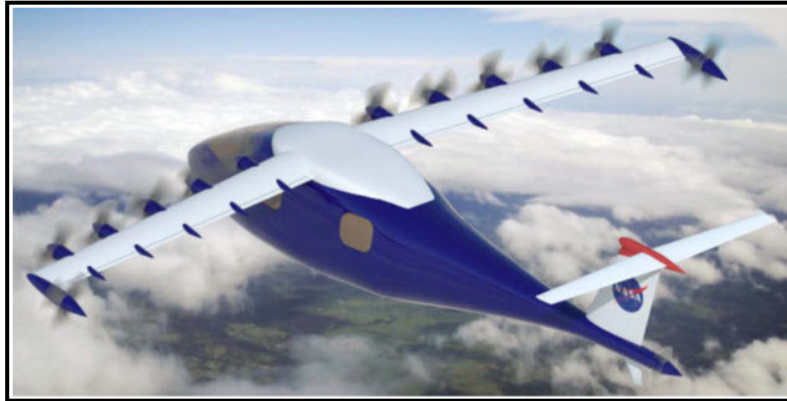
Vadim Lvovich



Army Research Center

Oleg Borodin

Green Aviation at NASA



Efficient Aircraft: NASA LEAPTech



UAVs: NASA "Greased-Lightning"

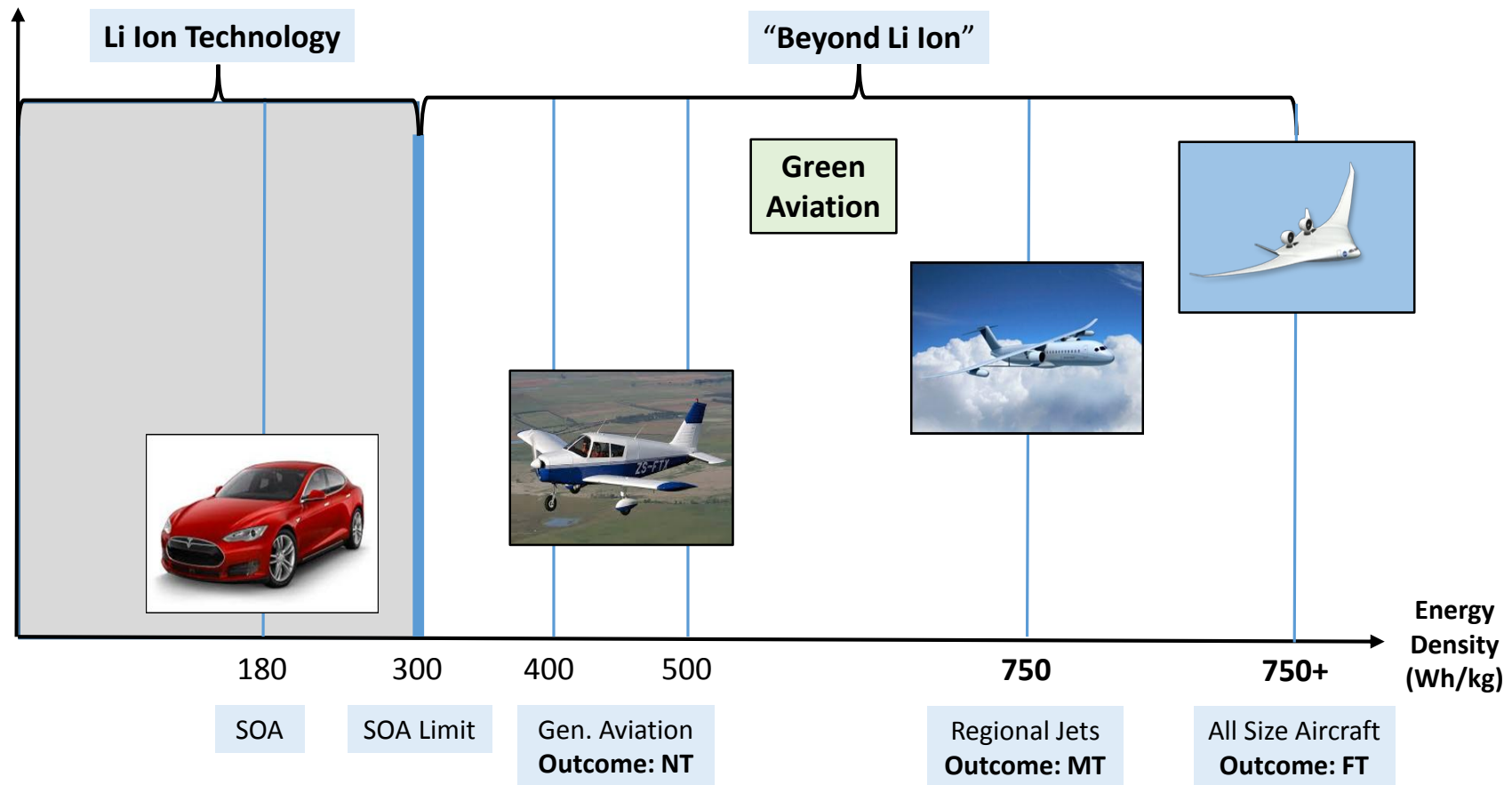
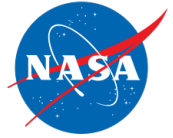


Solar-Battery Hybrid: NASA "Pathfinder"



Battery-Gas Hybrid: Boeing "SUGAR Volt"

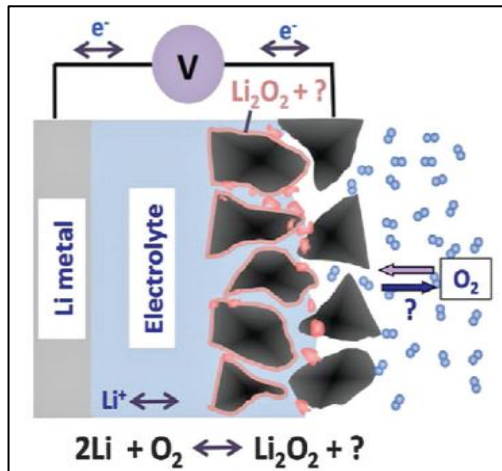
Battery Energy Density Limitations on Green Aviation



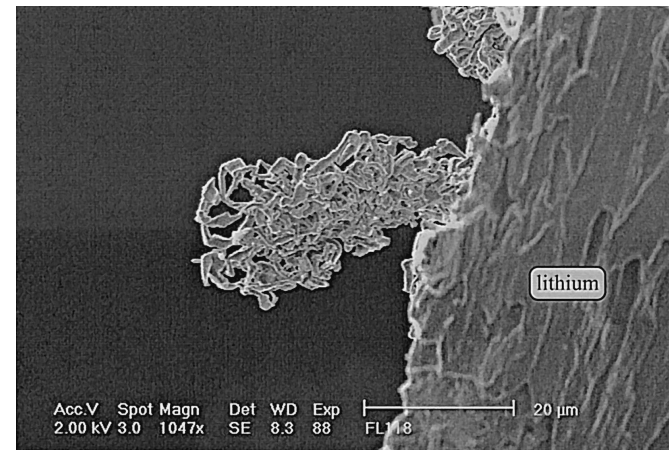
Major requirement is: High Energy Density

Other requirements are **rechargeable**, **safety**, power, recharge time, cost, etc.

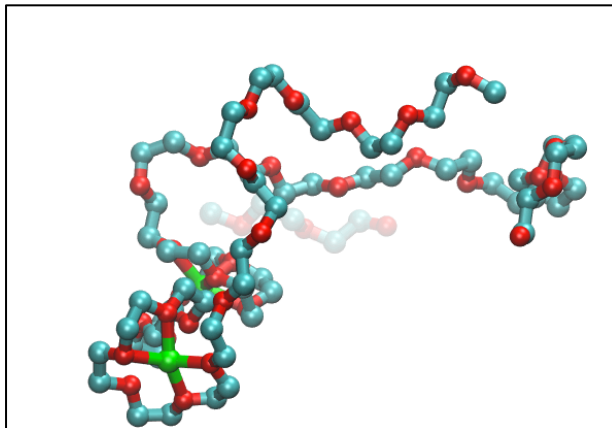
Battery Research for Green Aviation at NASA



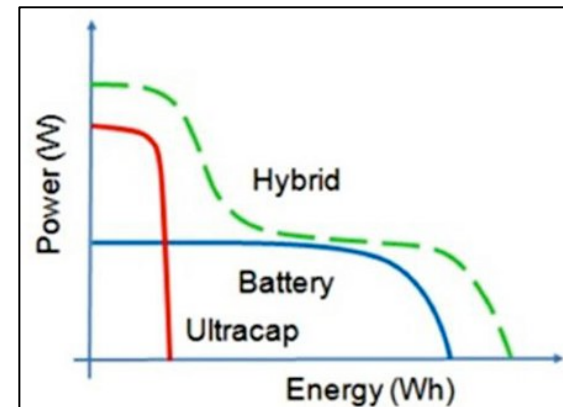
Li-Air Battery Chemistry



Electrolytes for Li-metal

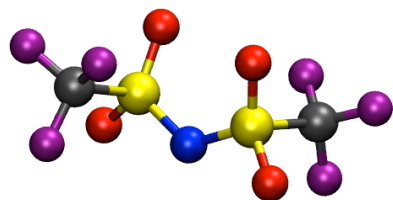
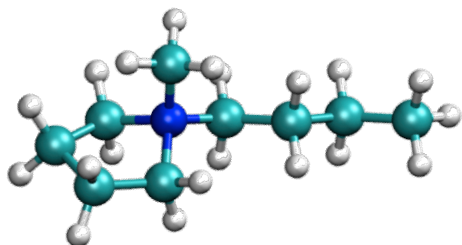


Structural Electrolytes

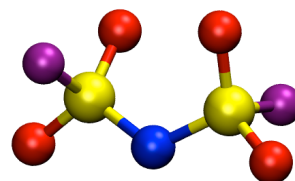
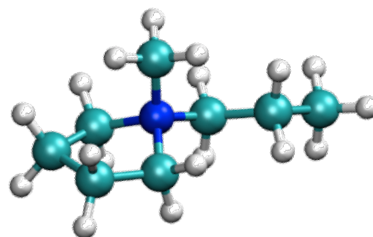


Hybrid Battery/Supercapacitors

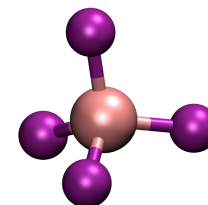
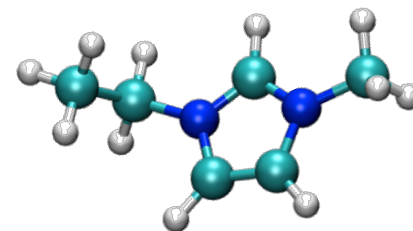
Ionic Liquid Electrolytes for Li-metal Electrodes



[pyr14][TFSI]



[pyr13][FSI]

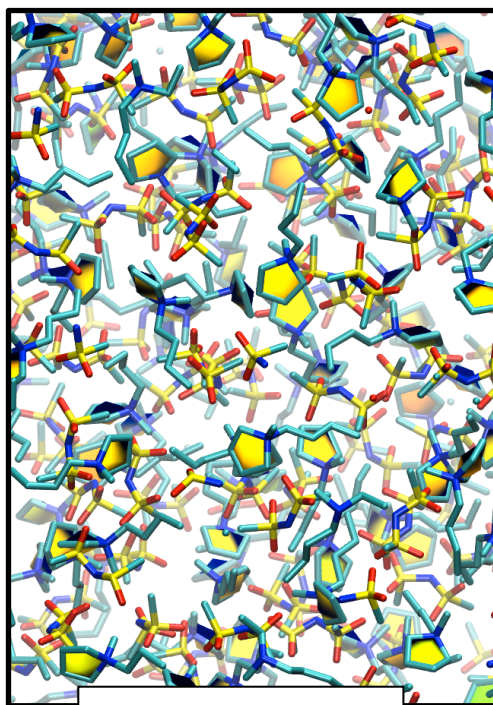


[EMIM][BF₄]

C (green)
N (blue)
S (yellow)
O (red)
F (purple)
B (pink)
H (white)

Chosen for suppression of dendrites on Li⁺ metal anodes

Computational Study of Electrolytes

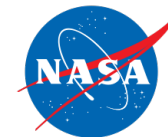


[pyr14][TFSI]

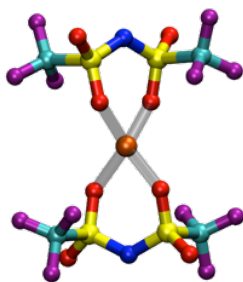
- Quantum simulations for **structure**:
 - small systems
 - Li/Anion cluster structure/energetics
 - Li-salt in liquid MD simulation
 - validation of classical approaches
- Classical Polarizable-MD (APPLE&P) simulation for **transport**:
 - large systems
 - diffusion and ionic conductivity
 - influence of Li-networks
 - transport mechanisms

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

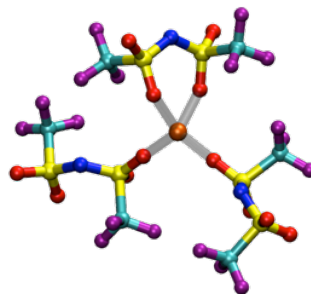
Stable Solvation Shells of Li[TFSl] (Quantum)



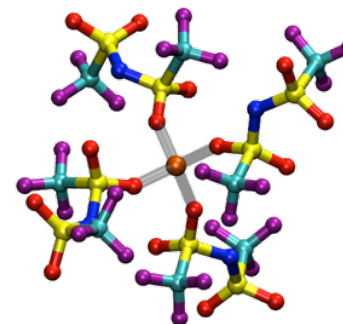
2-anion



3-anion

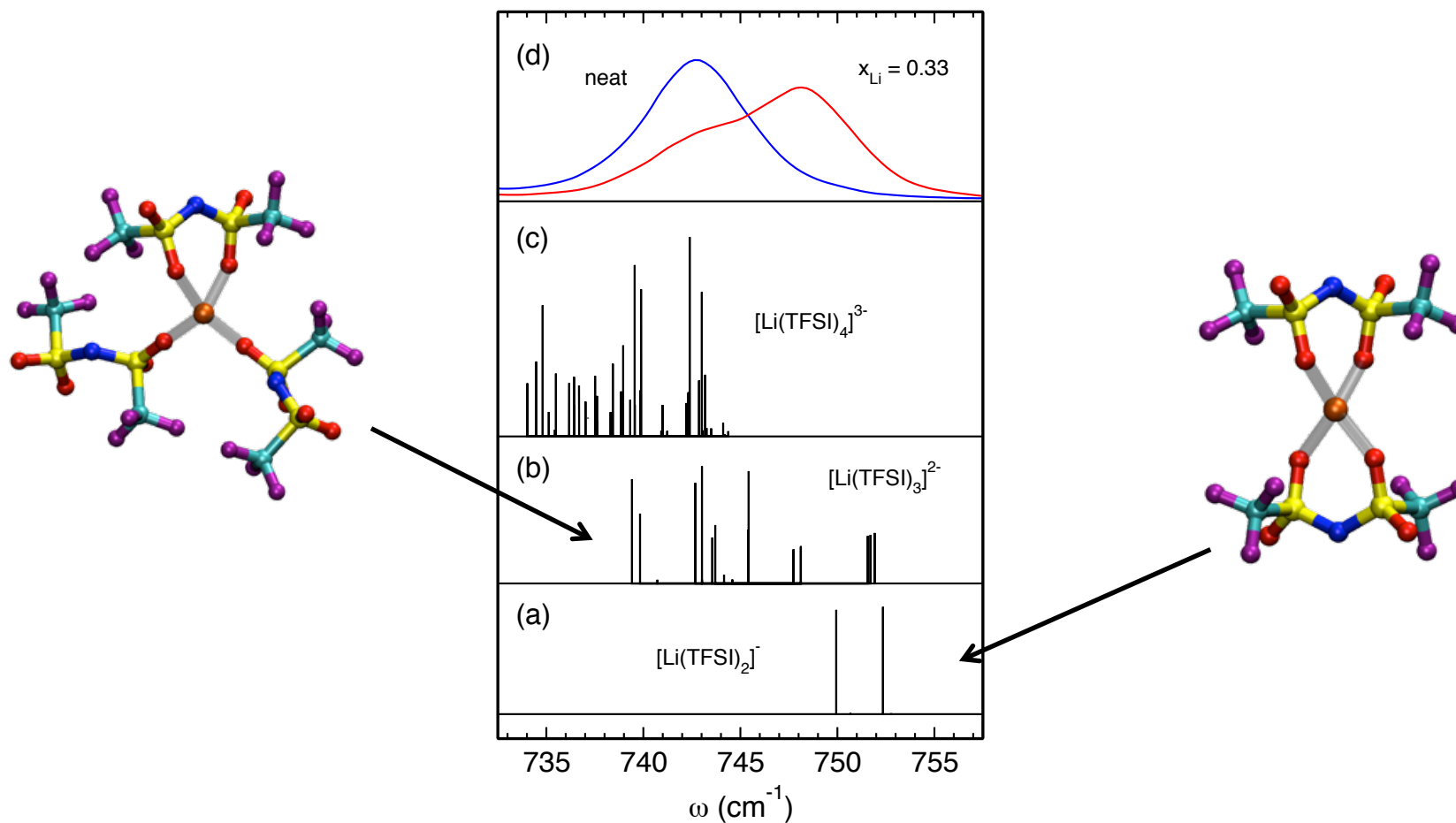


4-anion



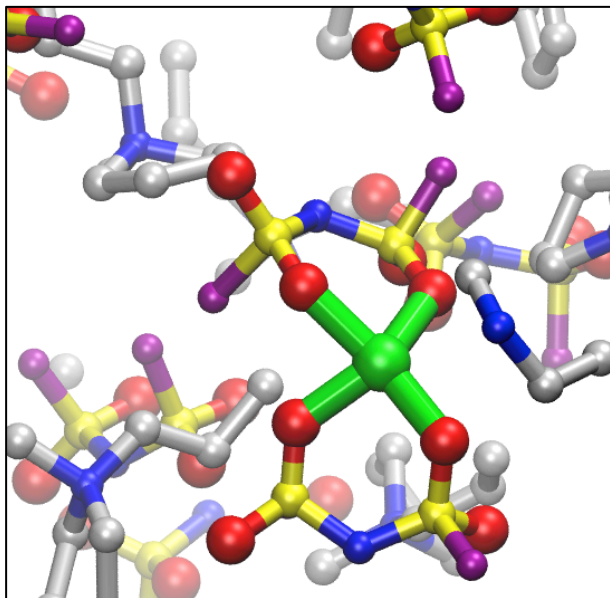
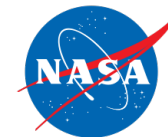
Many potential 2, 3, and 4 anion Li⁺ solvation shells

Raman Analysis of Li[TFSI] (Quantum)

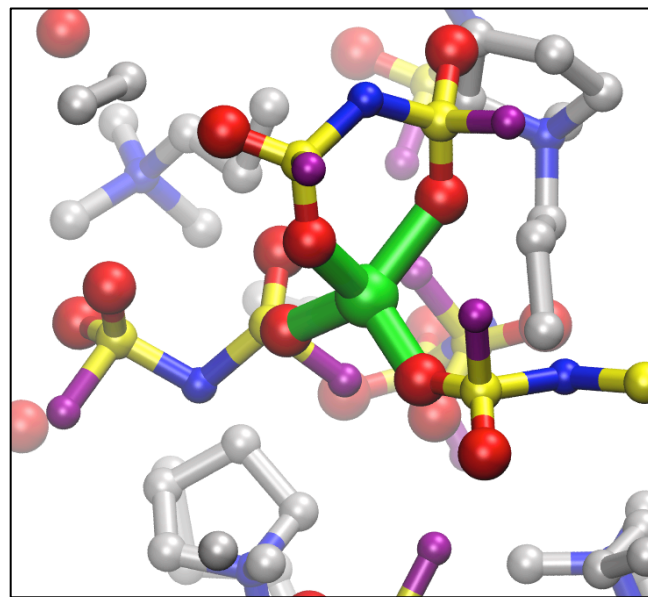


2 and 3 [TFSI] coordination are shifted

Li Solvation Shell Stability (Quantum)



20-100 ps; 12-16 pairs; $T = 363 \text{ K}$

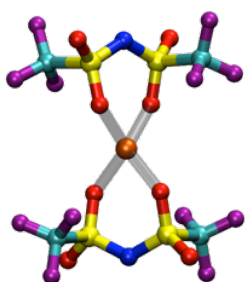


Highly unfavorable configurations exchange anions within 20 ps

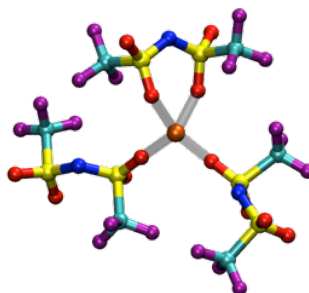
Stable Solvation Shells of Li[TFSI] (Quantum)



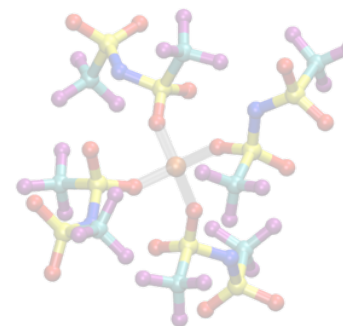
2-anion



3-anion

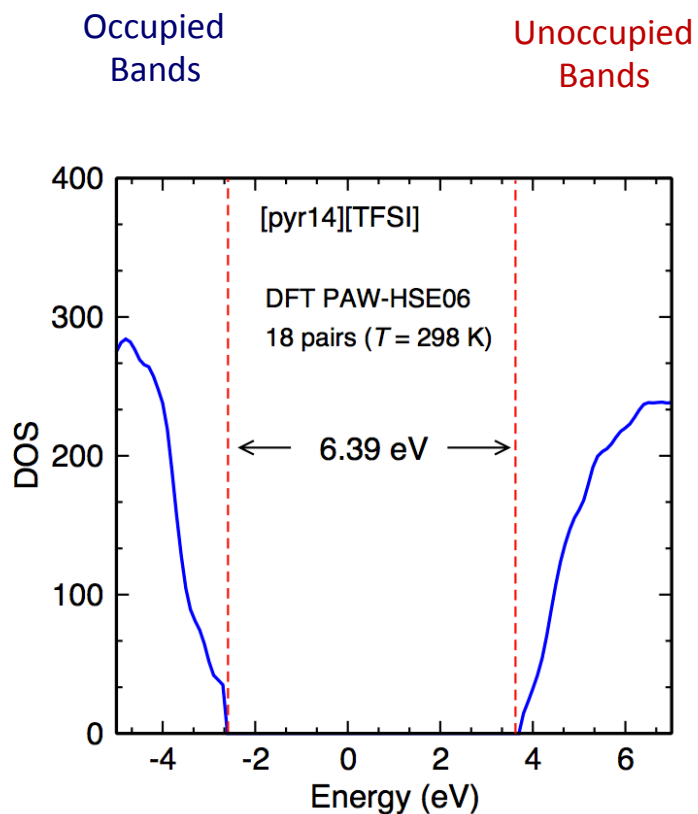


4-anion



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

Electrochemical Window (Quantum)



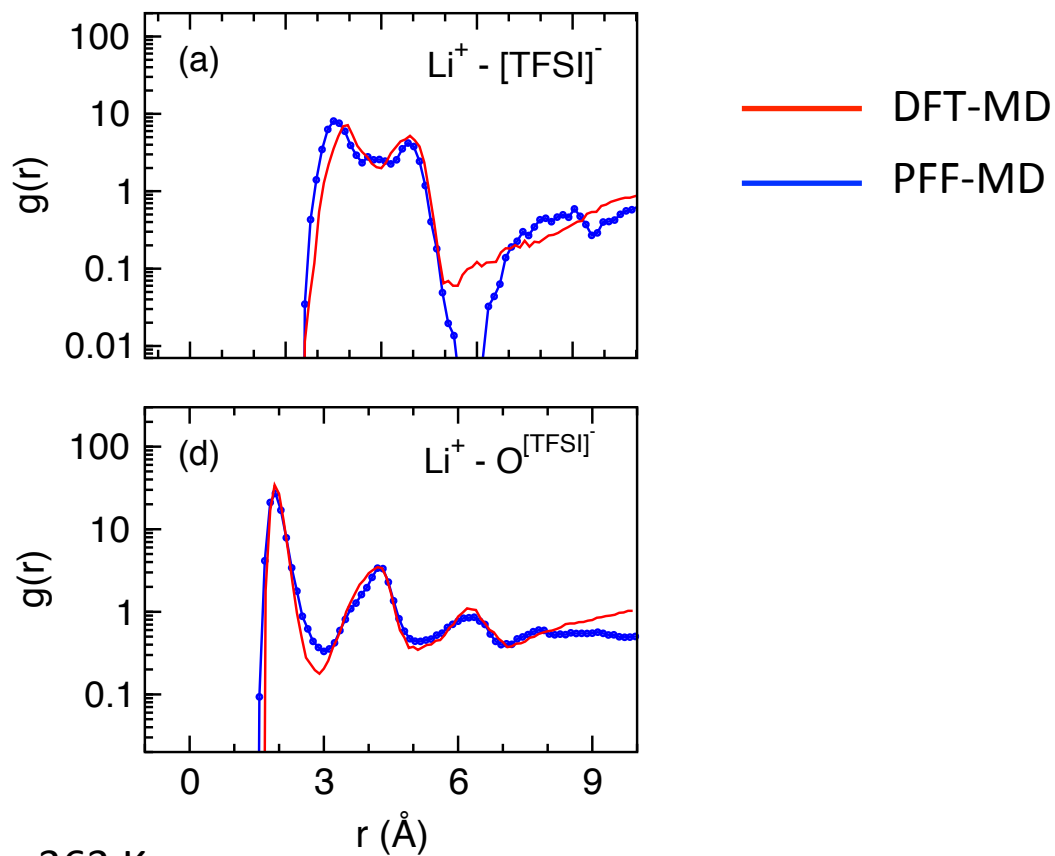
Electrochemical Windows (eV)

	DFT (PBE)	DFT (HSE06)	Exp.
[pyr14][TFSI]	4.6	6.5	6
[pyr13][FSI]	4.7	6.7	6
[EMIM][BF ₄]	3.9	5.4	4.3

10 PFF-MD configurations; 24 pairs; $T = 298$ K

Electrochemical window of liquids with pure and hybrid functional bounds experiment

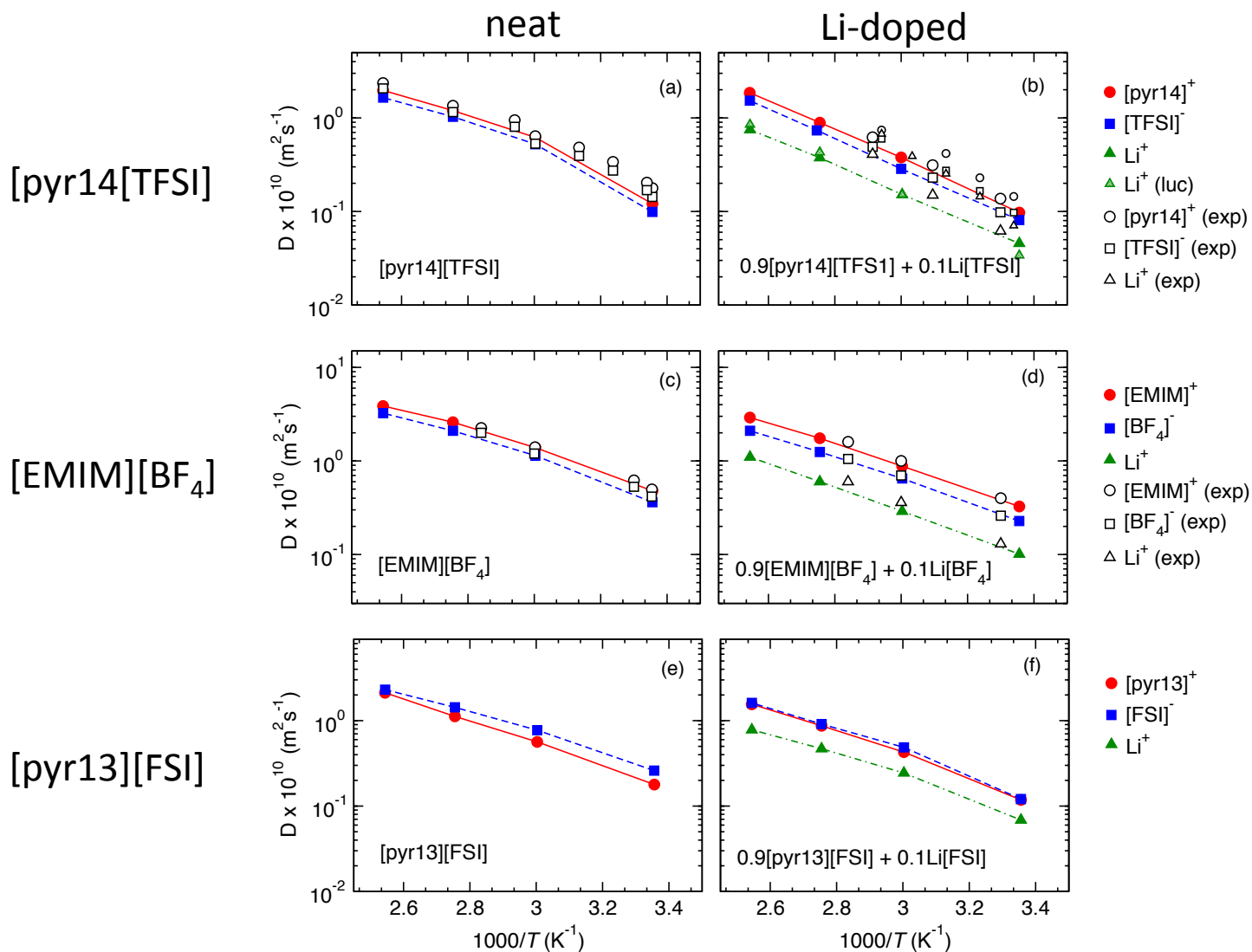
High Accuracy Comparison (Quantum/Classical)



8-12 pairs; $T = 363$ K

Classical radial distributions in good agreement with DFT-MD

Diffusion (Classical)

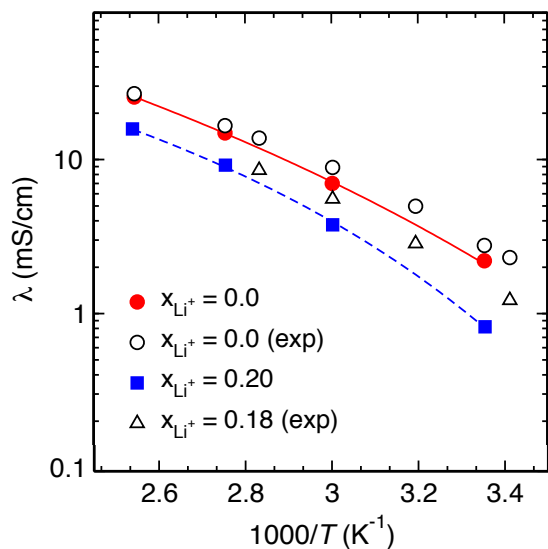


Measures within 10% of experiment

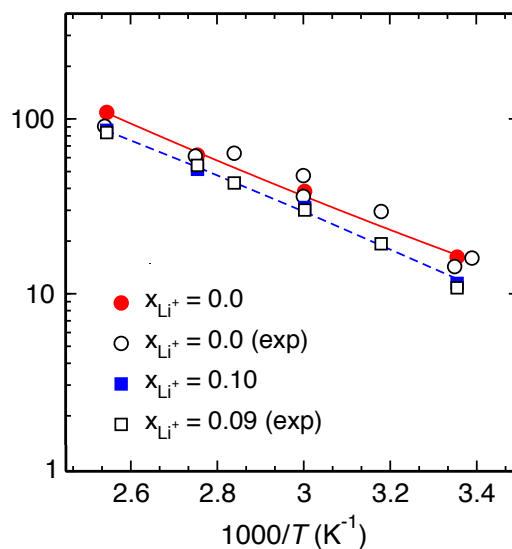
Ionic Conductivity (Classical)



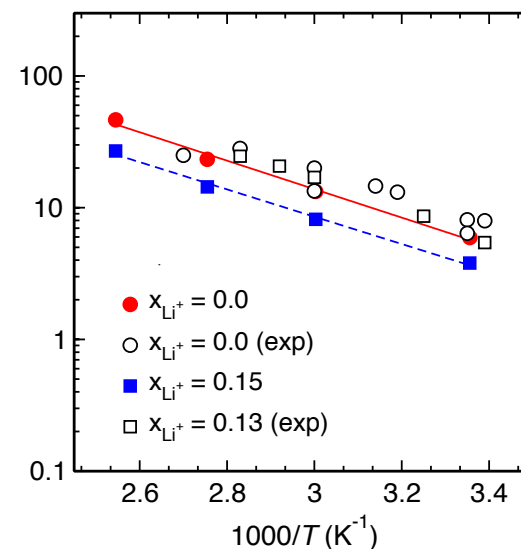
[pyr14][TFSI]



[EMIM][BF₄]

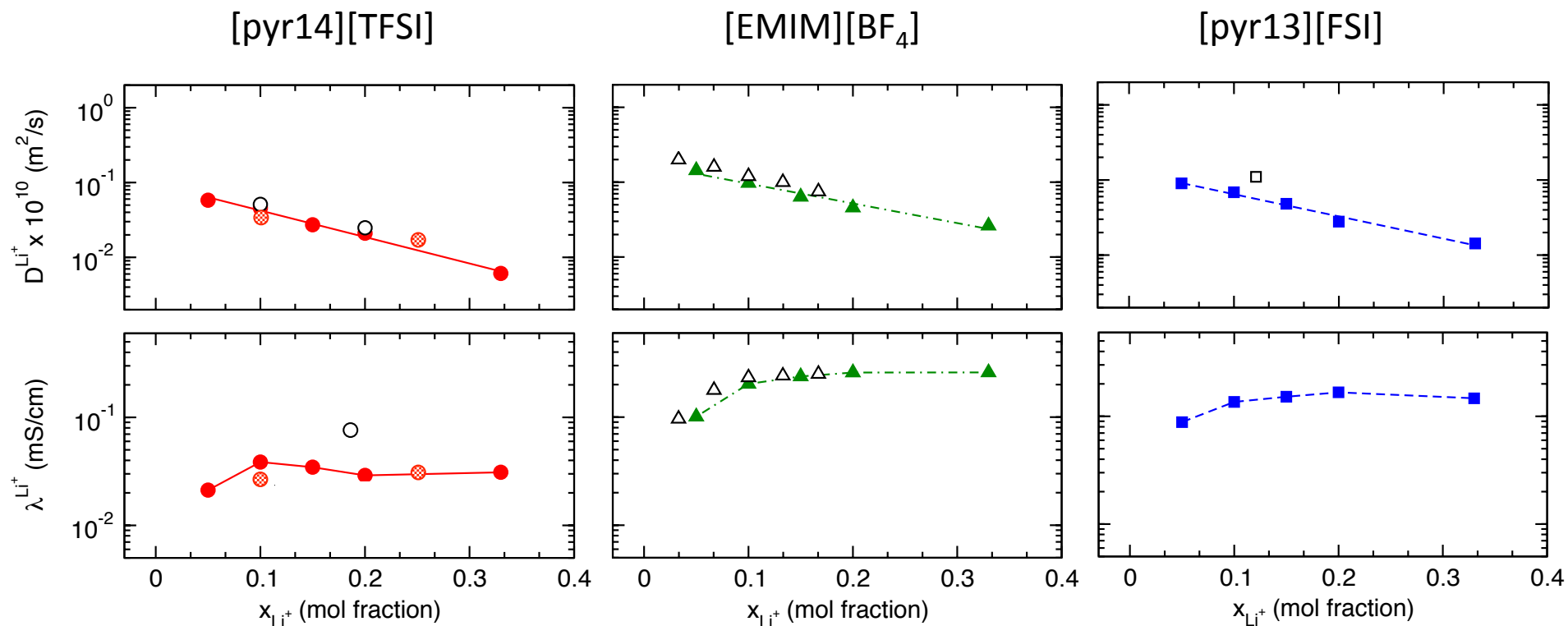


[pyr13][FSI]



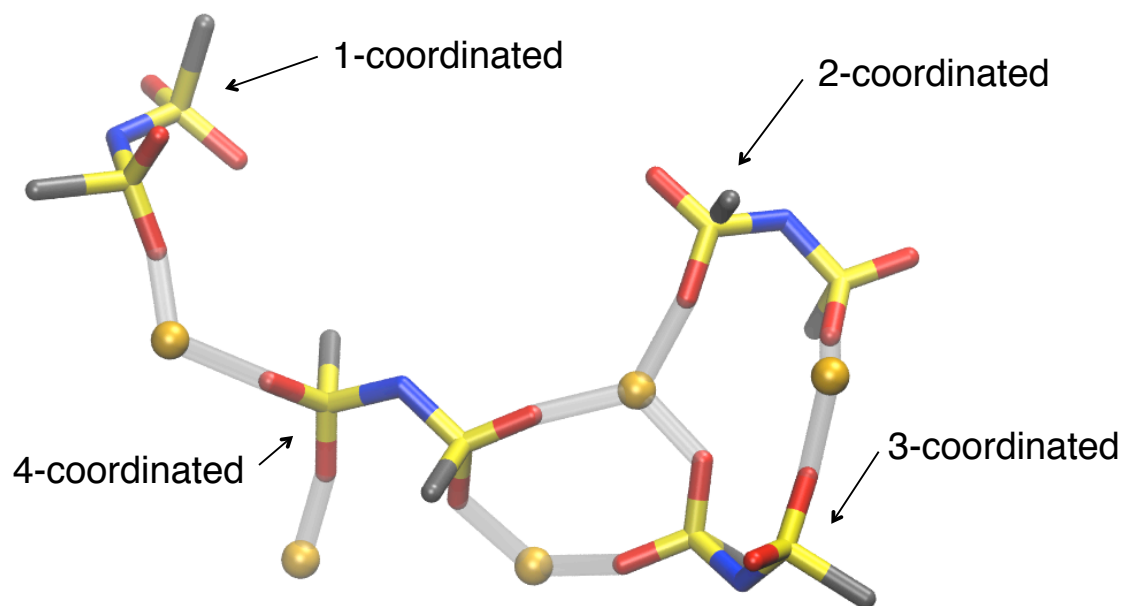
Li-doping suppresses conductivity of all systems

Room-T Li Transport (Classical)



Li⁺ contribution to conduction plateaus at high salt doping

Li⁺ ... Li⁺ networks (PFF-MD)



Network Li⁺ 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**