

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



Justin B. Haskins¹ and John W. Lawson²

¹AMA, Inc., NASA Ames Research Center

²NASA Ames Research Center

Collaborators



NASA Ames Research Center

John W. Lawson

Charles W. Bauschlicher

Justin B. Haskins

Josh D. Monk



NASA Glenn Research Center

James J. Wu

Dionne M. Hernandez

William R. Bennett

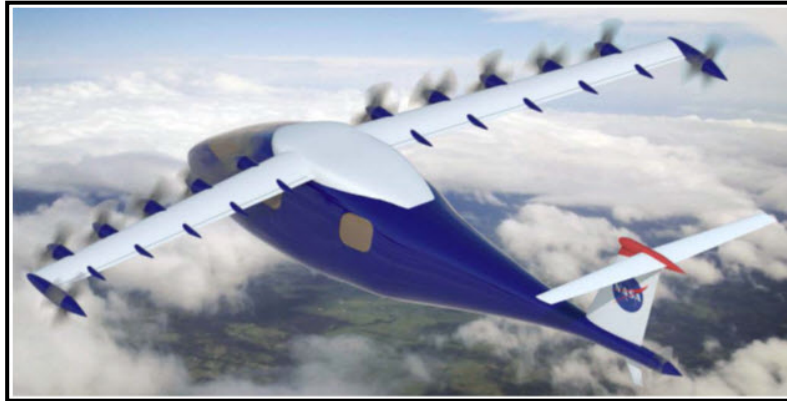
Vadim Lvovich



Army Research Center

Oleg Borodin

Green Aviation at NASA



Efficient Aircraft: NASA LEAPTech



UAVs: NASA "Greased-Lightning"

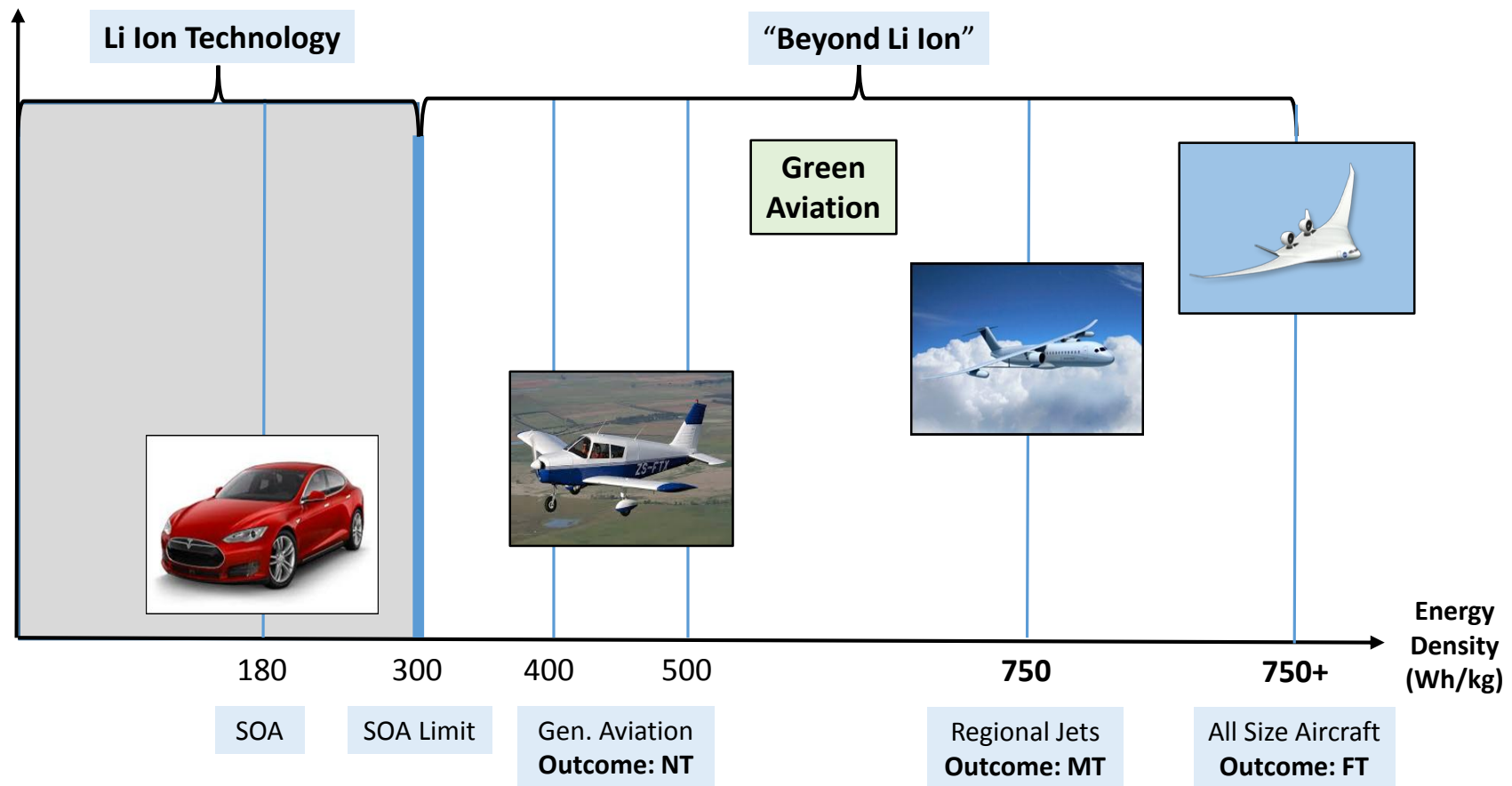
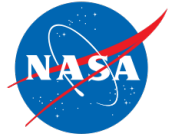


Solar-Battery Hybrid: NASA "Pathfinder"



Battery-Gas Hybrid: Boeing "SUGAR Volt"

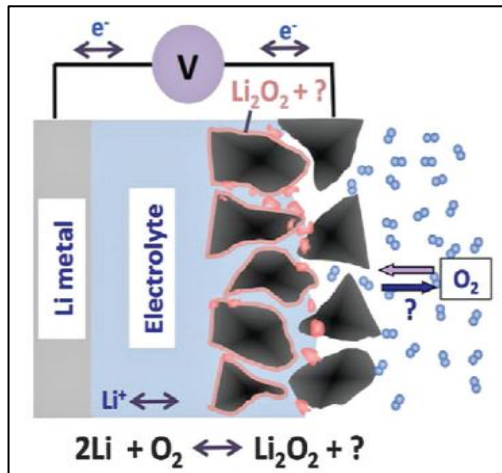
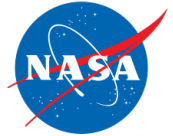
Battery Energy Density Limitations on Green Aviation



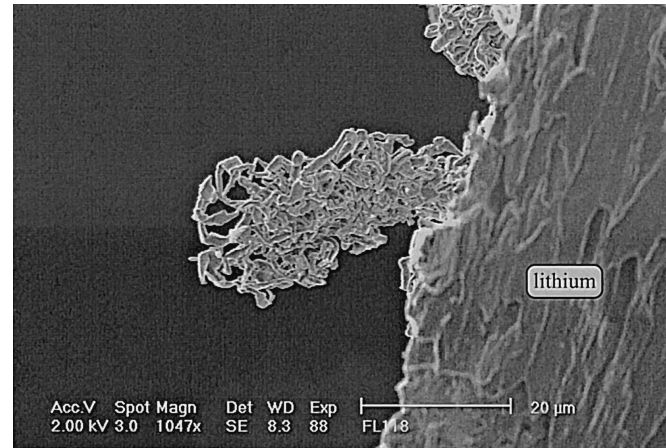
Major requirement is: High Energy Density

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

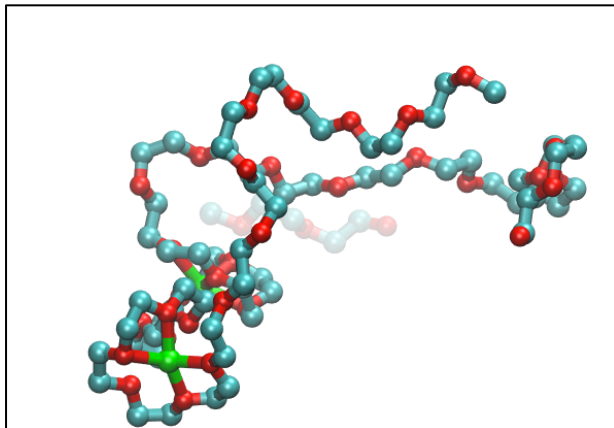
Battery Research for Green Aviation at NASA



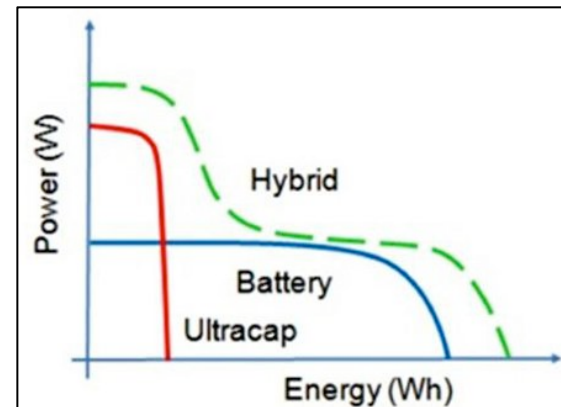
Li-Air Battery Chemistry



Electrolytes for Li-metal

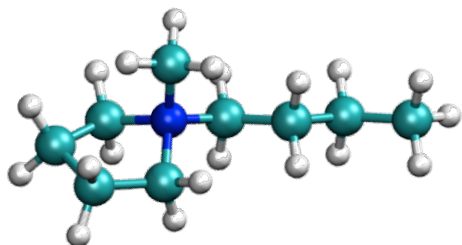


Structural Electrolytes

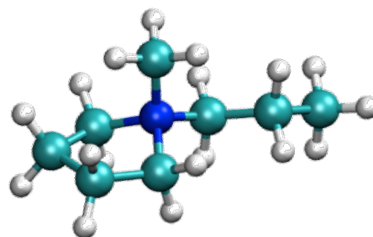


Hybrid Battery/Supercapacitors

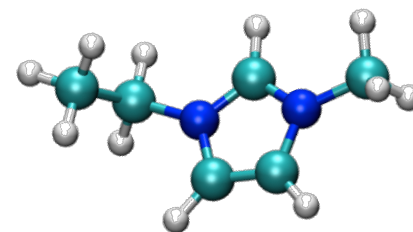
Ionic Liquid Electrolytes for Supercapacitors



[pyr14][TFSI]



[pyr13][FSI]



[EMIM][BF₄]

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

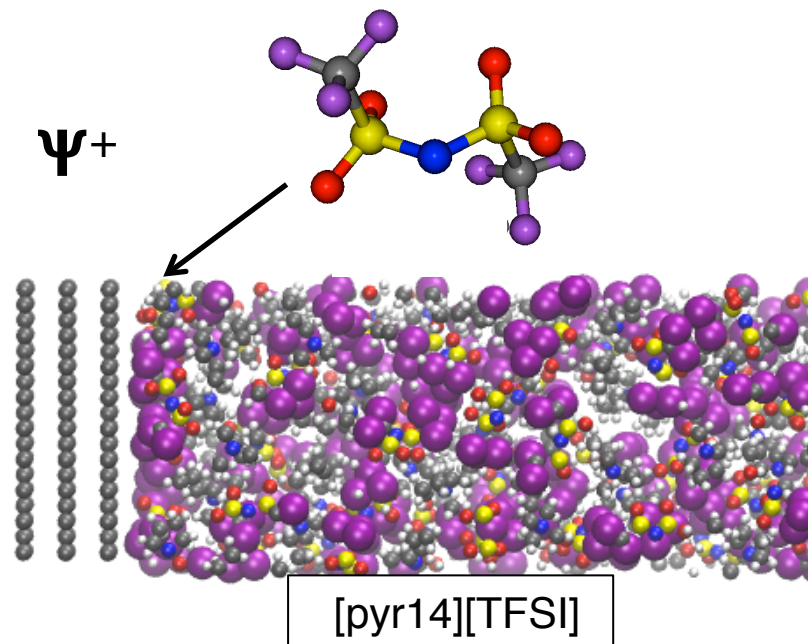
Chosen for potential use in both batteries and supercapacitors

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

Computational Study of Ionic liquids Electrolytes

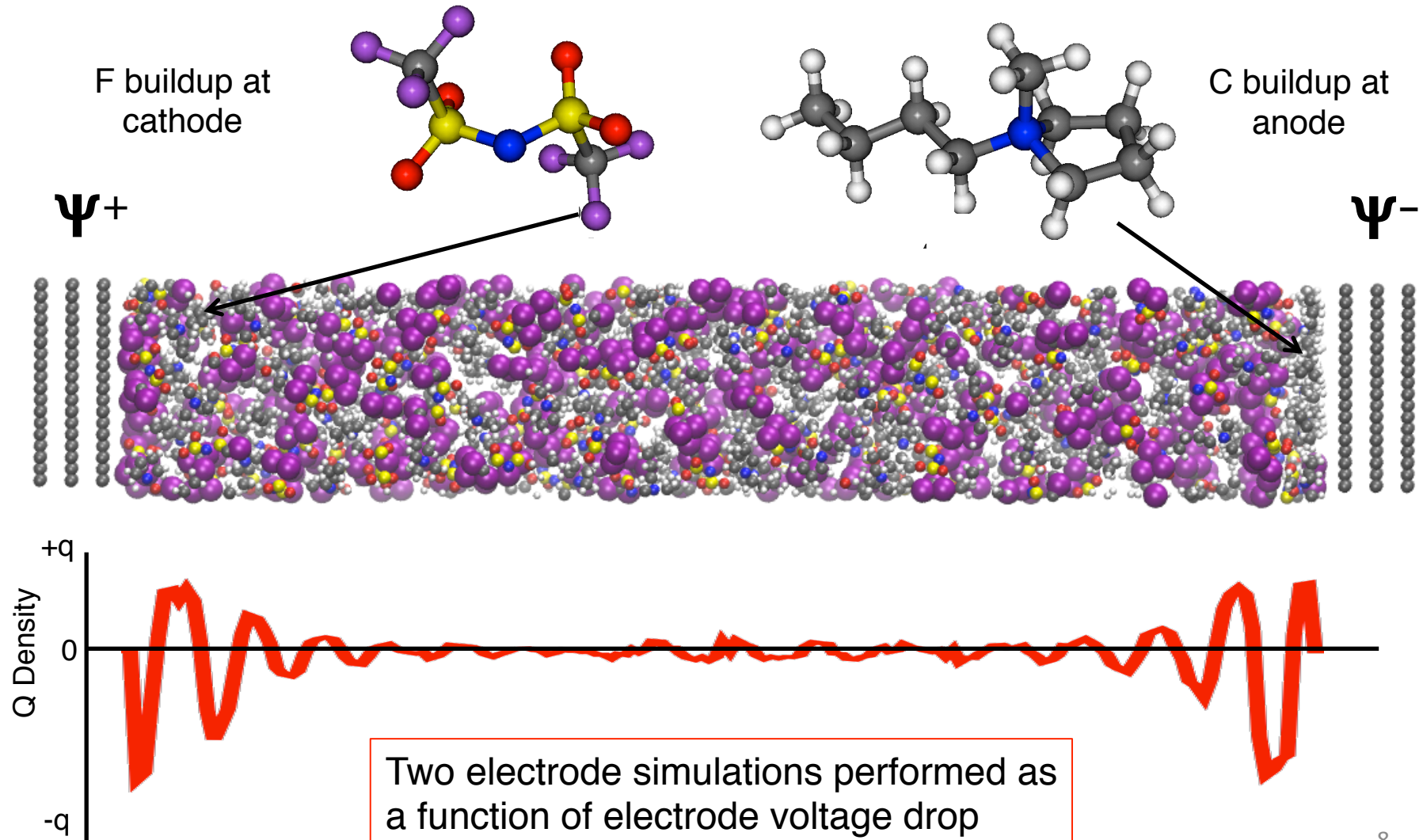
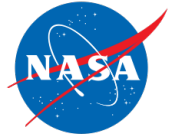


- **Classical Polarizable-MD (APPLE&P) simulation for capacitance:**
 - large systems
 - constant potential electrodes
 - structural origin of capacitance
 - influence of Li-salt
- **Quantum simulations for electrochemical window:**
 - small liquid systems
 - density functional theory molecular dynamics simulation
 - influence of Li-salt

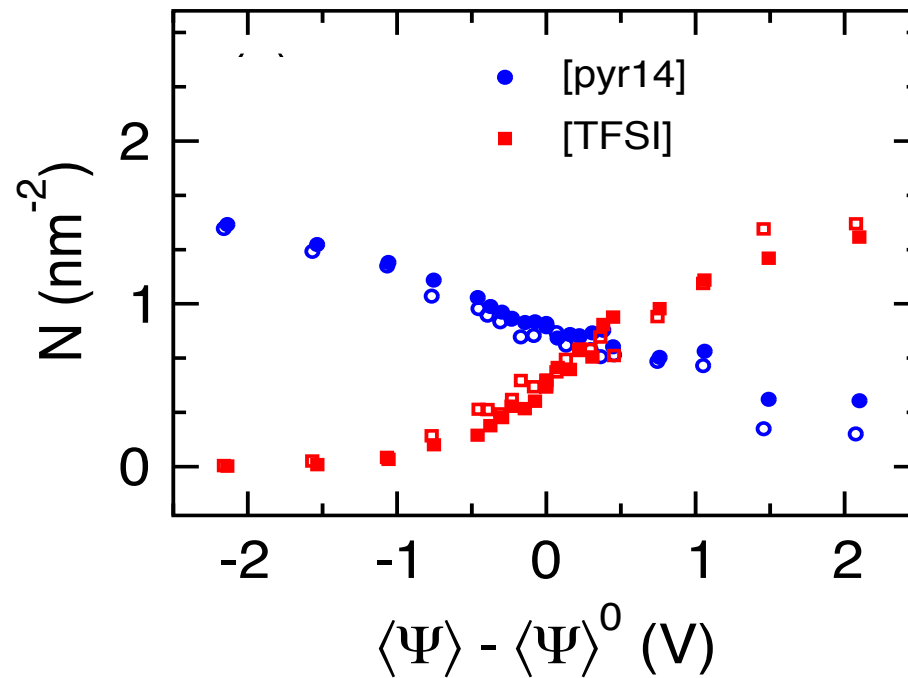


First all-simulation approach to supercapacitors:
capacitance, operation range, and energy density

Electric Double Layer (EDL)

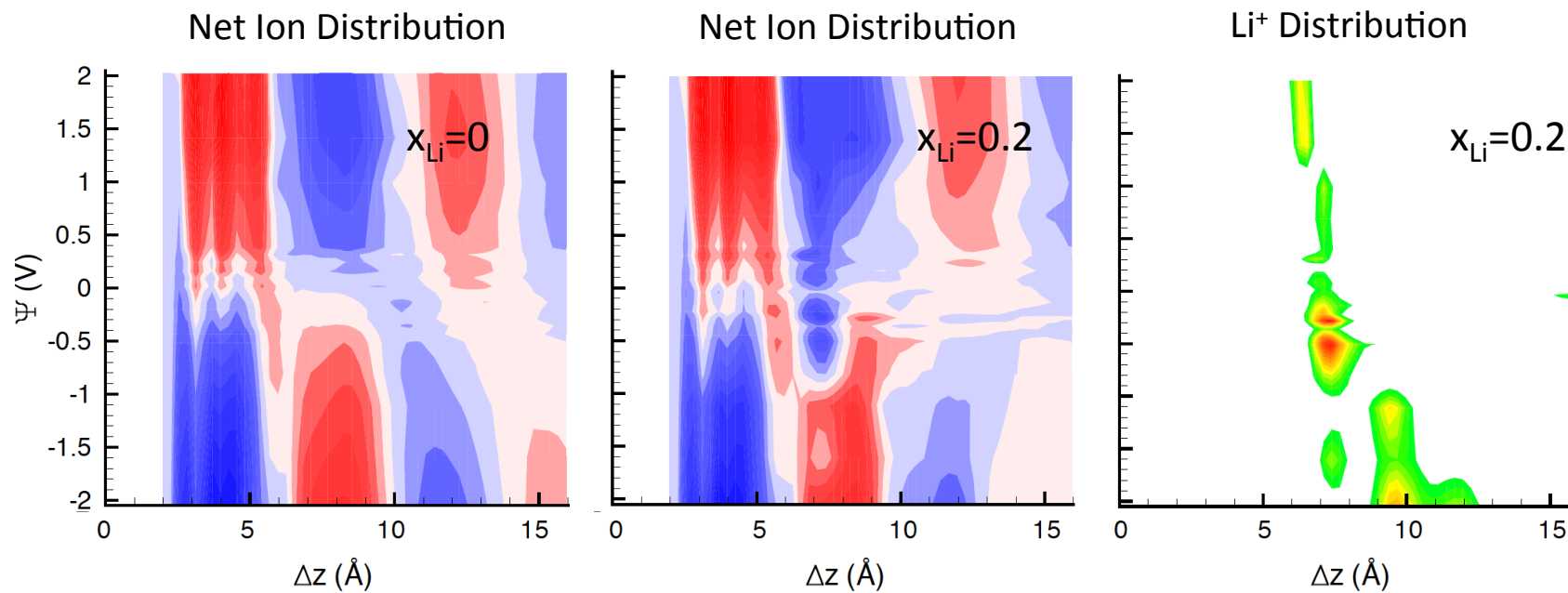


Ion accumulation at the surface: [pyr14][TFSI]



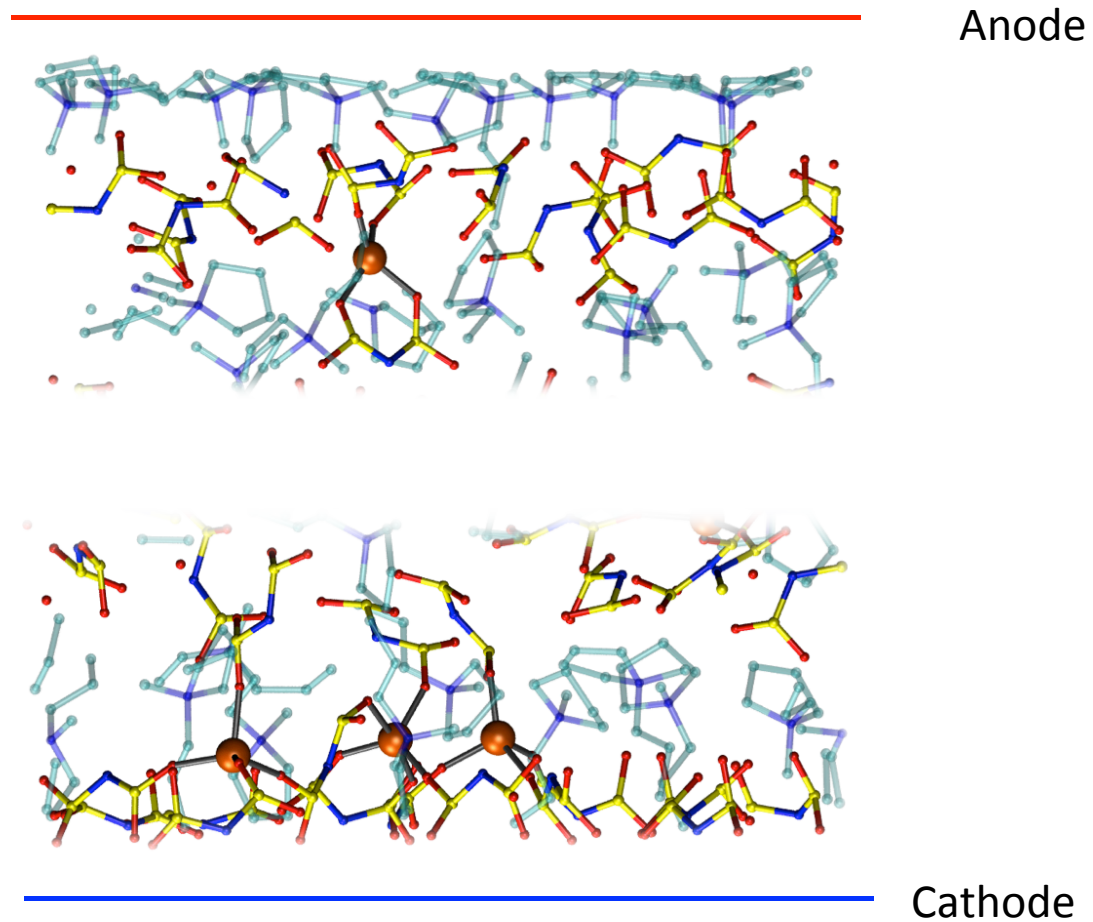
Ion depletion at high voltage

Li⁺ Influence on the EDL



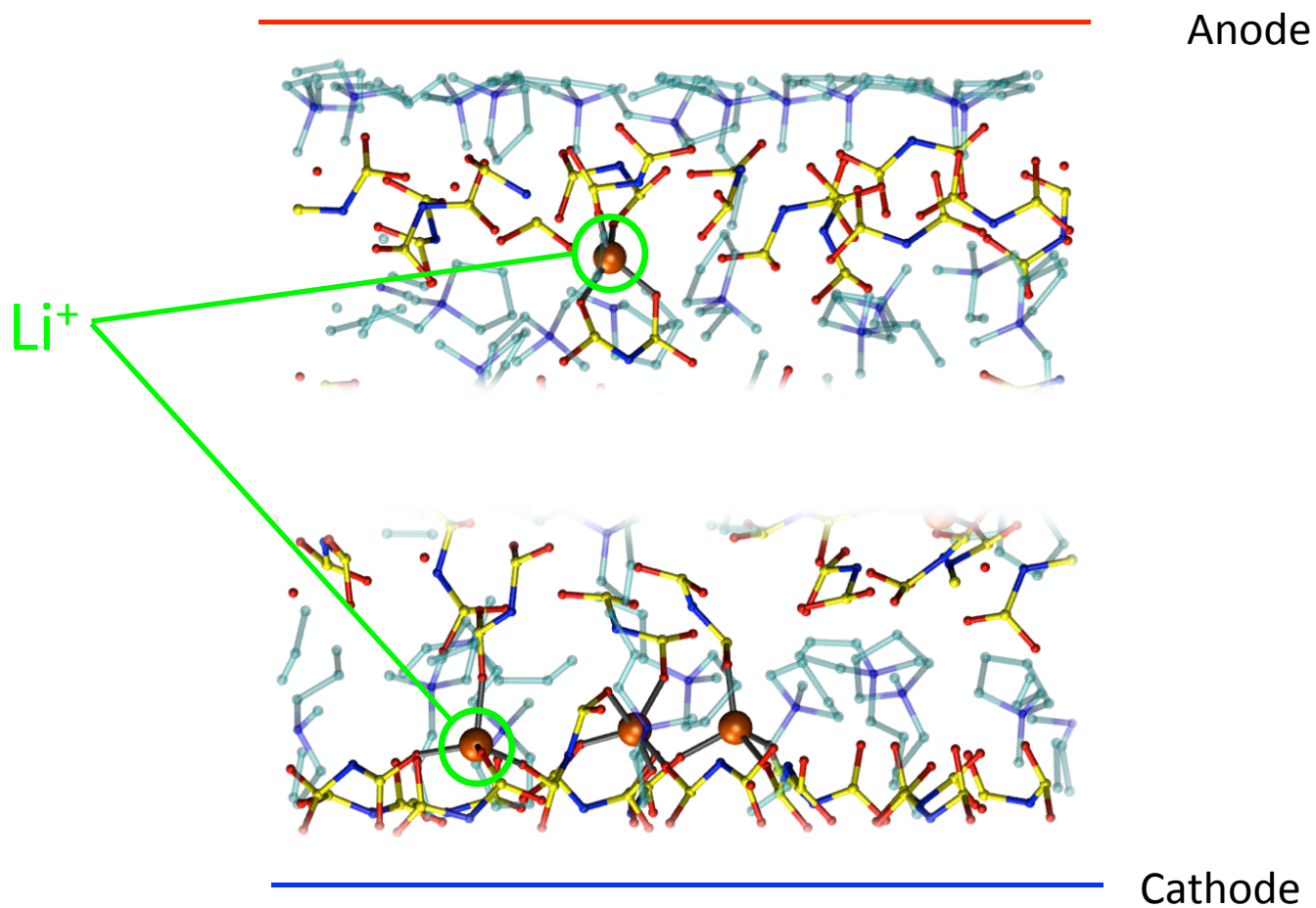
Li⁺ disrupts the EDL and accumulates in 2nd layer

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



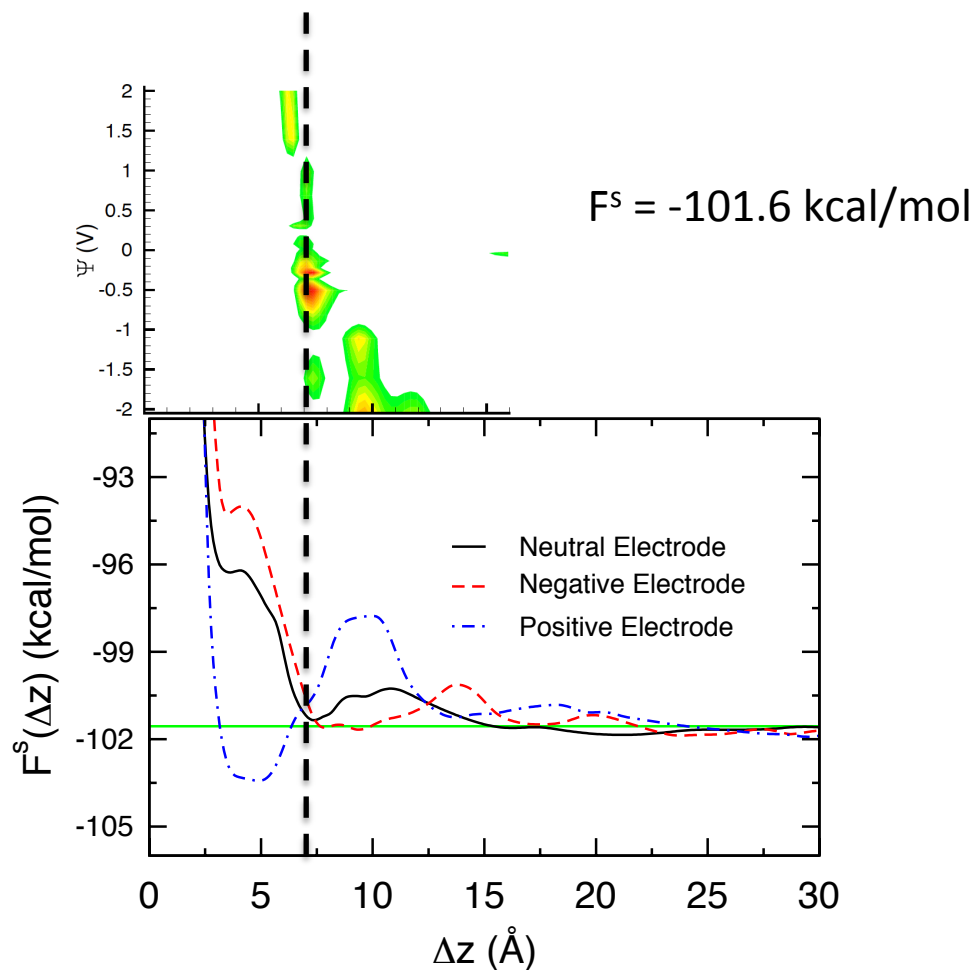
Li⁺ accumulates in the second molecular layer

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



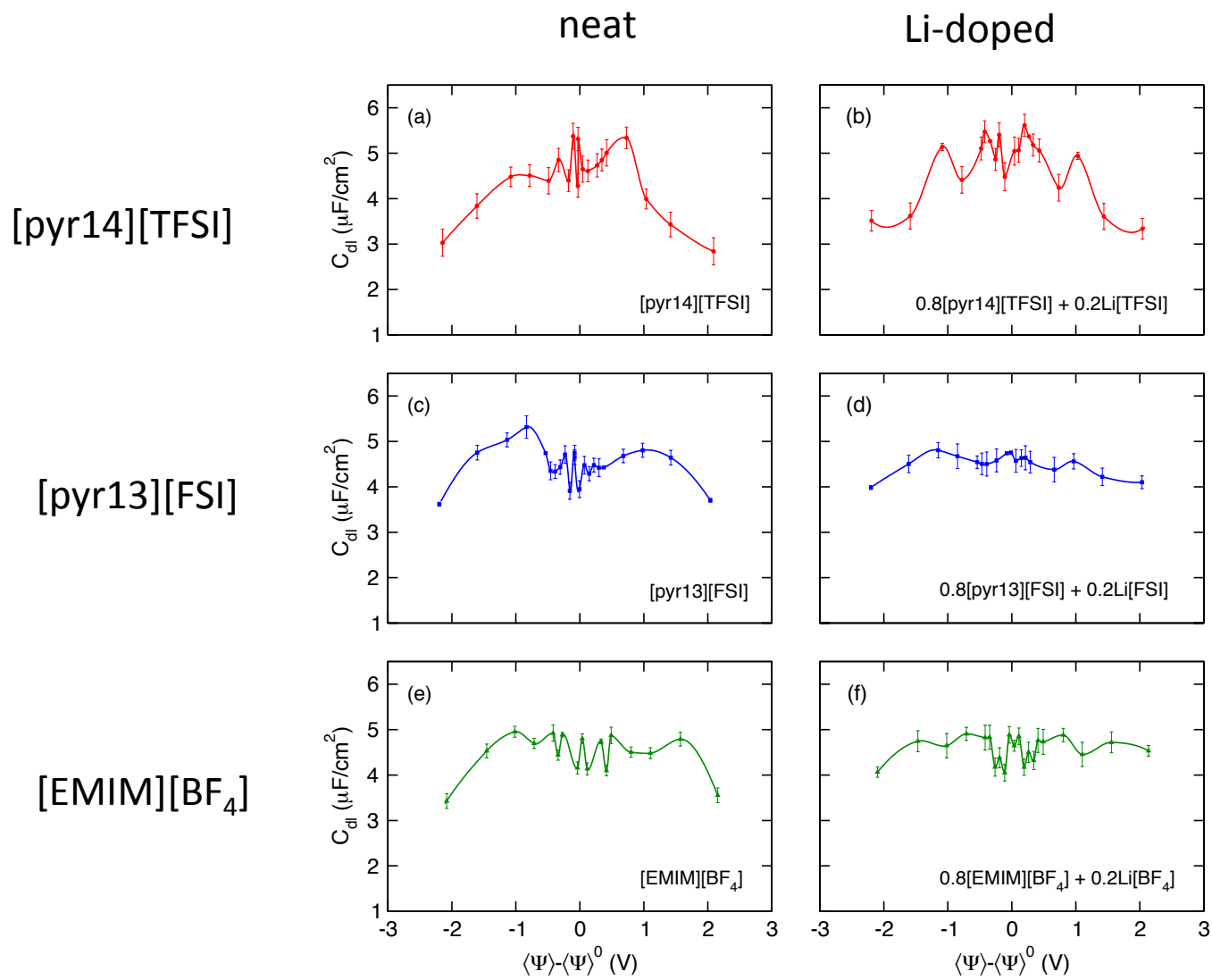
Li⁺ accumulates in the second molecular layer

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

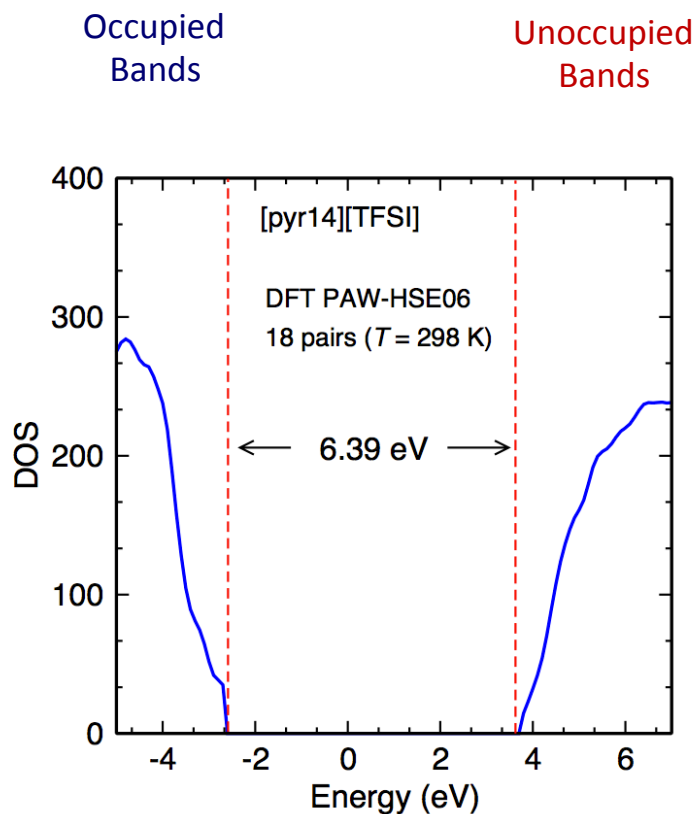


Solvation free energy concurs with Li-density

Influence of Li⁺ on capacitance



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

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 m²/g

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

Specific energy estimates predict experimental trends

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**