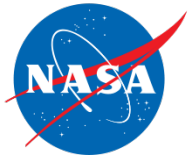
Interfacial Structure and Capacitance of Li-doped Ionic Liquid Electrolytes from Molecular Simulation



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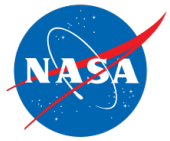
Collaborators



NASA Ames Research Center

John W. Lawson
Charles W. Bauschlicher
Justin B. Haskins
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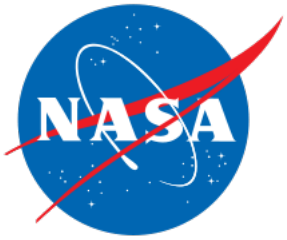


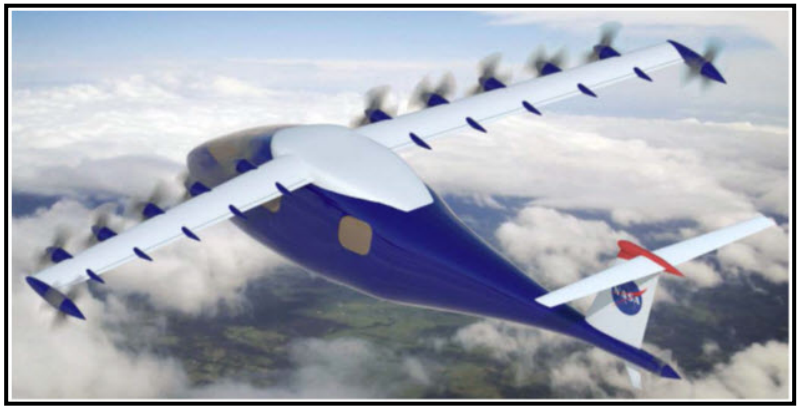
NASA Glenn Research Center

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

Army Research Center

Oleg Borodin

Green Aviation at NASA



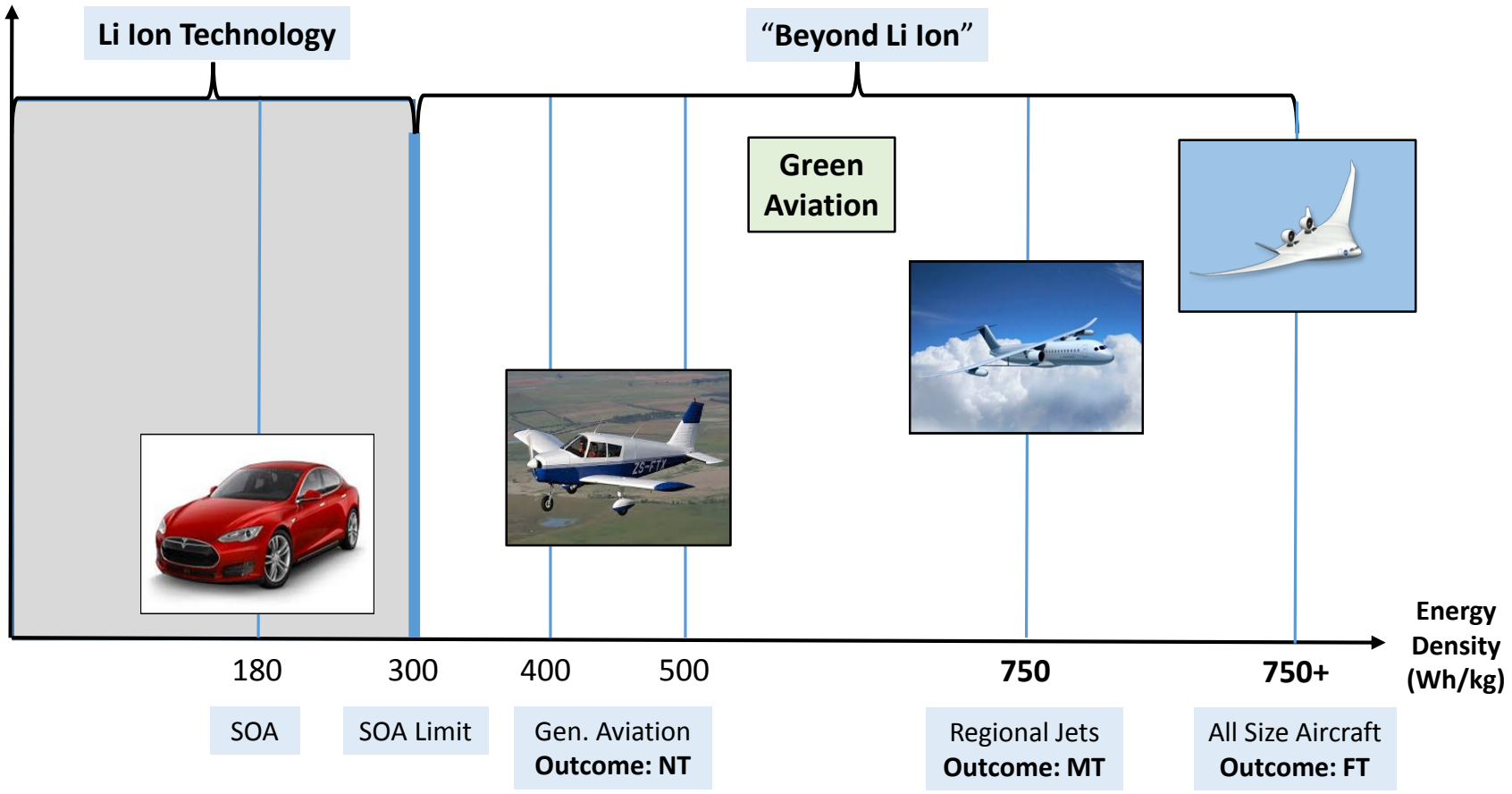
Efficient Aircraft: NASA LEAPTech

UAVs: NASA “Greased-Lightning”

Solar-Battery Hybrid: NASA “Pathfinder”

Battery-Gas Hybrid: Boeing “SUGAR Volt”

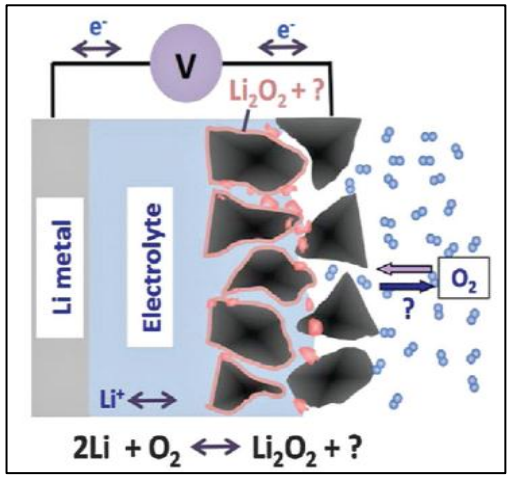
Battery Energy Density Limitations on Green Aviation



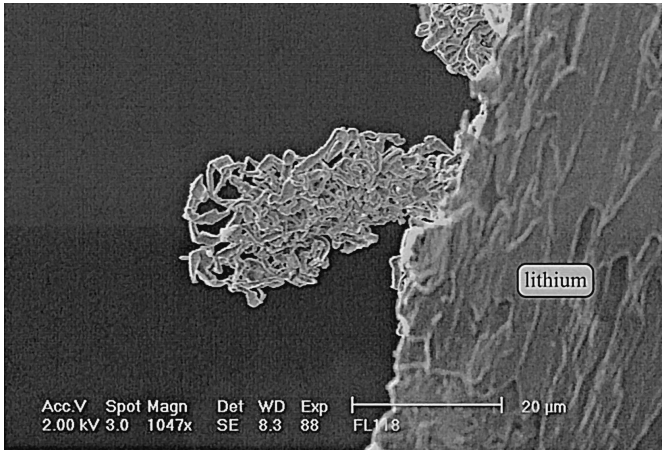
Major requirement is: High Energy Density

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

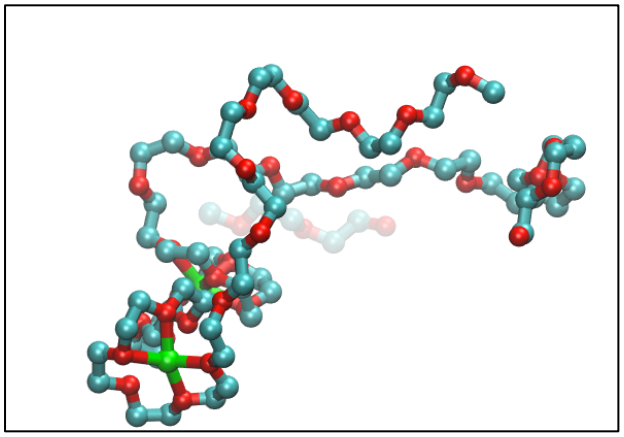
Battery Research for Green Aviation at NASA



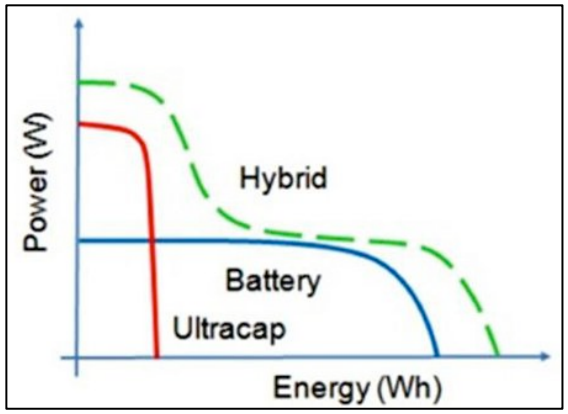
Li-Air Battery Chemistry



Electrolytes for Li-metal

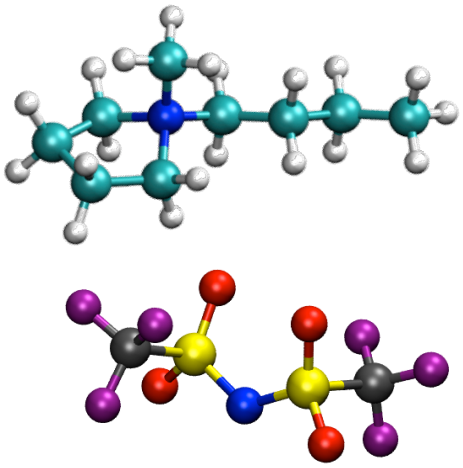


Structural Electrolytes

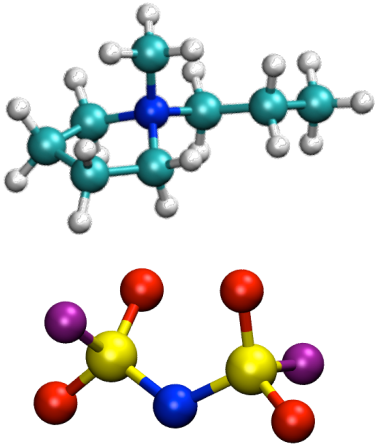


Hybrid Battery/Supercapacitors

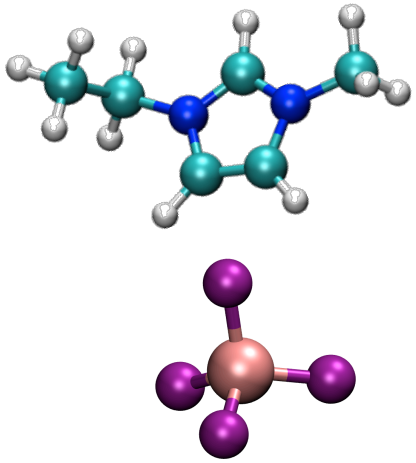
Ionic Liquid Electrolytes for Supercapacitors



[pyr14][TFSI]



[pyr13][FSI]



[EMIM][BF_4]

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

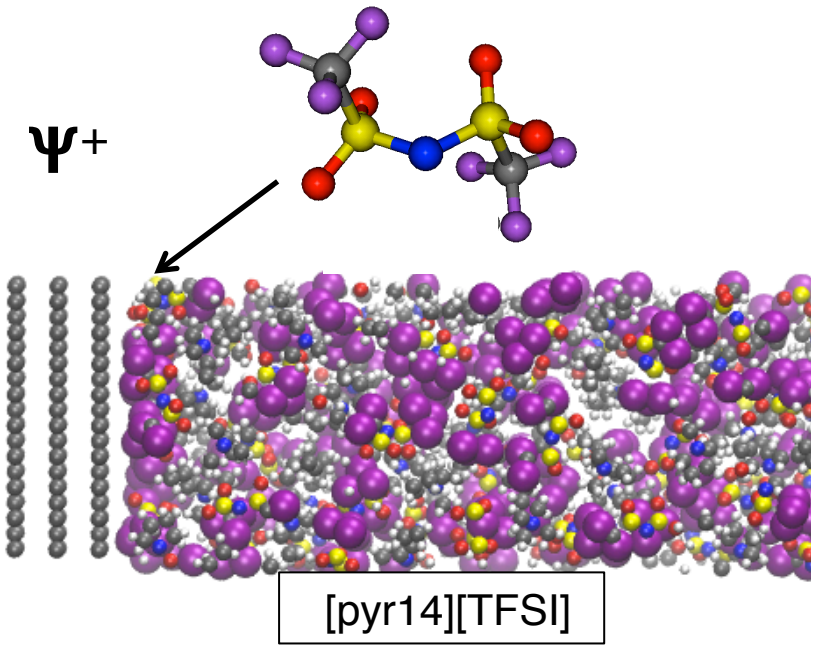
Chosen for potential use in both batteries and supercapacitors

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

Computational Study of Ionic liquids Electrolytes

- **Classical Polarizable-MD (APPLE&P) simulation for capacitance**:
  - large systems
  - constant potential electrodes
  - structural origin of capacitance
  - influence of Li-salt

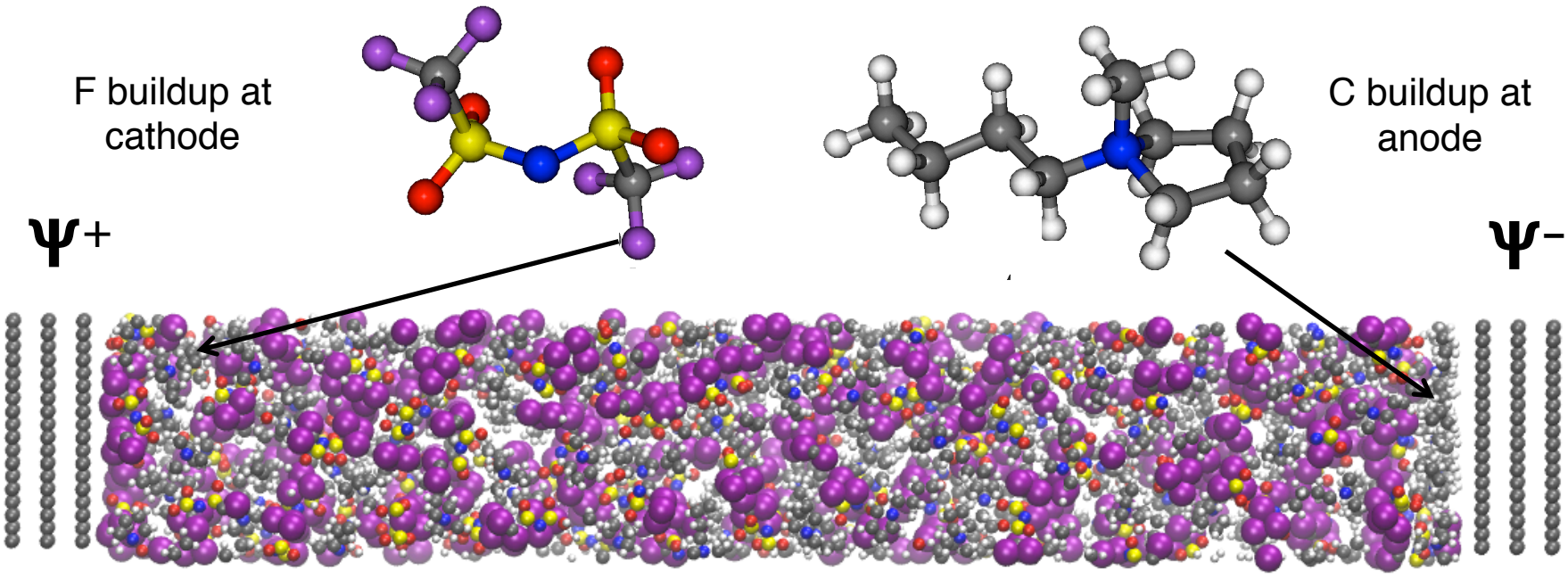
- **Quantum simulations for electrochemical window**:
  - small liquid systems
  - density functional theory molecular dynamics simulation
  - influence of Li-salt

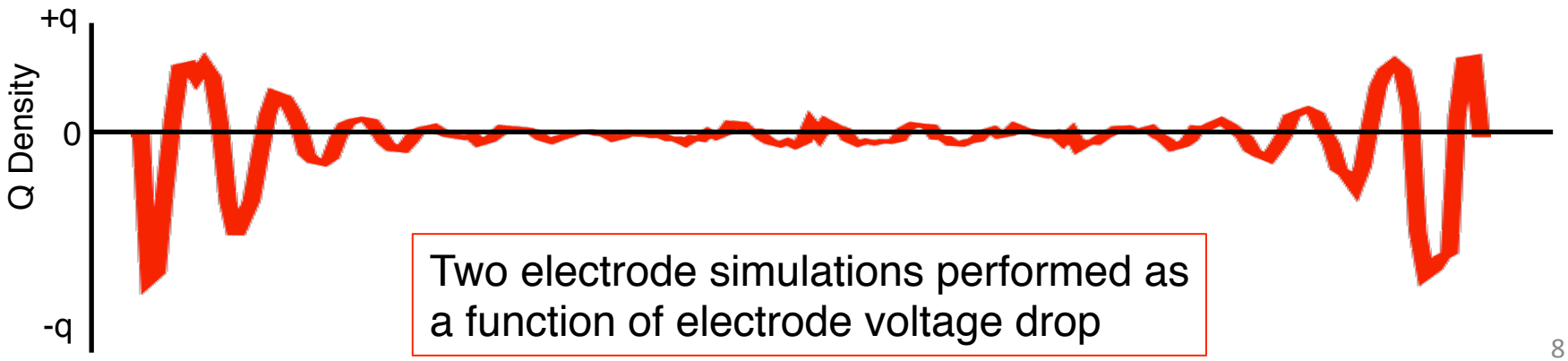


First all-simulation approach to supercapacitors: capacitance, operation range, and energy density

J Haskins, *et al.*, *J. Phys. Chem. C* (2016); J Haskins, J Lawson, *J. Chem. Phys.* (2016)

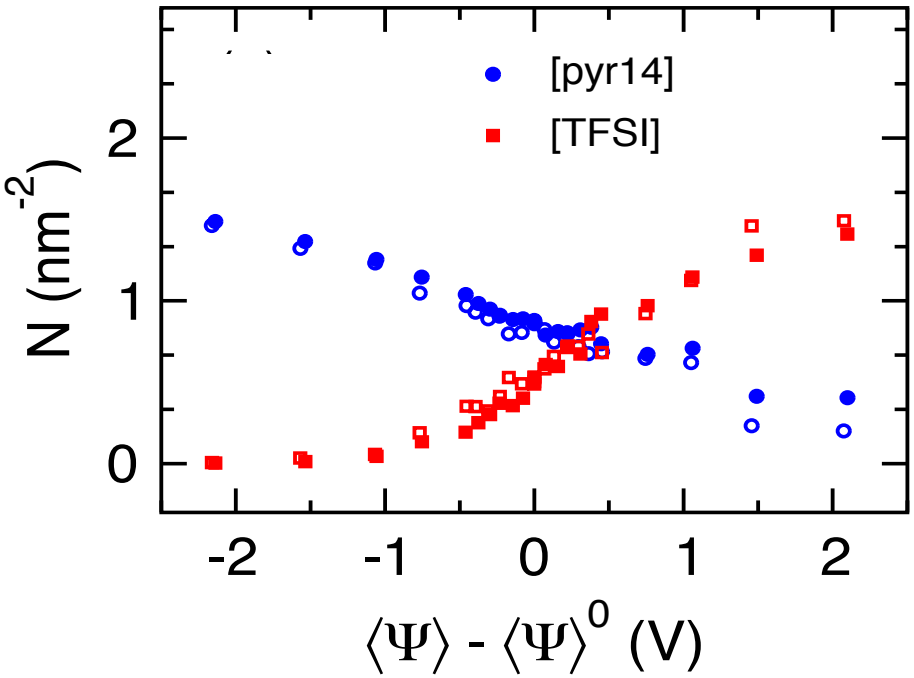
Electric Double Layer (EDL)





Two electrode simulations performed as a function of electrode voltage drop

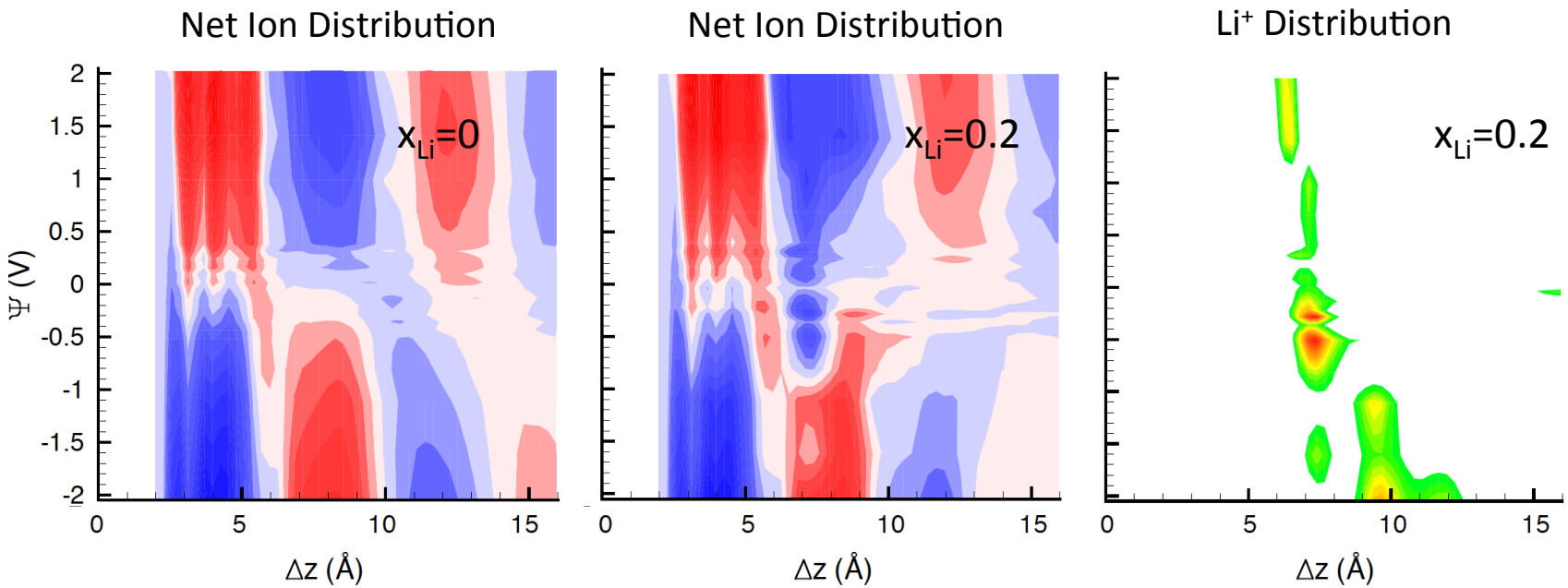
Ion accumulation at the surface: [pyr14][TFSI]



Ion depletion at high voltage

J Haskins, et al., *J. Phys. Chem. C* (2016)

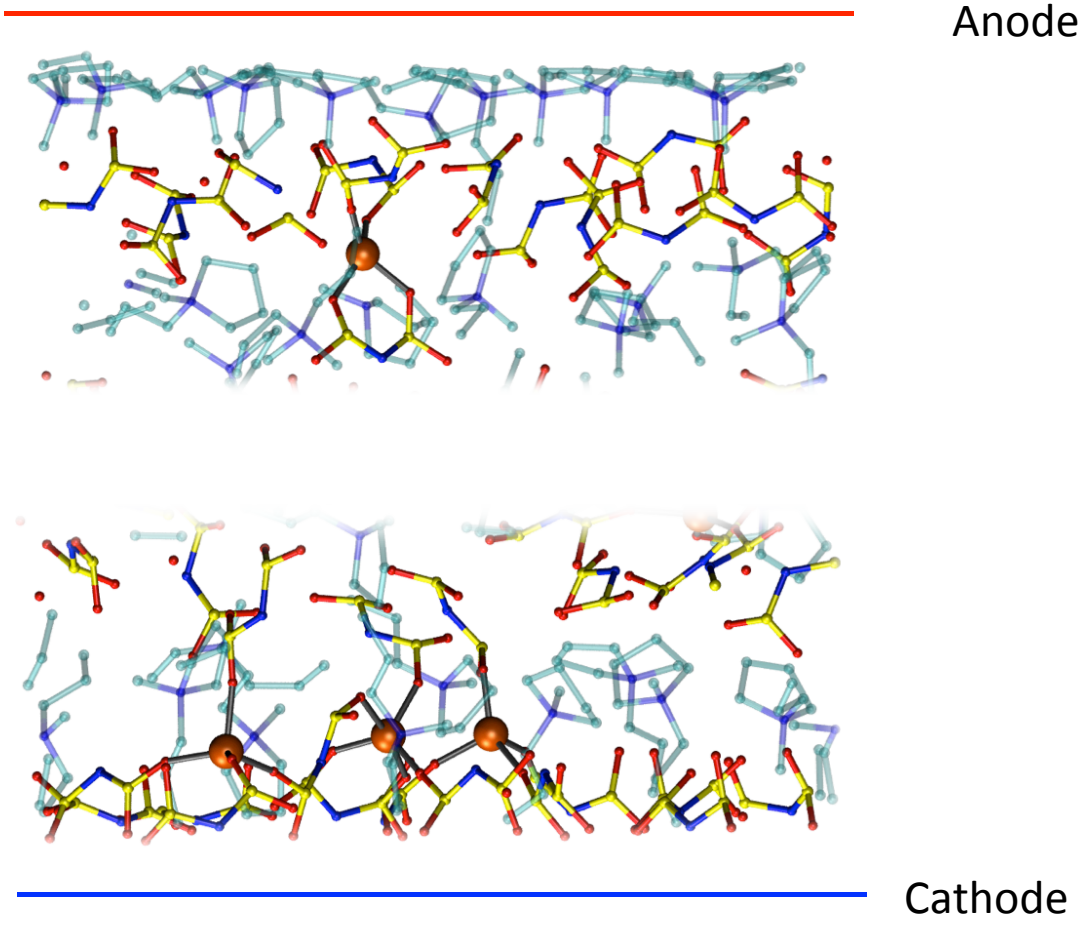
Li^+ Influence on the EDL



Li^+ disrupts the EDL and accumulates in 2nd layer

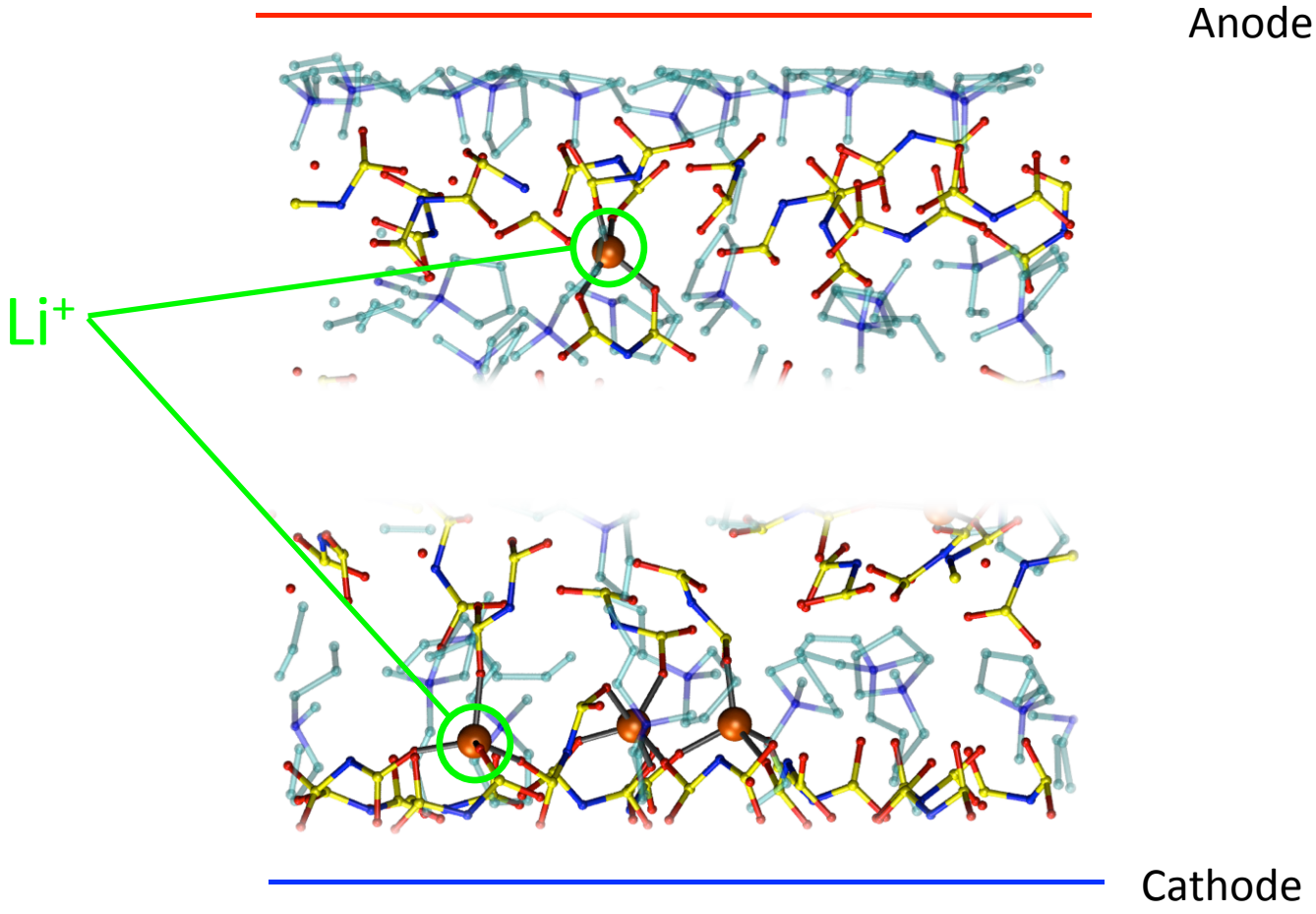
J Haskins, et al., *J. Phys. Chem. C* (2016)

Li^+ binding at the interface: [pyr14][TFSI]



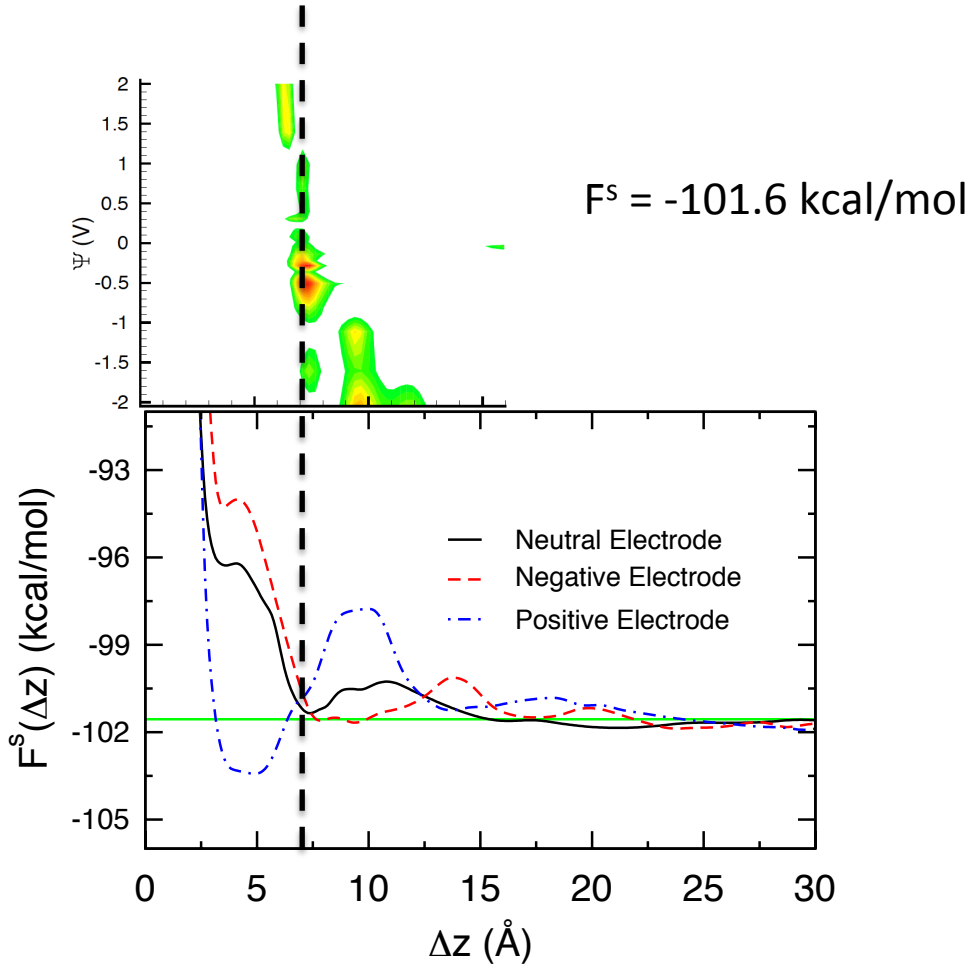
Li^+ accumulates in the second molecular layer

Li^+ binding at the interface: [pyr14][TFSI]



Li^+ accumulates in the second molecular layer

Free energy barrier to Li^+ intercalation: [pyr14][TFSI]

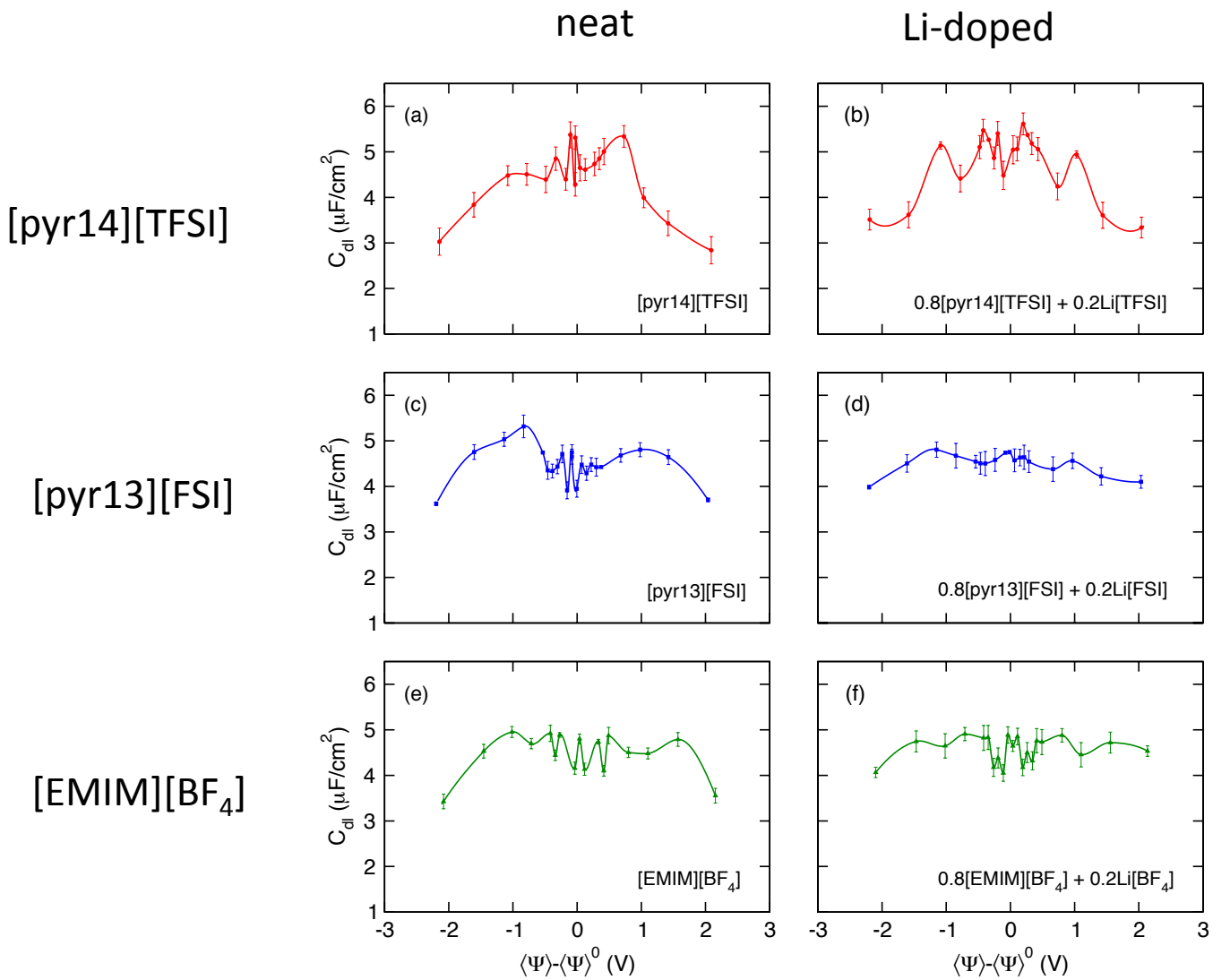


F^s = -101.6 kcal/mol

Solvation free energy concurs with Li-density

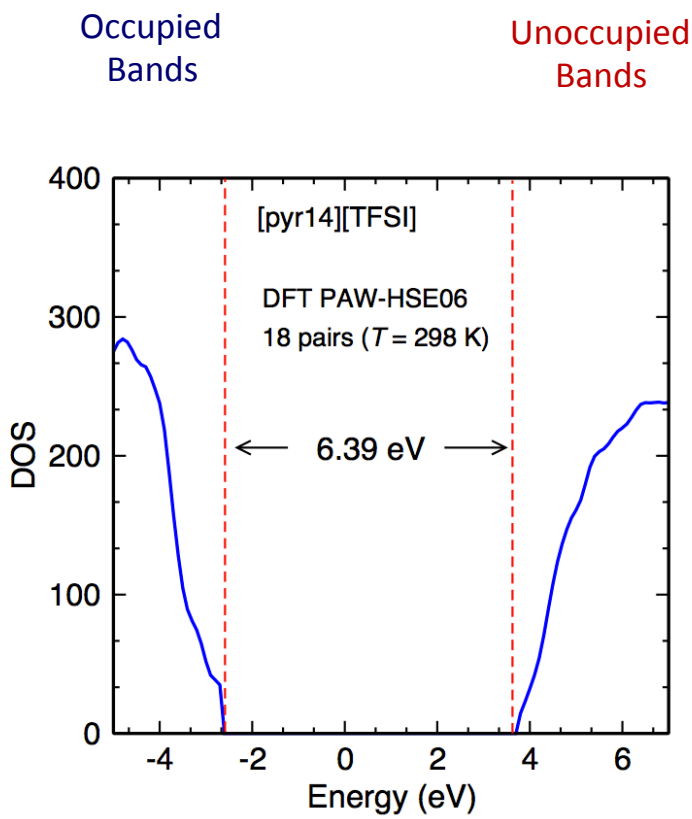
J.B. Haskins, et al., *J. Phys. Chem. C* (2016)

Influence of Li^+ on capacitance



J Haskins, , *et al.*, *J. Phys. Chem. C* (2016); J Haskins, *et al*, *J. Chem. Phys.* (2016); J Vatamanu, *et al.*, *J. Am. Chem. Soc.* (2010)

Electrochemical windows (DFT-MD Liquid)



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 windows bound experiment

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

Specific energy estimate

		E (Wh/m^2)	E (Wh/kg)
[pyr14][TFSI]	Theory	0.7-1.3	0.8-1.4
	Exp.	1.4-3.5	1.5-3.8
[pyr13][FSI]	Theory	0.7-1.4	0.8-1.5
	Exp.	3.5-6.8	3.8-7.3
[EMIM][BF_4]	Theory	0.5-0.9	0.5-1.0
	Exp.	1.3-1.5	1.4-1.6

Assume specific surface area 1074 m^2/g

Specific Energy = $0.5C_{dl}(EW)^2$

Specific energy estimates predict experimental trends

J Haskins, *et al.*, *J. Phys. Chem. C* (2016)

Conclusions

- Li^+ disruption of the electric double layer
- Magnitude of capacitance is a weak function of Li-doping
- Capacitance profile shows variation with Li-doping
- Electrochemical stability a weak function of Li-doping
- Computed specific energy in good agreement with experiment