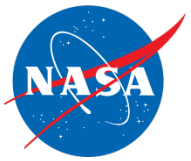
Simulation of Li^+ in Ionic Liquids

Structure, Transport, and Electrochemical Windows



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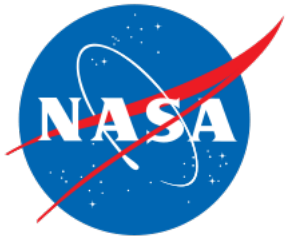
[2]NASA Ames Research Center

Collaborators

NASA Ames Research Center

John W. Lawson
Charles W. Bauschlicher
Justin B. Haskins
Josh D. Monk



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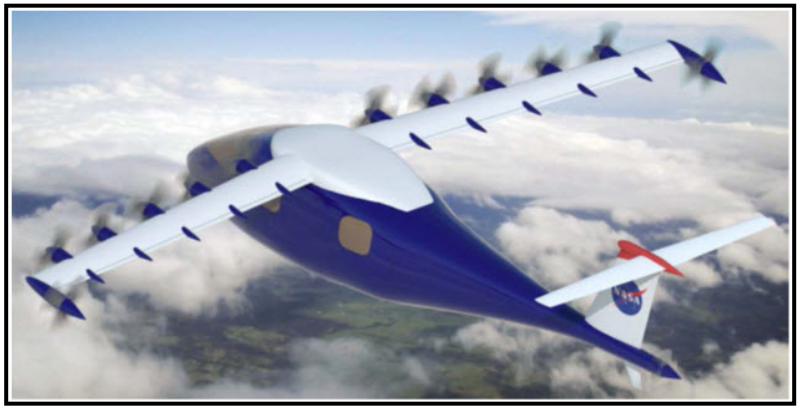
James J. Wu
Dionne M. Hernandez
William R. Bennett
Vadim Lvovich

Army Research Center

Oleg Borodin

Green Aviation at NASA



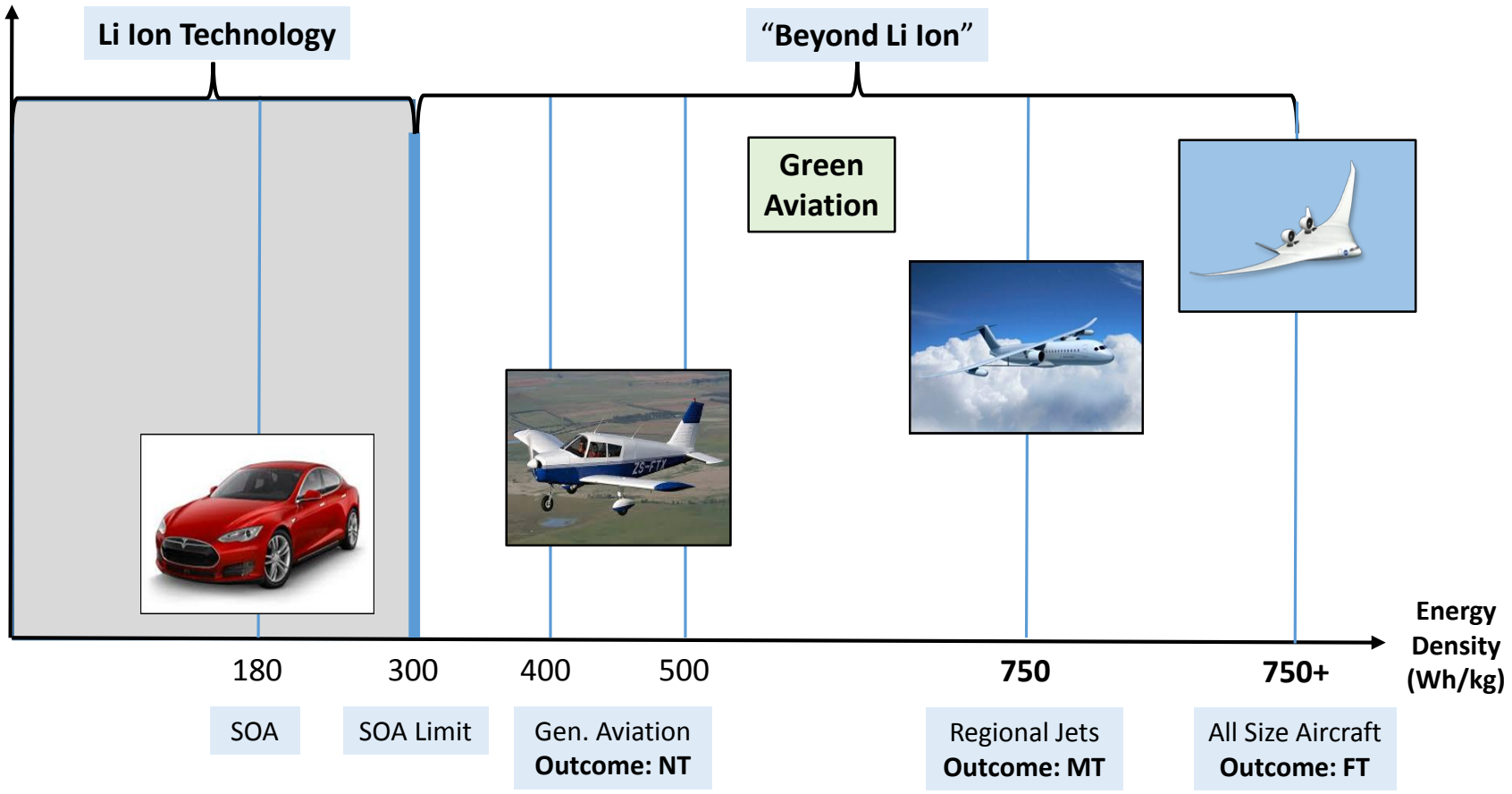
Efficient Aircraft: NASA LEAPTech

UAVs: NASA “Greased-Lightning”

Solar-Battery Hybrid: NASA “Pathfinder”

Battery-Gas Hybrid: Boeing “SUGAR Volt”

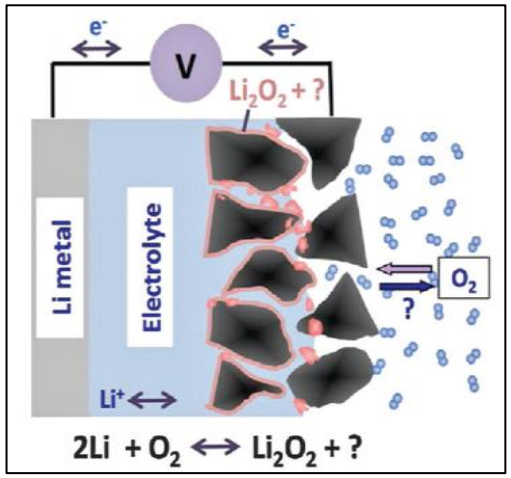
Battery Energy Density Limitations on Green Aviation



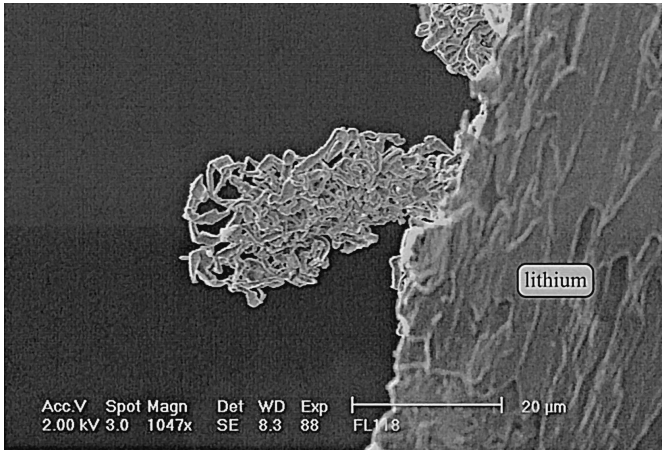
Major requirement is: High Energy Density

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

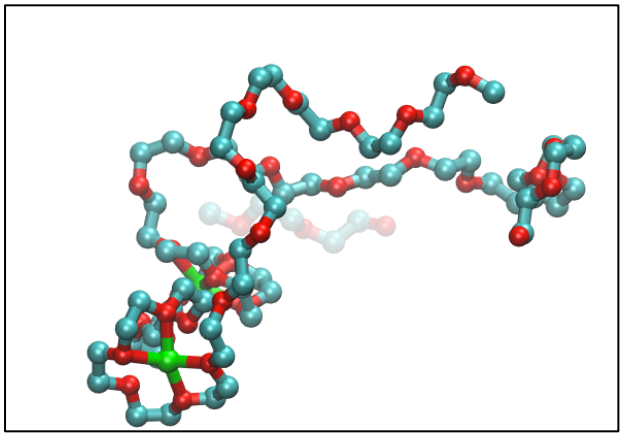
Battery Research for Green Aviation at NASA



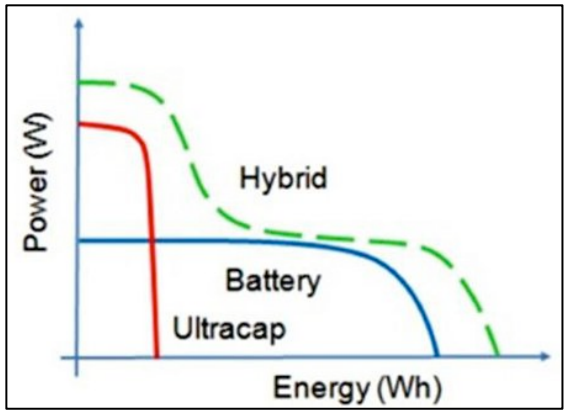
Li-Air Battery Chemistry



Electrolytes for Li-metal

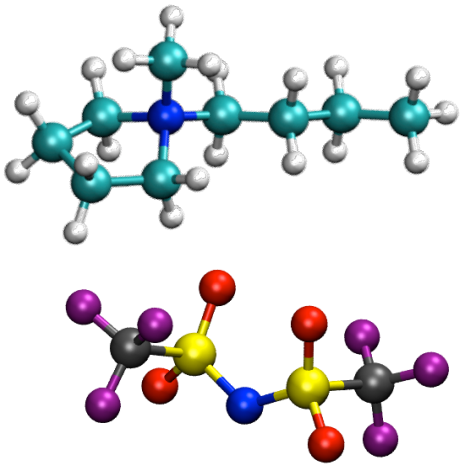


Structural Electrolytes

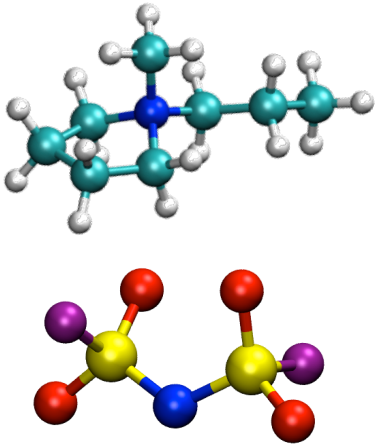


Hybrid Battery/Supercapacitors

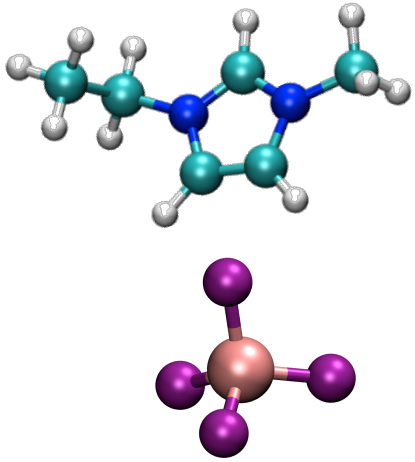
Ionic Liquid Electrolytes for Li-metal Electrodes



[pyr14][TFSI]



[pyr13][FSI]



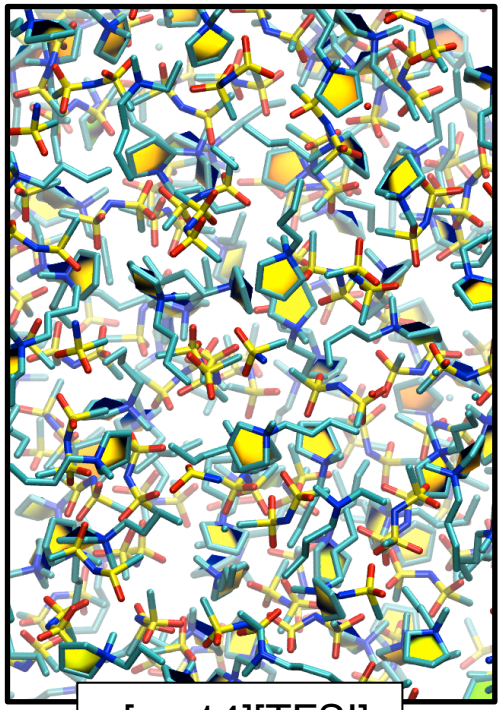
[EMIM][BF_4]

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

Chosen for suppression of dendrites on Li^+ metal anodes

Bhattacharyya et al., Nature Mater. (2010); Basile, et al., Electrohem. Commun. (2013)

Computational Study of Electrolytes


[pyr14][TFSI]

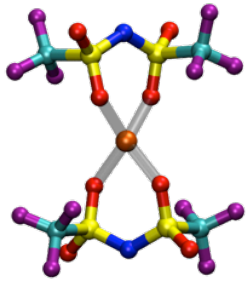
- **Quantum simulations for structure:**
  - small systems
  - Li/Anion cluster structure/energetics
  - Li-salt in liquid MD simulation
  - validation of classical approaches
- **Classical Polarizable-MD (APPLE&P) simulation for transport:**
  - large systems
  - diffusion and ionic conductivity
  -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

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

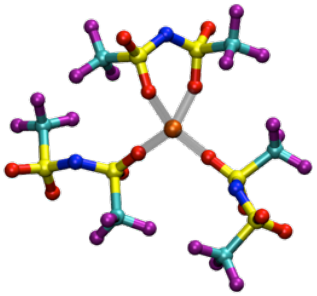
Borodin, *J. Phys. Chem. B* **113**, 11463 (2009); J Haskins, et al., *J. Phys. Chem. B* **118**, 11295 (2014);
C Bauschlicher, et al., *J. Phys. Chem. B* **118**, 10785 (2014); J Haskins, et al., *J. Phys. Chem. B* **119**, 14705 (2015)

Stable Solvation Shells of Li[TFSI] (Quantum)

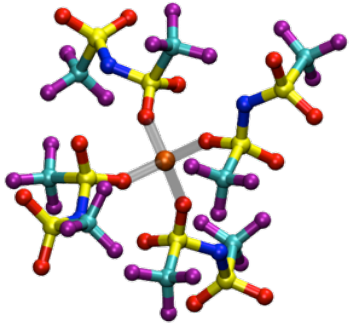
2-anion



3-anion



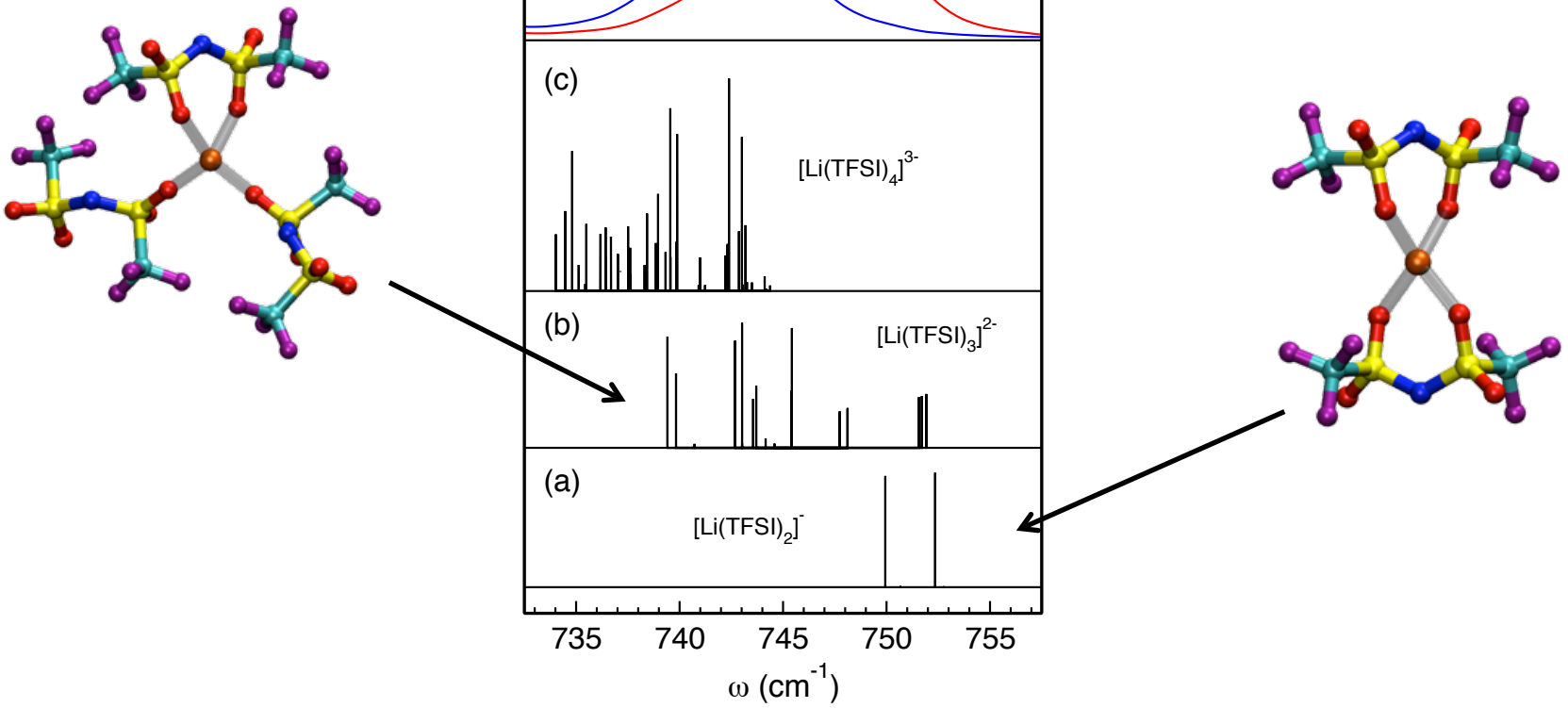
4-anion



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

C Bauschlicher, et al., *J. Phys. Chem. B* **118**, 10785 (2014); J Haskins, et al., *J. Phys. Chem. B* **119**, 14705 (2015)

Raman Analysis of Li[TFSI] (Quantum)

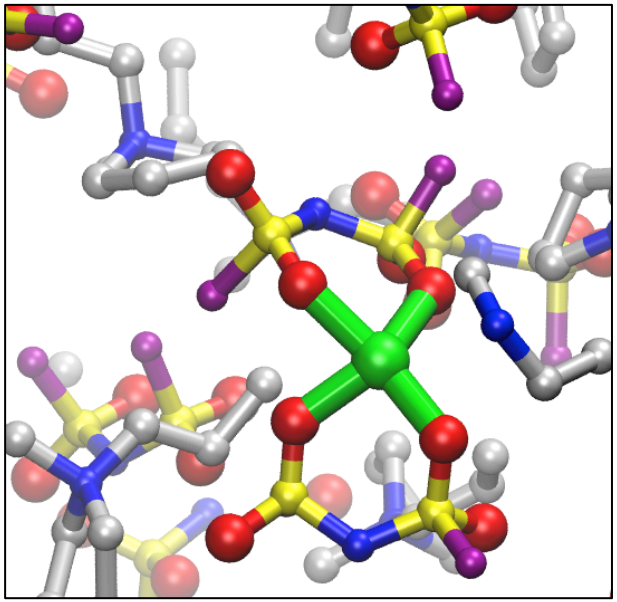


2 and 3 [TFSI] coordination are shifted

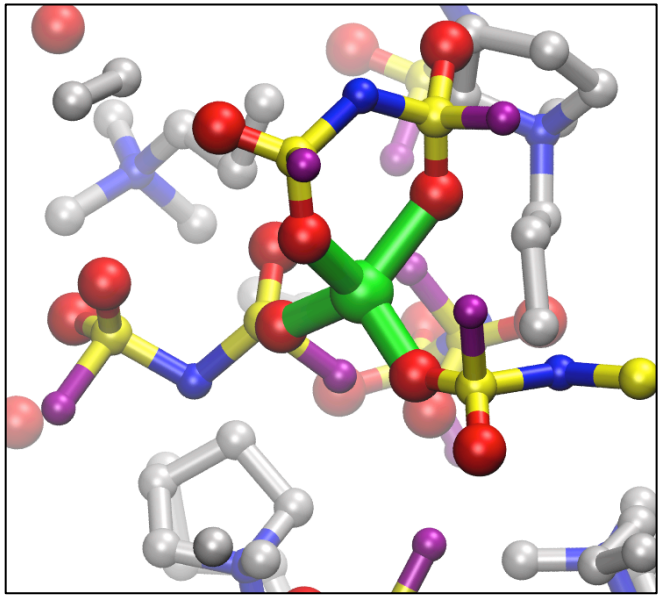
J Haskins, et al., *J. Phys. Chem. B* **119**, 14705 (2015); J Lassegues, et al., *J. Phys. Chem. A* **113**, 305 (2009)

Li Solvation Shell Stability (Quantum)

$Li[FSI]_2$



$Li[FSI]_3$



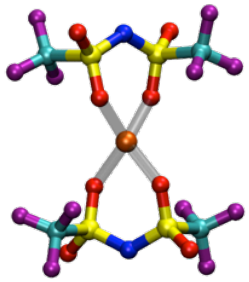
20-100 ps; 12-16 pairs; T = 363 K

Highly unfavorable configurations exchange anions within 20 ps

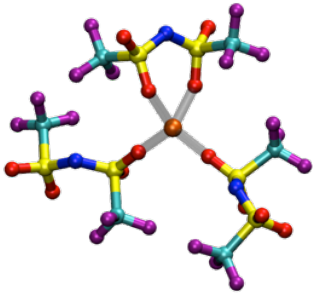
J Haskins, et al., *J. Phys. Chem. B* **119**, 14705 (2015)

Stable Solvation Shells of Li[TFSI] (Quantum)

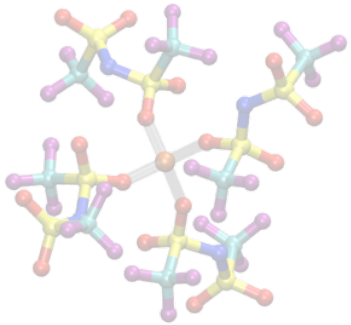
2-anion



3-anion



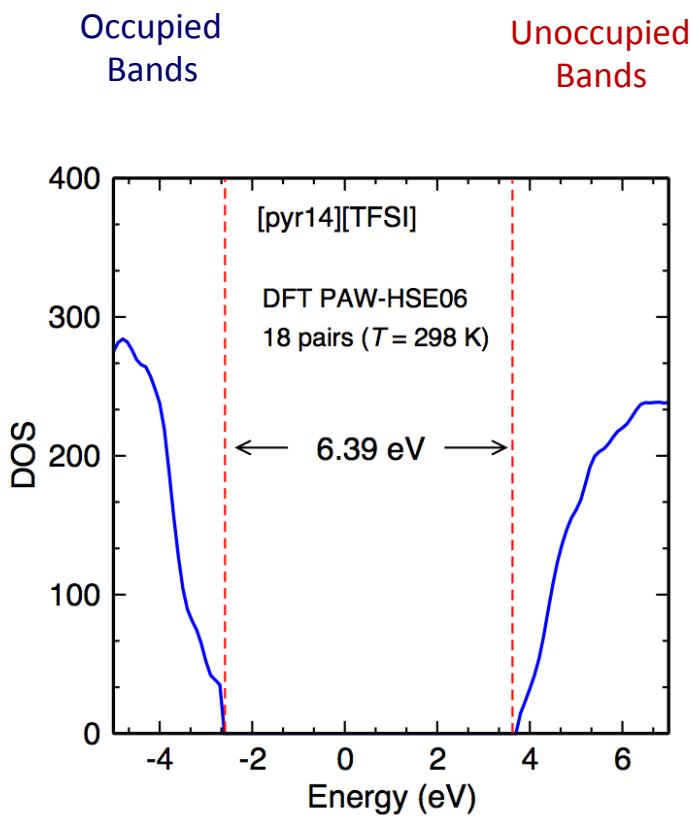
4-anion



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

C Bauschlicher, et al., *J. Phys. Chem. B* **118**, 10785 (2014); J Haskins, et al., *J. Phys. Chem. B* **119**, 14705 (2015)

Electrochemical Window (Quantum)



Electrochemical Windows (eV)

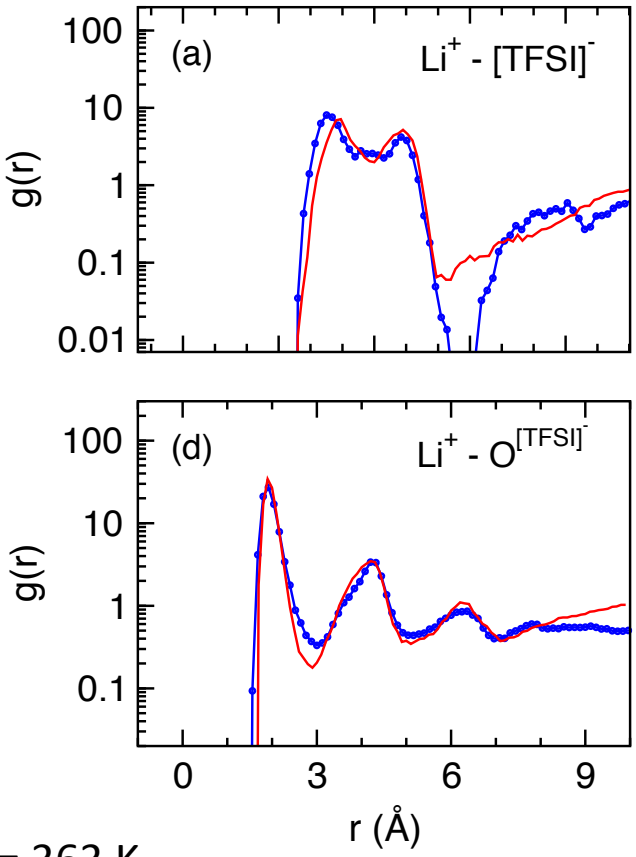
	DFT (PBE)	DFT (HSE06)	Exp.
[pyr14][TFSI]	4.6	6.5	6
[pyr13][FSI]	4.7	6.7	6
[EMIM][BF_4]	3.9	5.4	4.3

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

Electrochemical window of liquids with pure and hybrid functional bounds experiment

J Haskins, *et al.*, *J. Phys. Chem. B* **119**, 14705 (2015)

High Accuracy Comparison (Quantum/Classical)



8-12 pairs; T = 363 K

Classical radial distributions in good agreement with DFT-MD

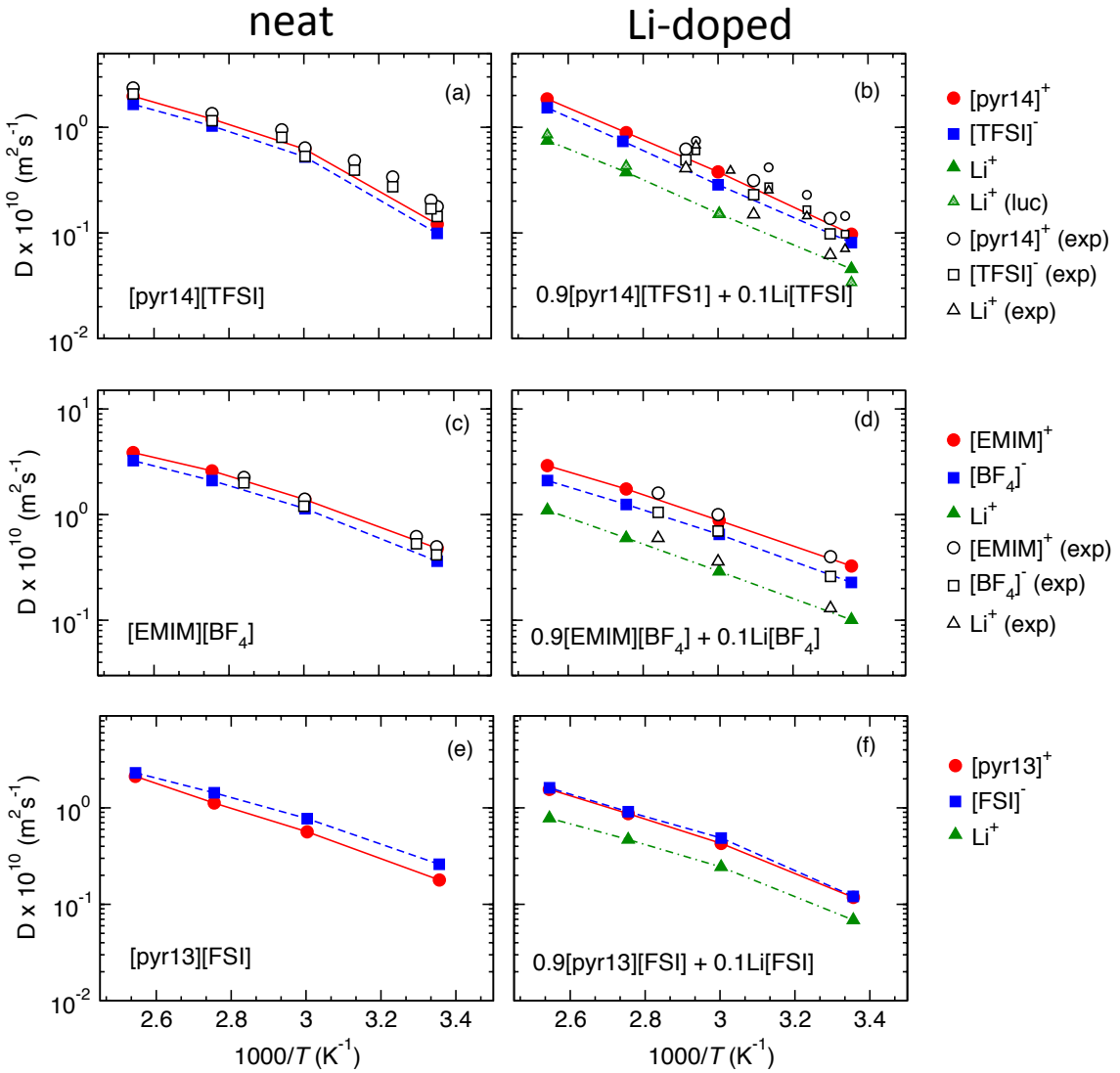
J Haskins, et al., *J. Phys. Chem. B* **119**, 14705 (2015)

Diffusion (Classical)

[pyr14[TFSI]

[EMIM][BF_4]

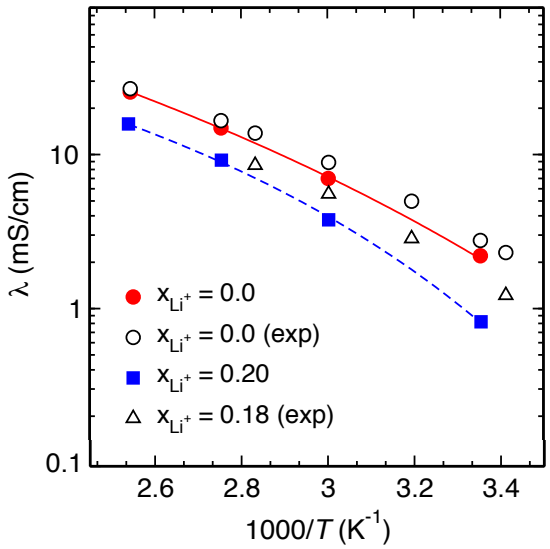
[pyr13][FSI]



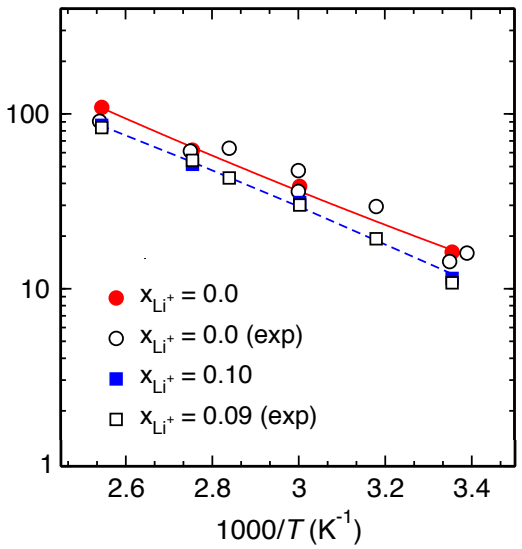
Measures within 10% of experiment

Ionic Conductivity (Classical)

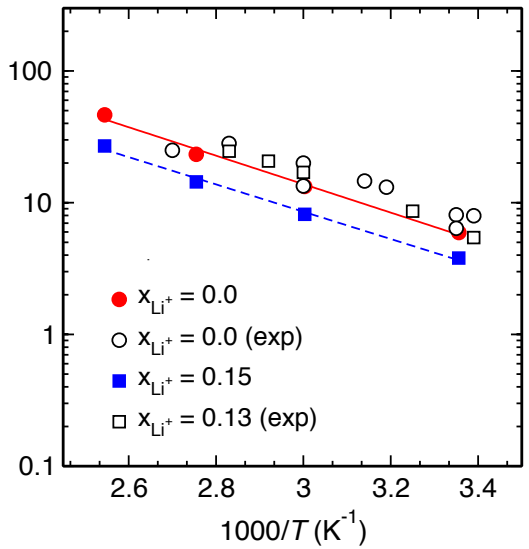
[pyr14[TFSI]



[EMIM][BF_4]



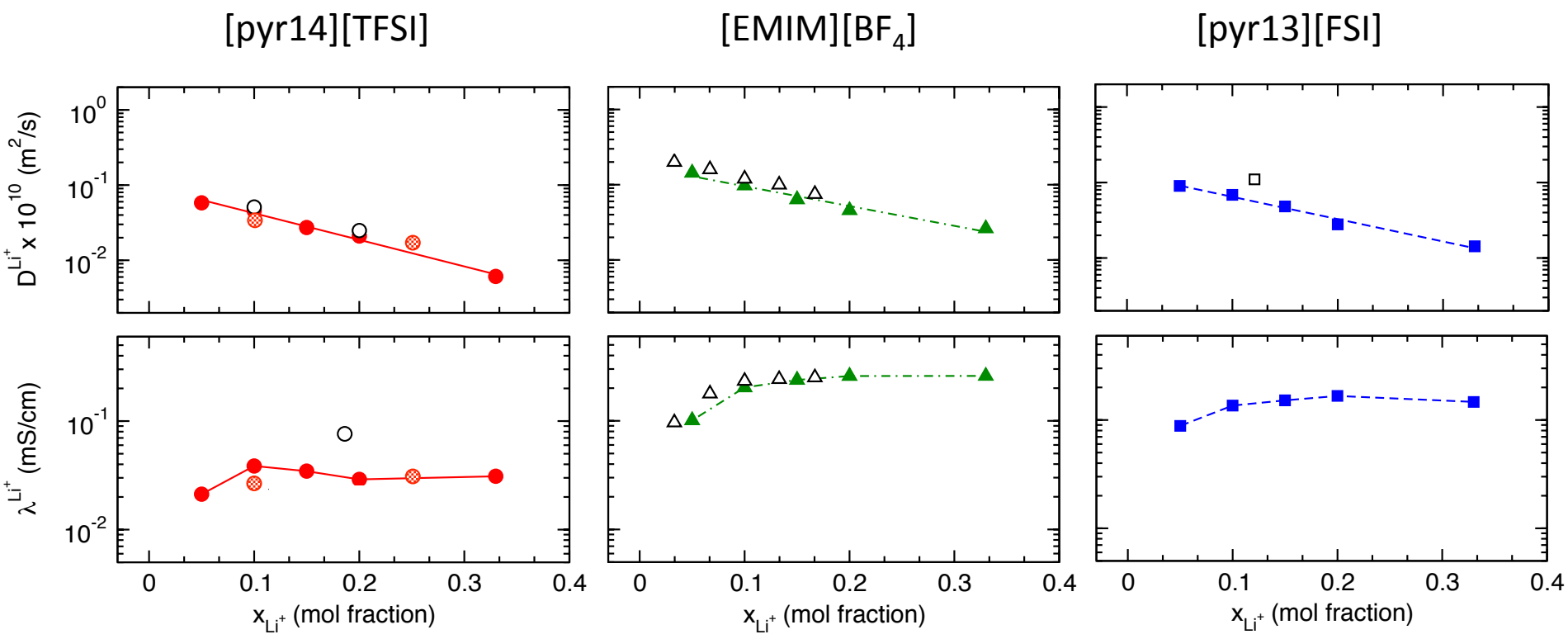
[pyr13][FSI]



Li-doping suppresses conductivity of all systems

J Haskins, et al., *J. Phys. Chem. B* **118**, 11295 (2014)

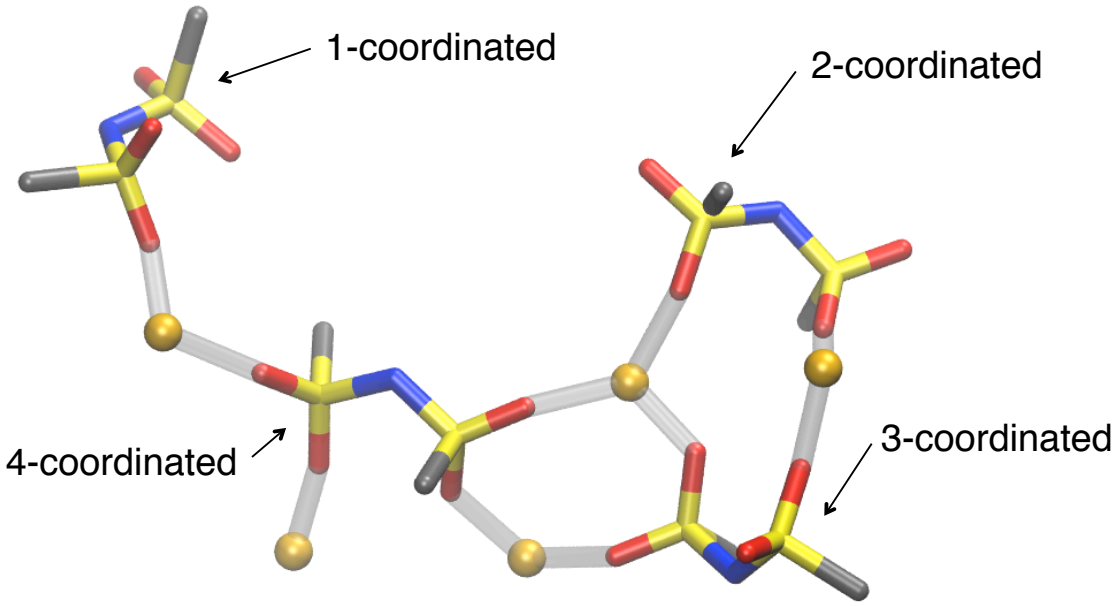
Room-T Li Transport (Classical)



Li⁺ contribution to conduction plateaus at high salt doping

J Haskins, et al., *J. Phys. Chem. B* **118**, 11295 (2014); O Borodin, et al., *J. Phys. Chem. B* **110**, 16879 (2006)

Li^+ … Li^+ networks (PFF-MD)



Network Li^+ share bridging anions

J Haskins, et al., *J. Phys. Chem. B* **118**, 11295 (2014)

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