https://ntrs.nasa.gov/search.jsp?R=20160005028 2019-08-31T03:44:13+00:00Z

Li-doped Ionic Liquid Electrolytes

From Bulk Phase to Interfacial Behavior

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James J. Wu

Dionne M. Hernandez

William R. Bennett

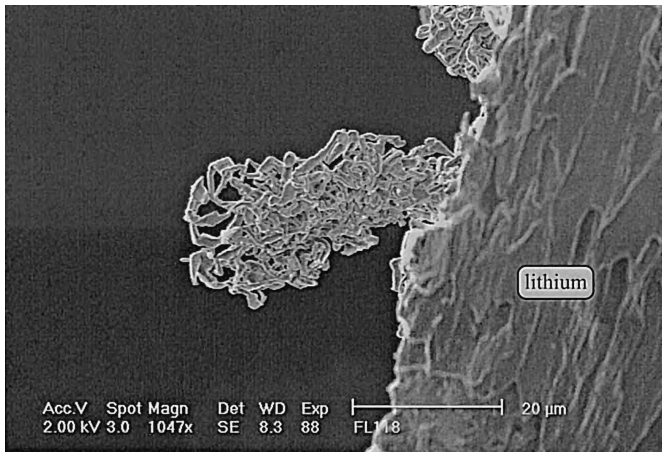
Vadim Lvovich

Army Research Center

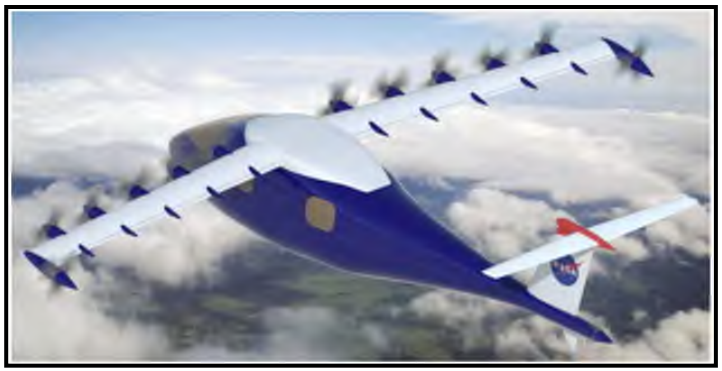
Oleg Borodin

Ionic liquids for electrochemical applications

- **Advanced electrodes**: help stabilize cycling against Li-metal
- **Li-ion batteries**: possible safer alternative to organic electrolytes
- **Supercapacitors:** double layer capacitor electrolyte
- **Electrodeposition**: wide electrochemical window solvent
- **Biofuel cells**: replace water as more stable solvent

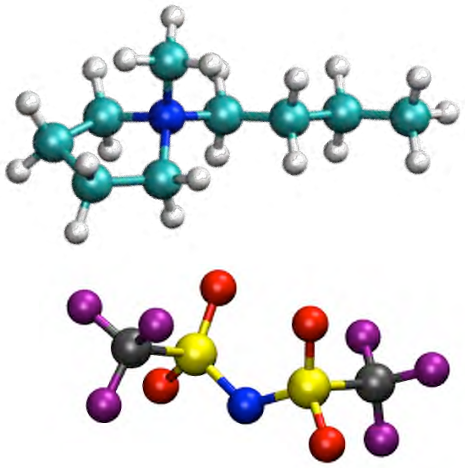


F. Orsini et al., J. Power Sources 76, 19-29 (1998)

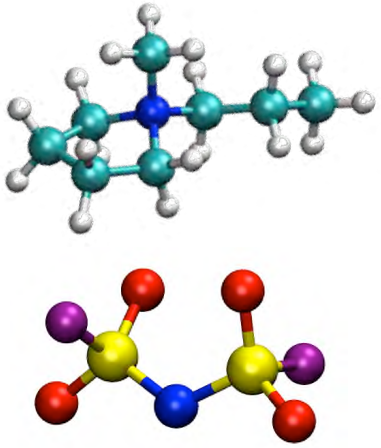


NASA Electric Aircraft

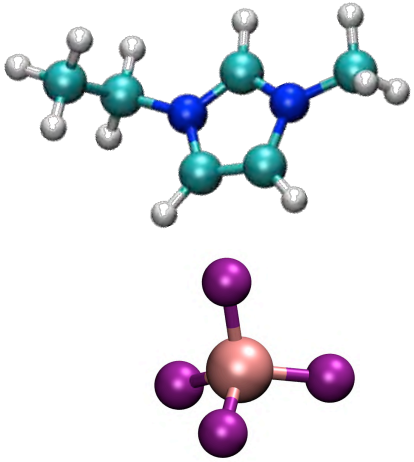
Ionic liquids (ILs)



[pyr14][TFSI]



[pyr13][FSI]



[EMIM][BF_4]

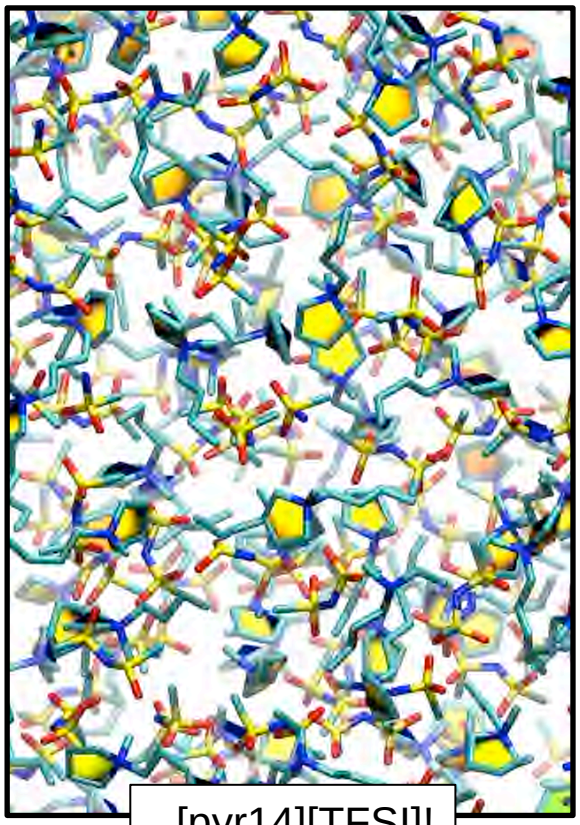
C (green)
N (blue)
S (yellow)
O (red)
F (purple)
B (pink)
H (white)

Chosen for supression of dendrites on Li^+ metal anodes!

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

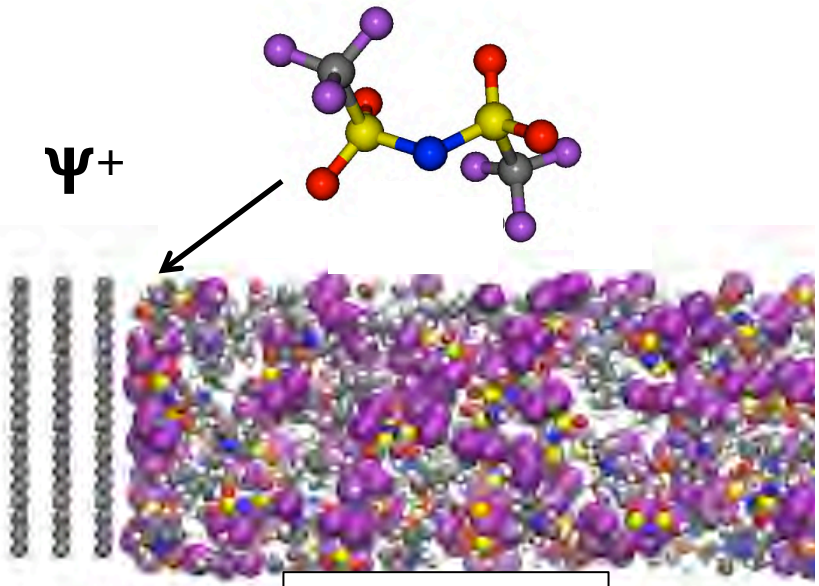
Computational Study of Li-doped ILs with Experimental Validation

Bulk Properties



[pyr14][TFSI]!

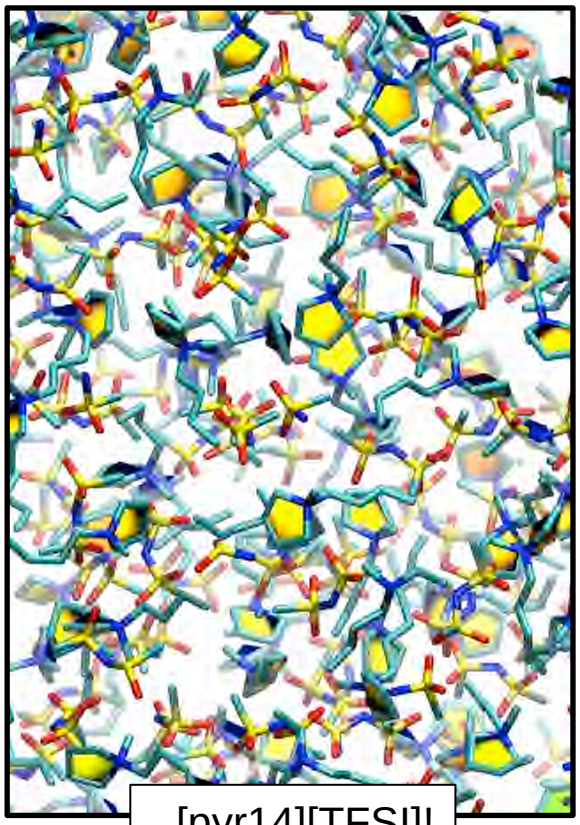
Interfacial Properties



[pyr14][TFSI]!

Computational Study of Li-doped ILs with Experimental Validation

Bulk Properties

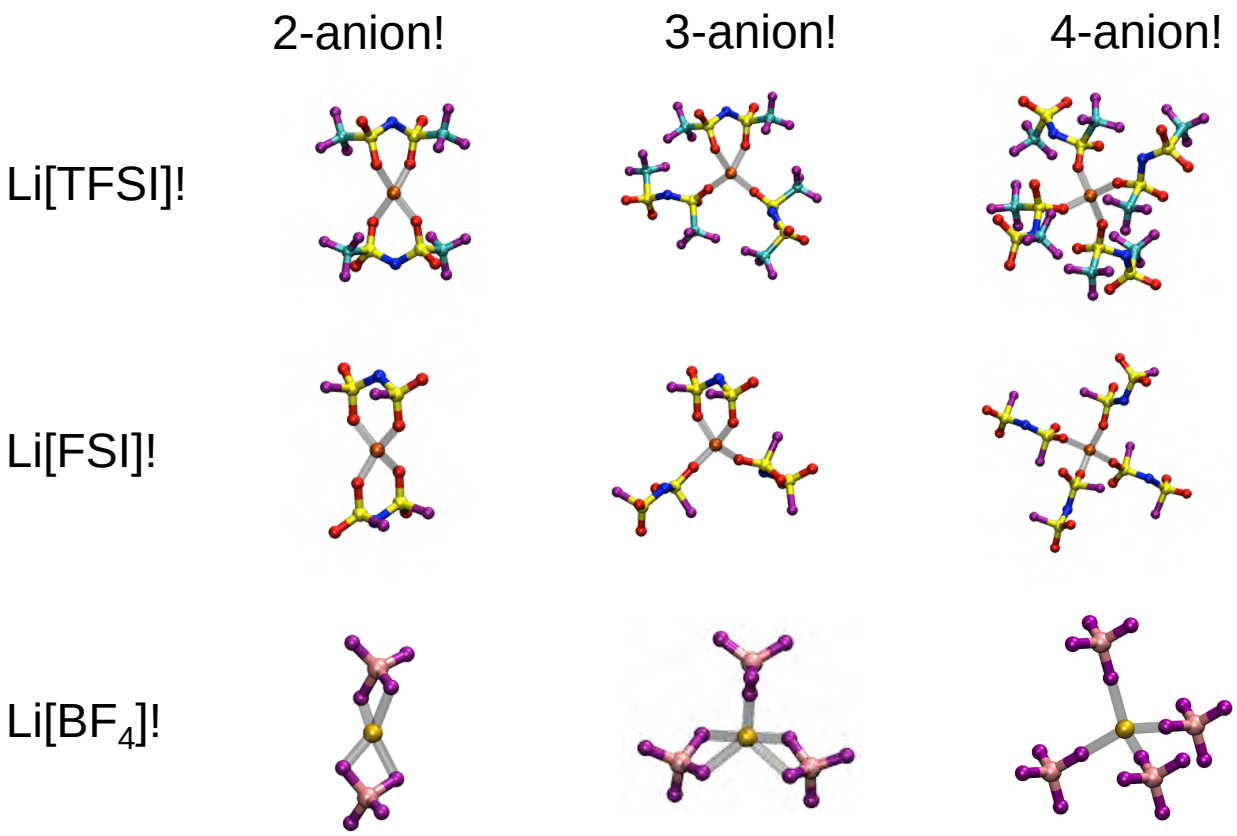


[pyr14][TFSI]!

- **Quantum chemistry (QC) of Li/Anion clusters**:
  - Li solvation structure/energetics
  - IR/Raman spectra
  - electrochemical windows
- **DFT-MD simulation of Li-doped liquid**:
  - Li solvation structure
  - IR spectra
  - electrochemical windows
- **Polarizable-MD (APPLE&P) simulation of Li-doped liquid**:
  - Li network structure
  - transport properties
  - transport mechanisms

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

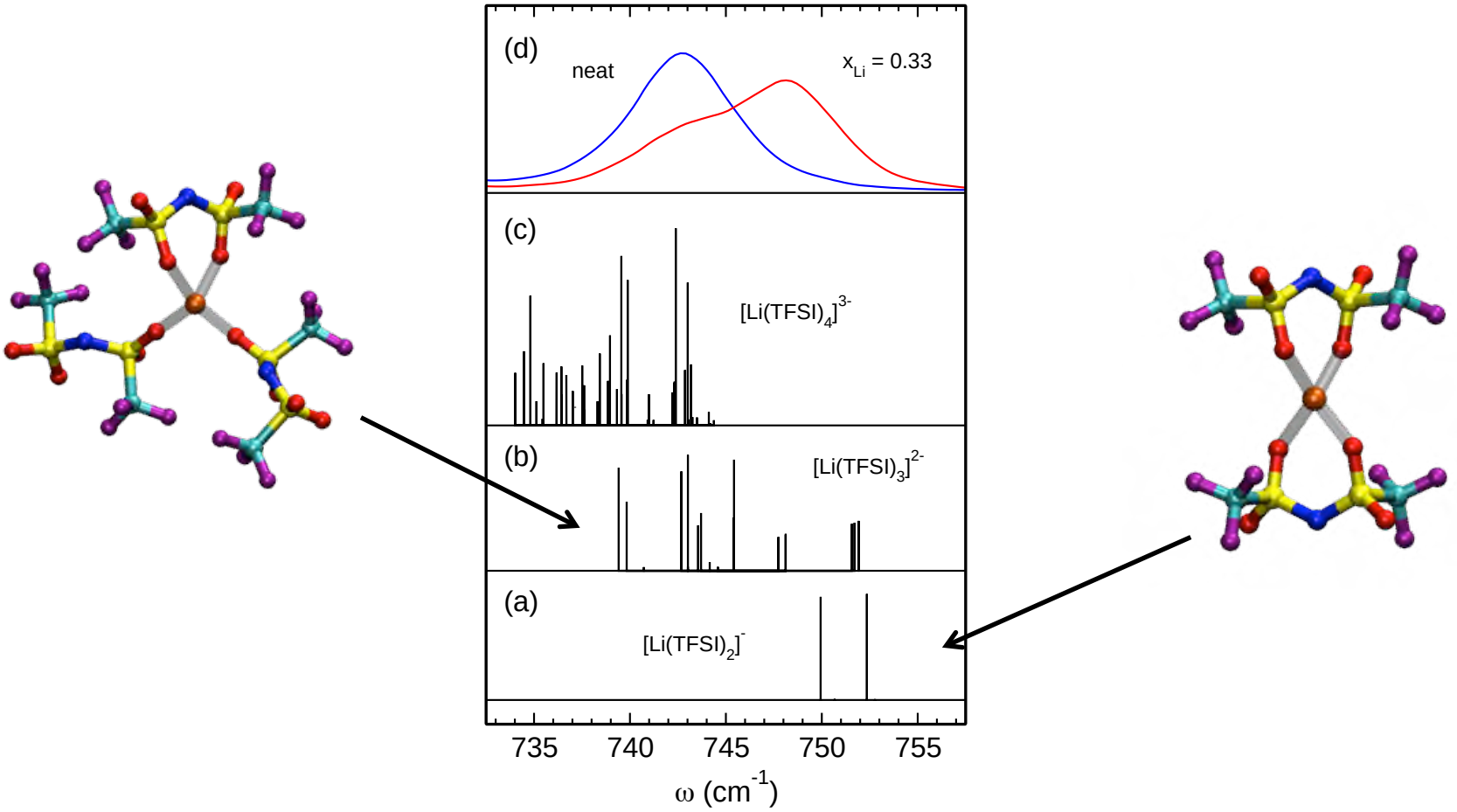
Stable solvation shells of Li^+ (QC Clusters)



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

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

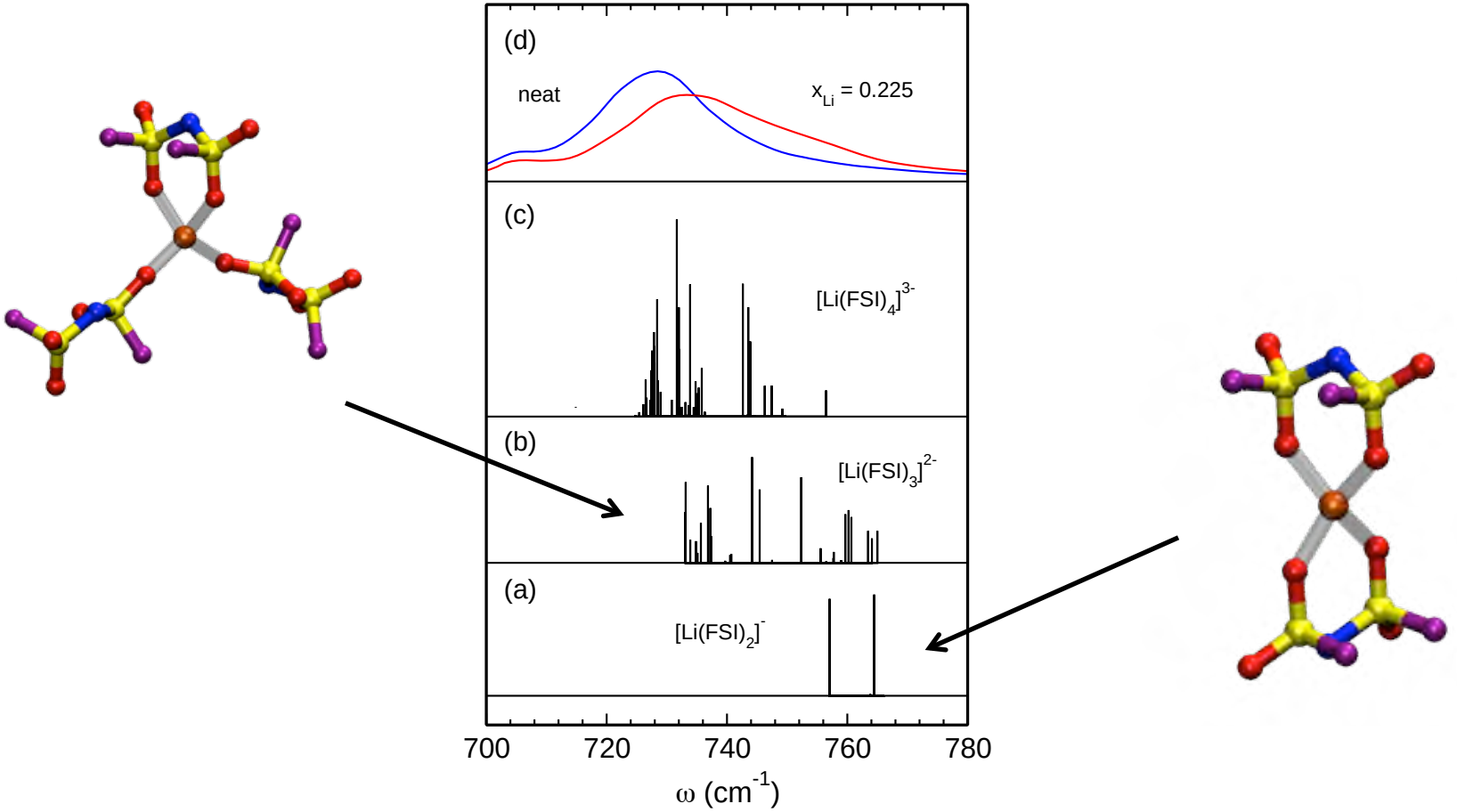
Raman analysis of Li[TFSI] (QC Clusters)



2 and 3 [TFSI] coordination are shifted!

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

Raman analysis of Li[FSI] (QC Clusters)

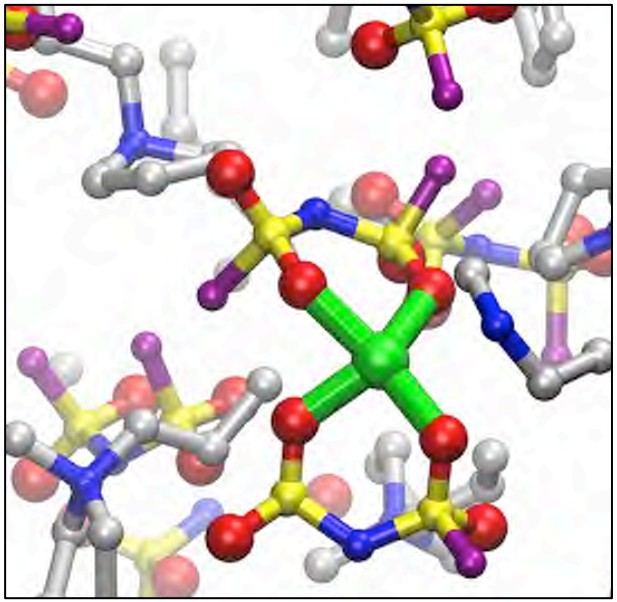


2 and 3 [FSI] coordination are shifted!

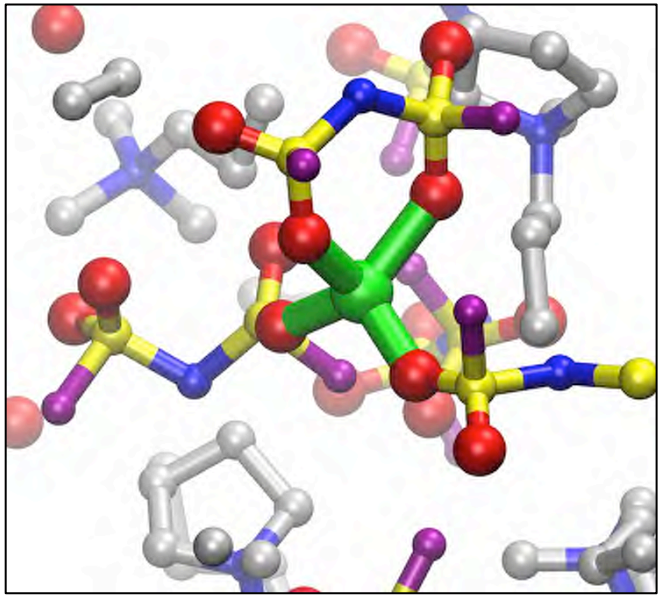
J.B. Haskins, et al., *J. Phys. Chem. B* **119**, 14705 (2015)
K. Fujii, et al., *J. Phys. Chem. C* **117**, 19314 (2013)

Li solvation shell stability (DFT-MD Liquid)

$Li[FSI]_2$



$Li[FSI]_3$

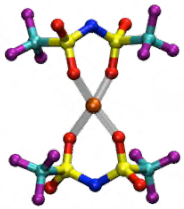
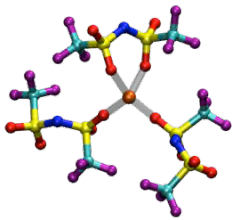
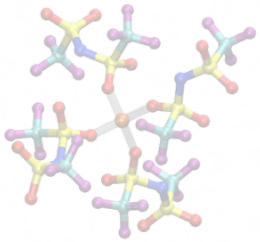
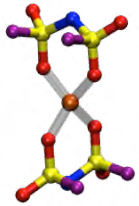
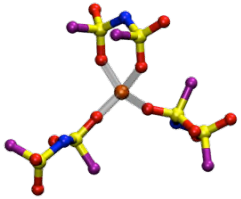
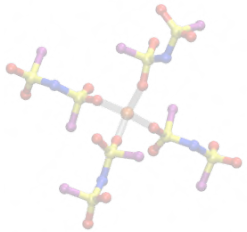
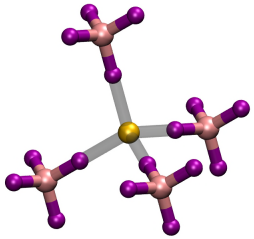


20-100 ps; 12-16 pairs; T = 363 K

Highly unfavorable configurations exchange anions within 20 ps!

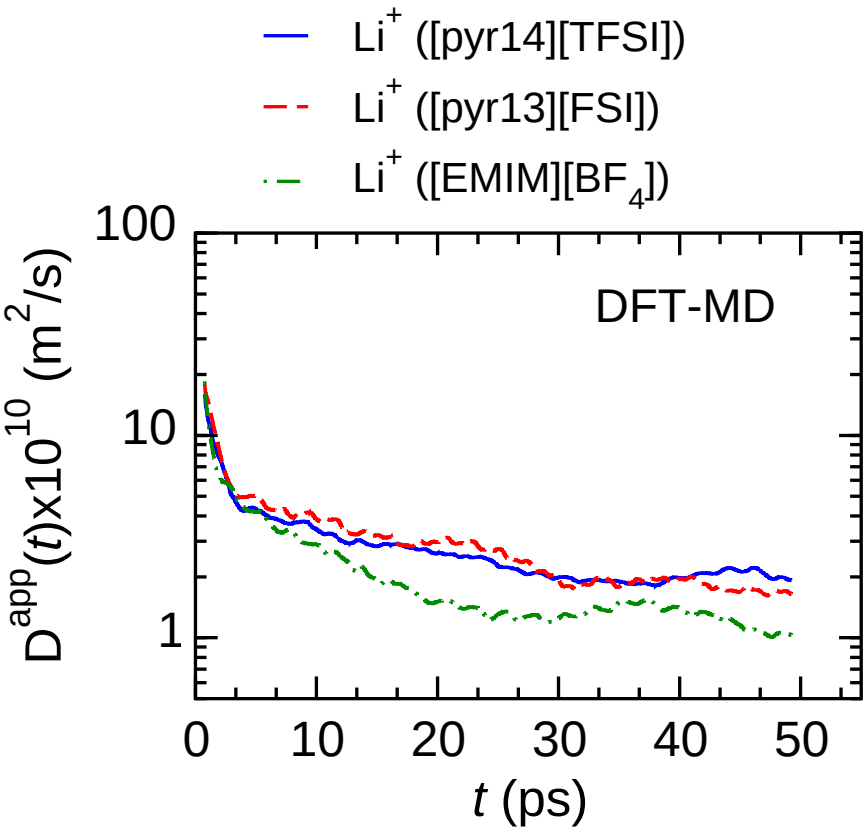
J.B. Haskins, et al., *J. Phys. Chem. B* **119**, 14705 (2015)

Stable solvation shells of Li^+ (DFT-MD Liquid)

	2-anion!	3-anion!	4-anion!
Li[TFSI]!			
Li[FSI]!			
Li[BF_4]!			

2, 3 anion Li^+ solvation shells for TFSI/FSI!
4 anion Li^+ solvation shell for BF_4 !

Li^+ Diffusion coefficients (DFT-MD Liquid)



Diffusion Coefficients x 10^{10} (m^2/s)

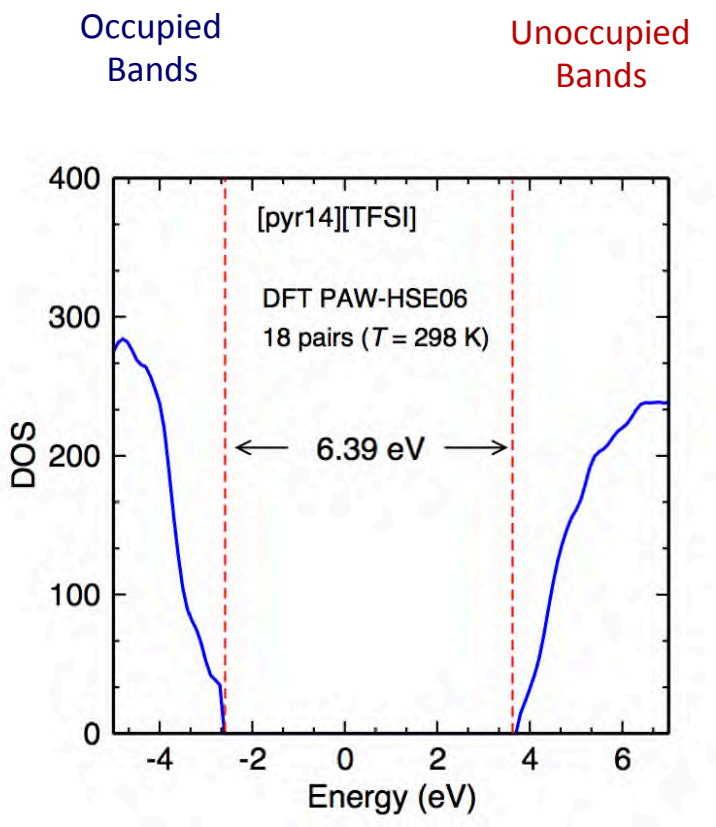
	DFT (50ps)	DFT (∞)	Exp.
[pyr14] [TFSI]	1.91	0.71	0.34
[pyr13] [FSI]	1.64	0.78	0.47
[emim] [BF_4]	1.03	0.79	0.65

100+ ps; 8-12 pairs; T = 363 K

Diffusion from ~100 ps DFT-MD order of magnitude agreement with experiment!

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

Electrochemical windows (DFT-MD Liquid)



Electrochemical Windows (eV)

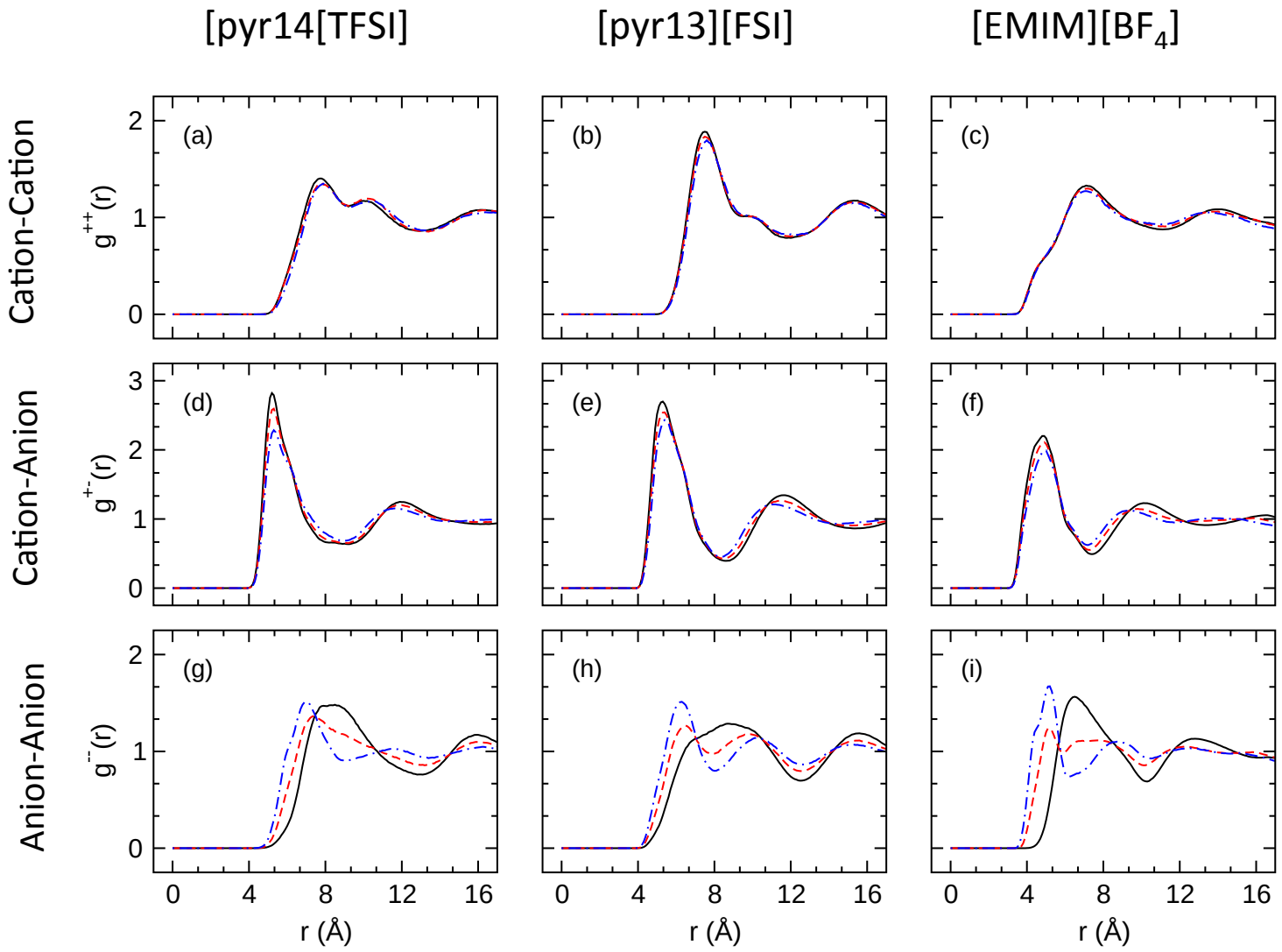
	DFT (PBE)	DFT (HSE06)	Exp.
[pyr14][TFSI]	4.6	6.5	3.8-6
[pyr13][FSI]	4.7	6.7	4.3-6
[EMIM][BF_4]	3.9	5.4	4.3

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

Electrochemical window of liquids with pure and hybrid functionals bounds experiment!

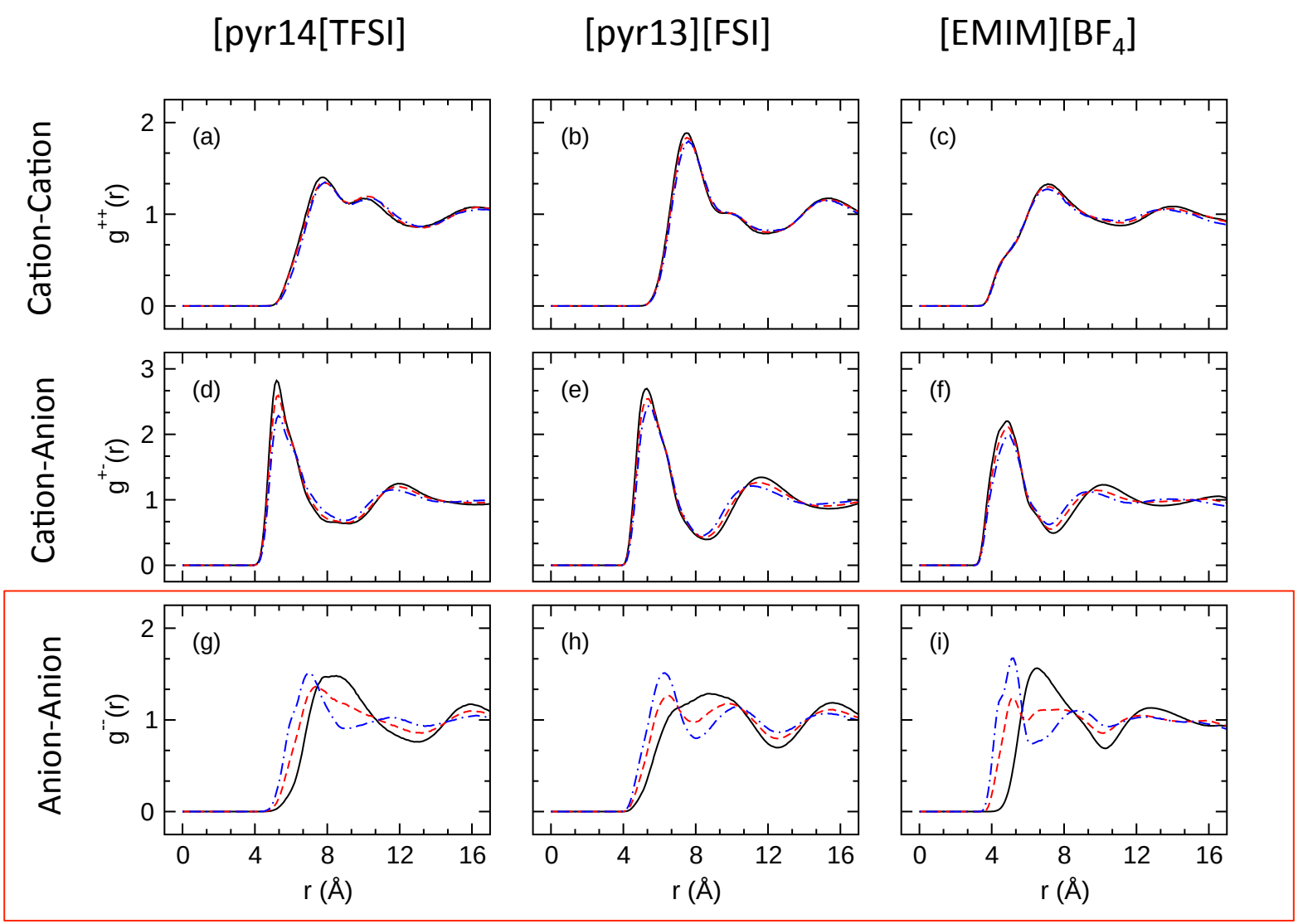
J.B. Haskins, et al., *J. Phys. Chem. B* **119**, 14705 (2015)

Radial distribution functions (PFF-MD)



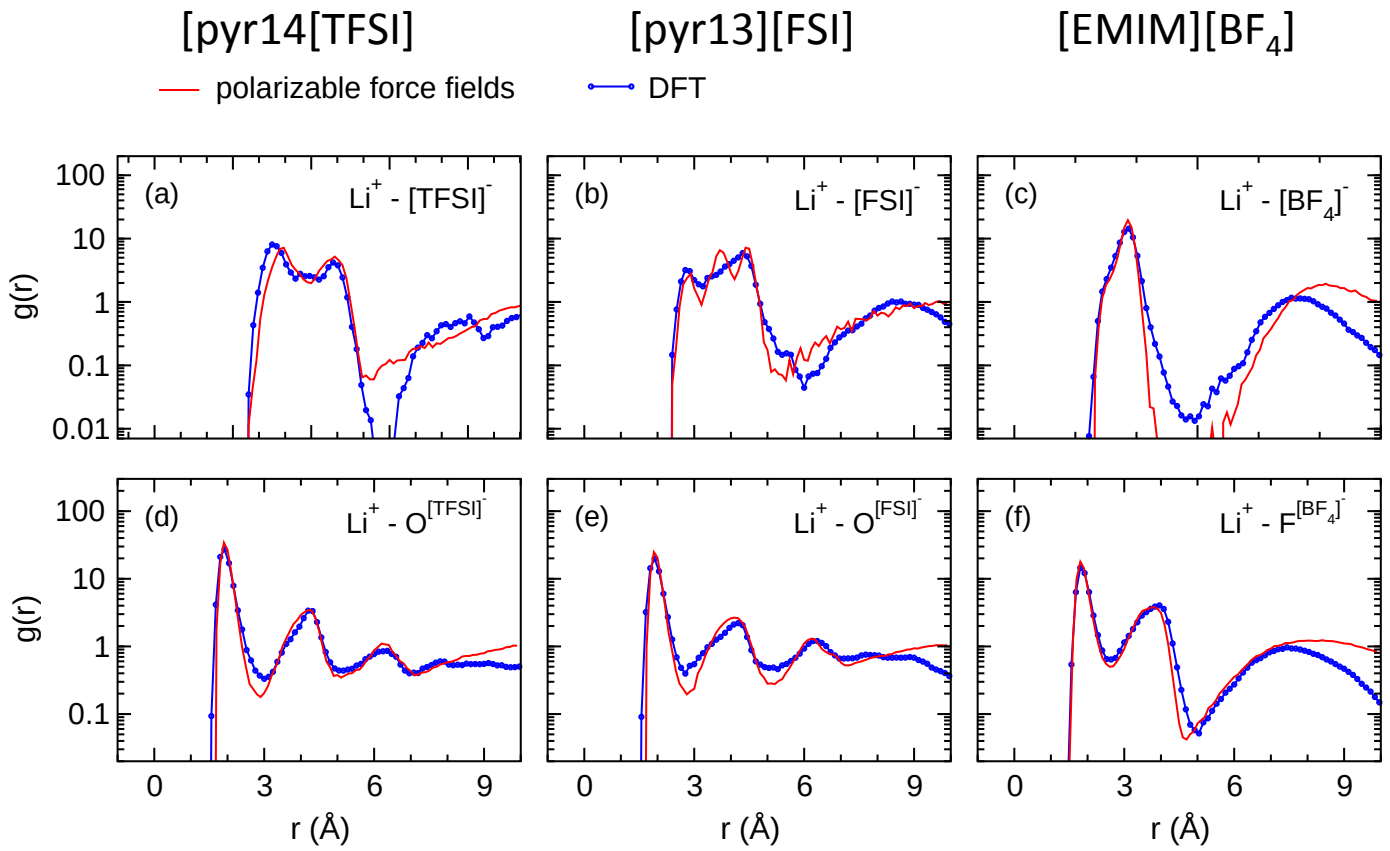
144-216 pairs

Radial distribution functions (PFF-MD)



144-216 pairs

High accuracy comparison (PFF-MD)



8-12 pairs; T = 363 K

PFF-MD radial distributions in good agreement with DFT-MD!

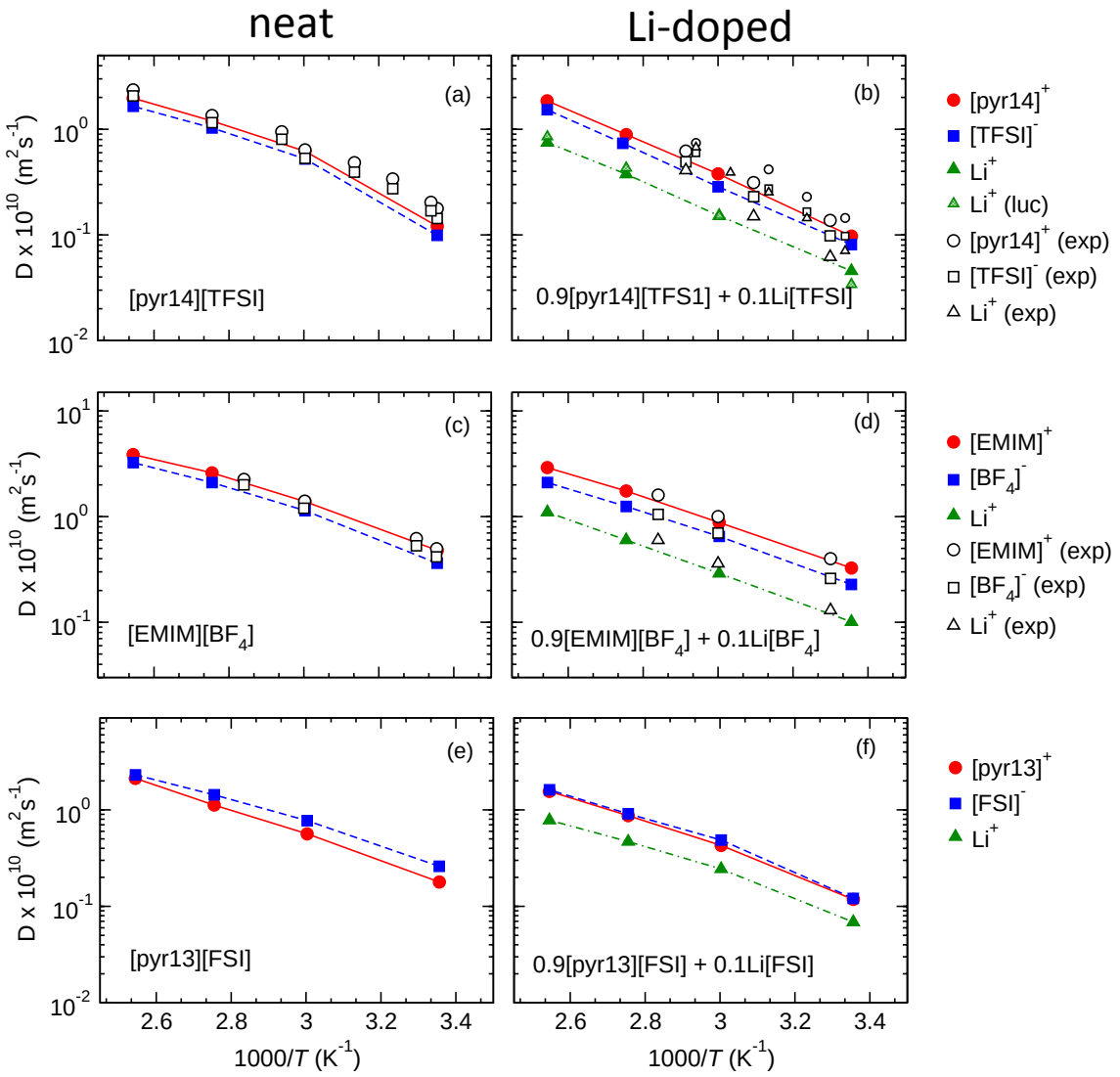
J.B. Haskins, et al., *J. Phys. Chem. B* **119**, 14705 (2015)
O. Borodin, *J. Phys. Chem. B* **113**, 11463 (2009)

Diffusion (PFF-MD)

[pyr14[TFSI]

[EMIM][BF_4]

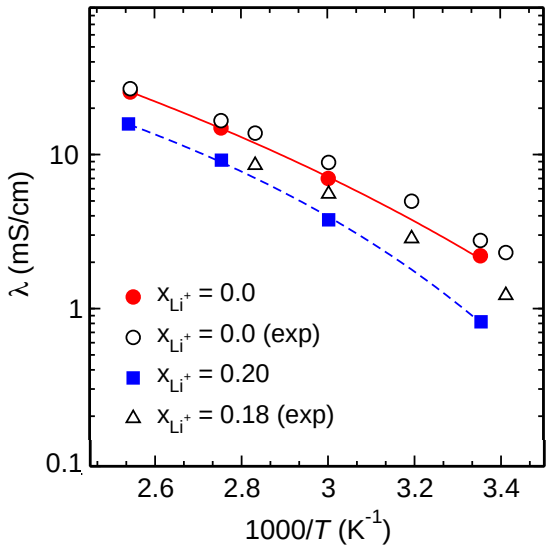
[pyr13][FSI]



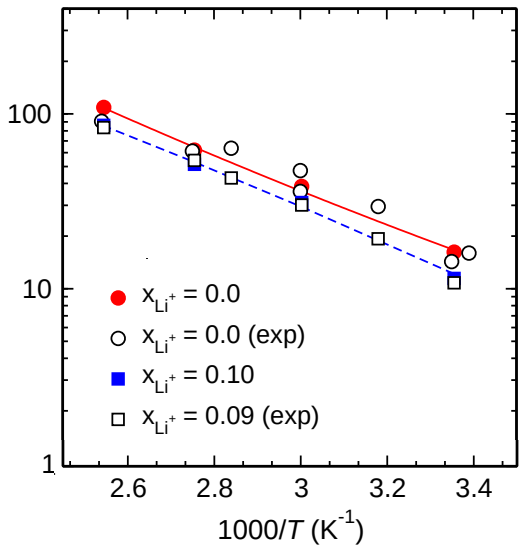
Li-doping suppresses diffusion of all ions!

Ionic conductivity (PFF-MD)

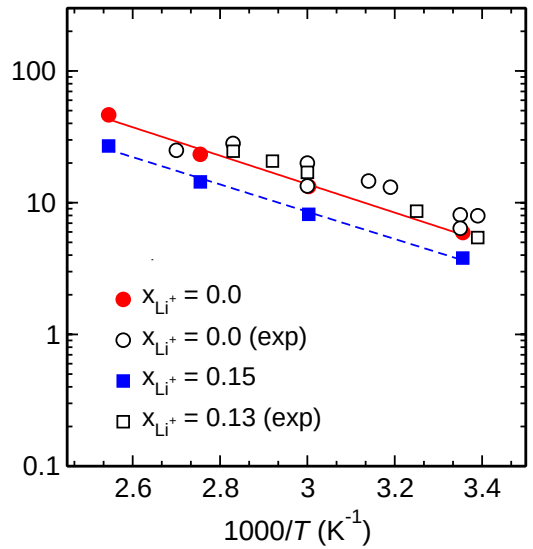
[pyr14[TFSI]



[EMIM][BF_4]



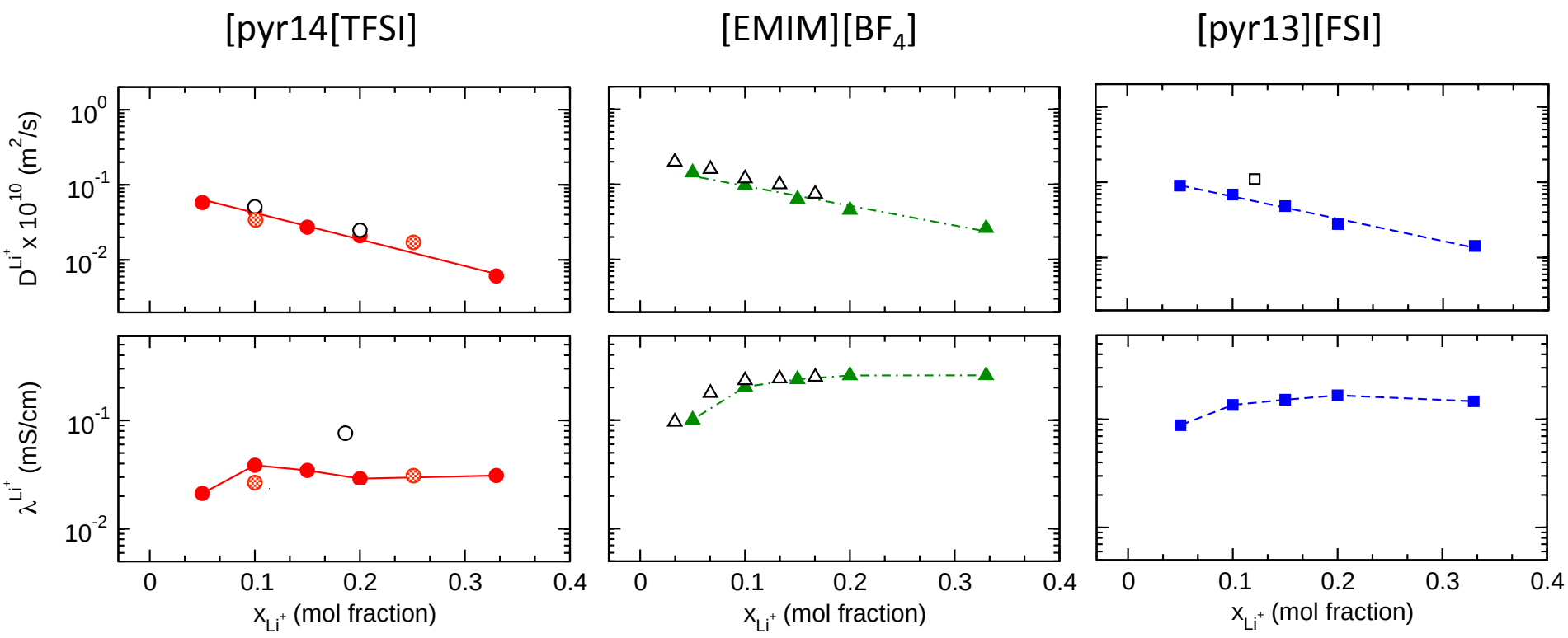
[pyr13][FSI]



Li-doping suppresses conductivity of all systems!

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

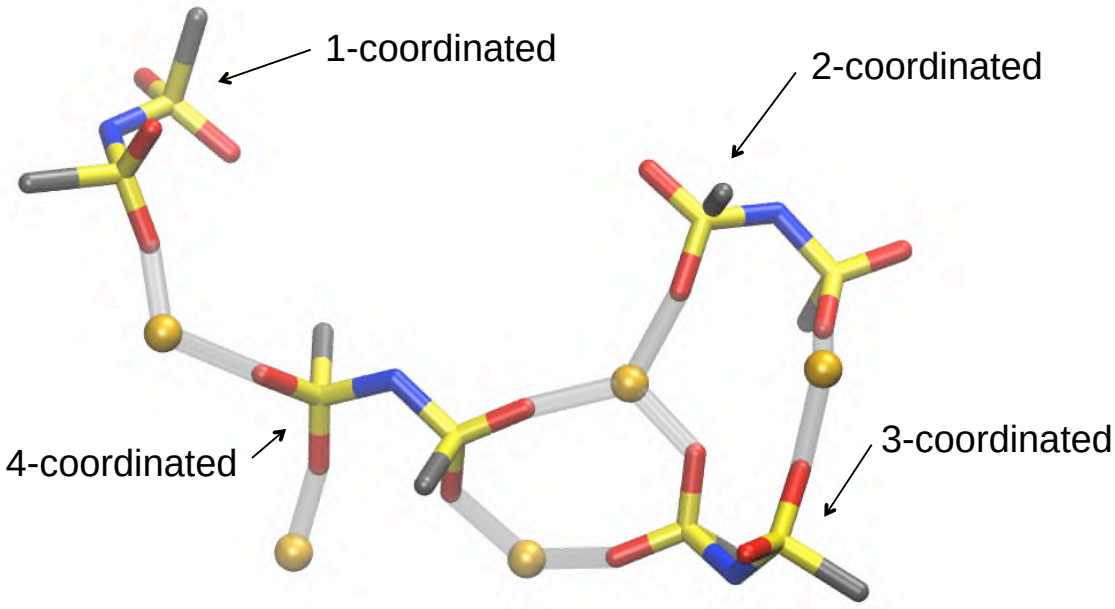
Room-T Li transport (PFF-MD)



Li⁺ contribution to conduction plateaus at high salt doping!

J.B. 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)

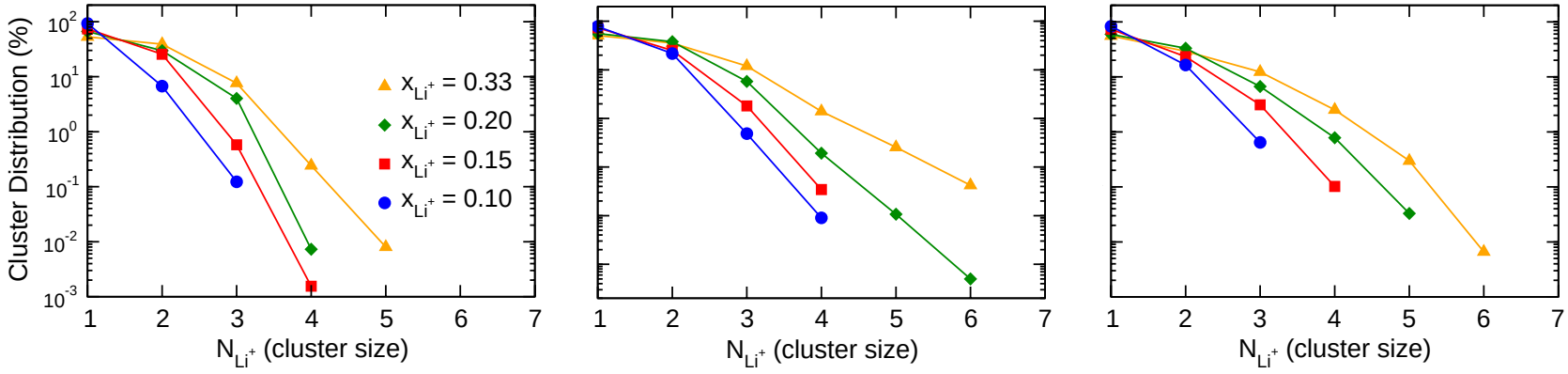


Network Li^+ share bridging anions!

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

Li^+ … Li^+ networks (PFF-MD)

[pyr14[TFSI] [EMIM][BF_4] [pyr13][FSI]



Li^+…Li^+ networks present at all levels of doping!

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

Li^+ … Li^+ networks (PFF-MD)

	x_{Li}	$\langle N_{Li\ldots Li}\rangle$	$\langle n\rangle$	$\langle N_s^-\rangle/N_{Li}$
[pyr14][TFSI]	0.05	1.1	3.3	3.3
	0.15	1.4	3.3	2.8
	0.33	1.5	3.6	2.2
[pyr13][FSI]	0.05	1.1	3.8	3.7
	0.15	1.4	3.9	3.1
	0.33	1.6	4.0	2.5
[EMIM][BF_4]	0.05	1.2	3.9	3.7
	0.15	1.4	3.9	3.2
	0.33	1.7	4.0	2.6

Apparent coordination decreases through Li-networks!

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

Room-T diffusion kinetics

x_{Li}	[pyr14][TFSI] D_{veh}/D_{tot}	[pyr13][FSI] D_{veh}/D_{tot}	[EMIM][BF_4] D_{veh}/D_{tot}
0.05	0.69	0.81	0.89
0.10	0.66	0.85	1.07
0.33	0.59	0.73	0.91

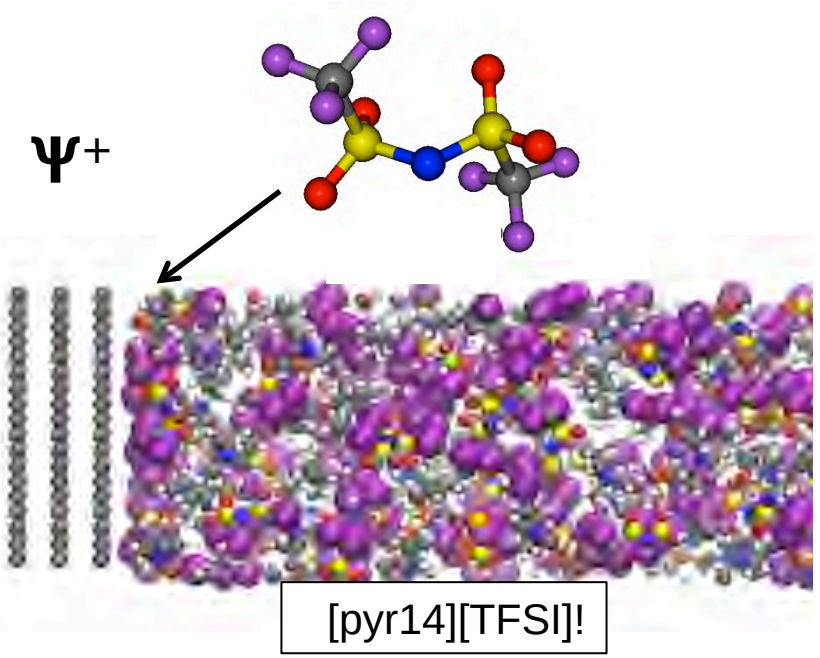
Vehicular mechanism dominates the diffusion and increases in importance with decreasing anion size !

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

Computational Study of Li-doped ILs with Experimental Validation

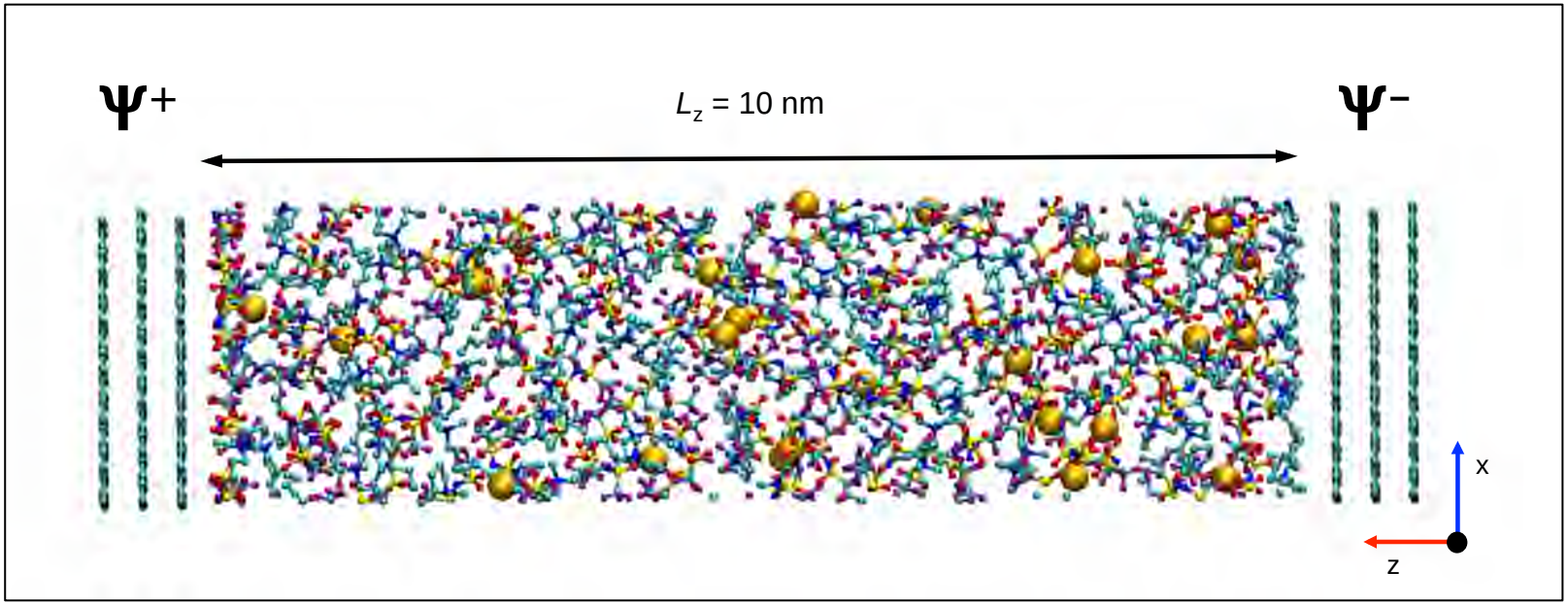
Interfacial Properties

- **Polarizable-MD for electrolytes**
- **Constant voltage electrodes**
- **Li^+/EDL property analysis**
  - structure
  - Li^+ solvation
  - differential capacitance
- **Free energy analysis of Li^+ solvation**



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

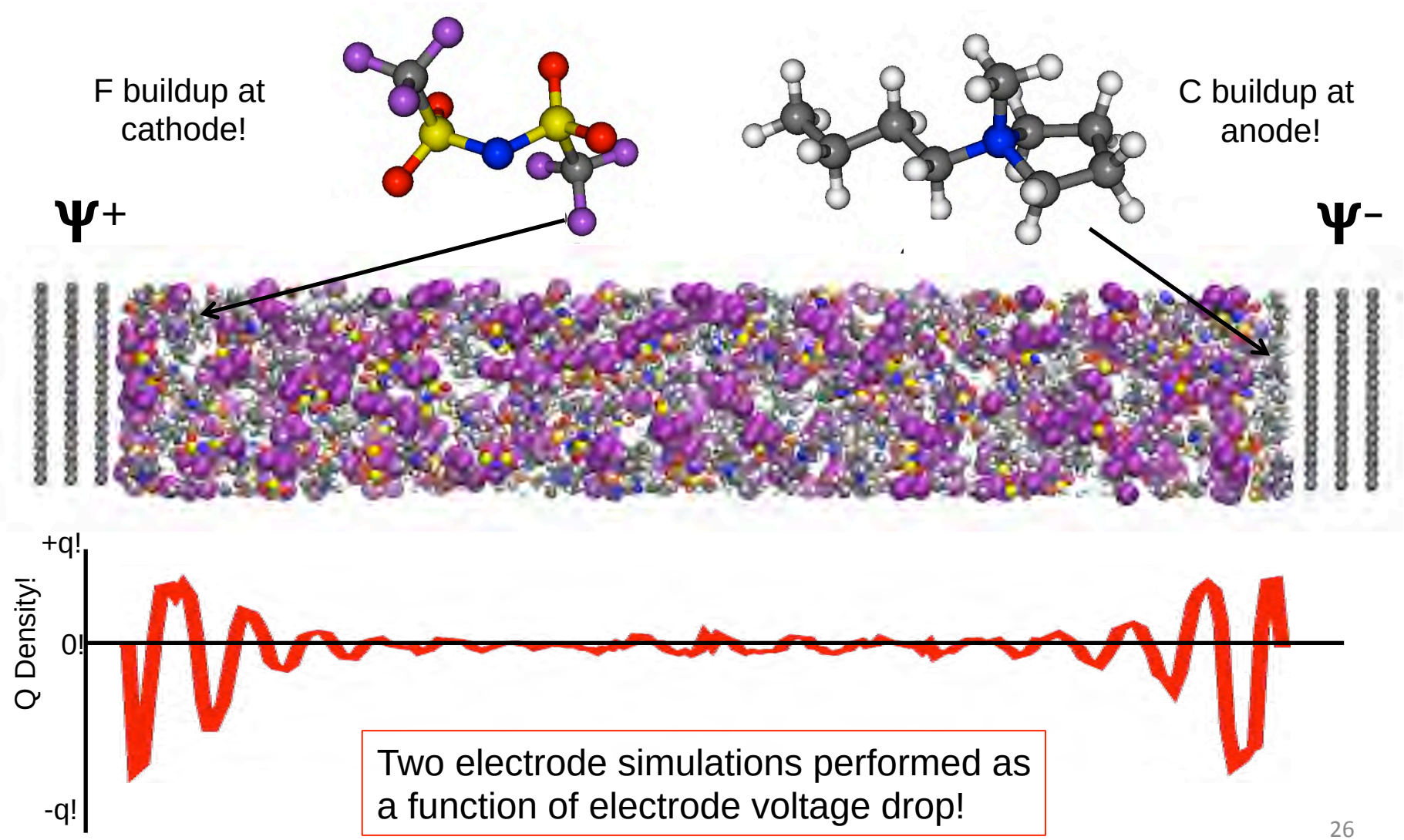
Interfacial Structure Simulations



$$\Delta\Psi = \Psi^{+} - \Psi^{-} = \text{constant}$$

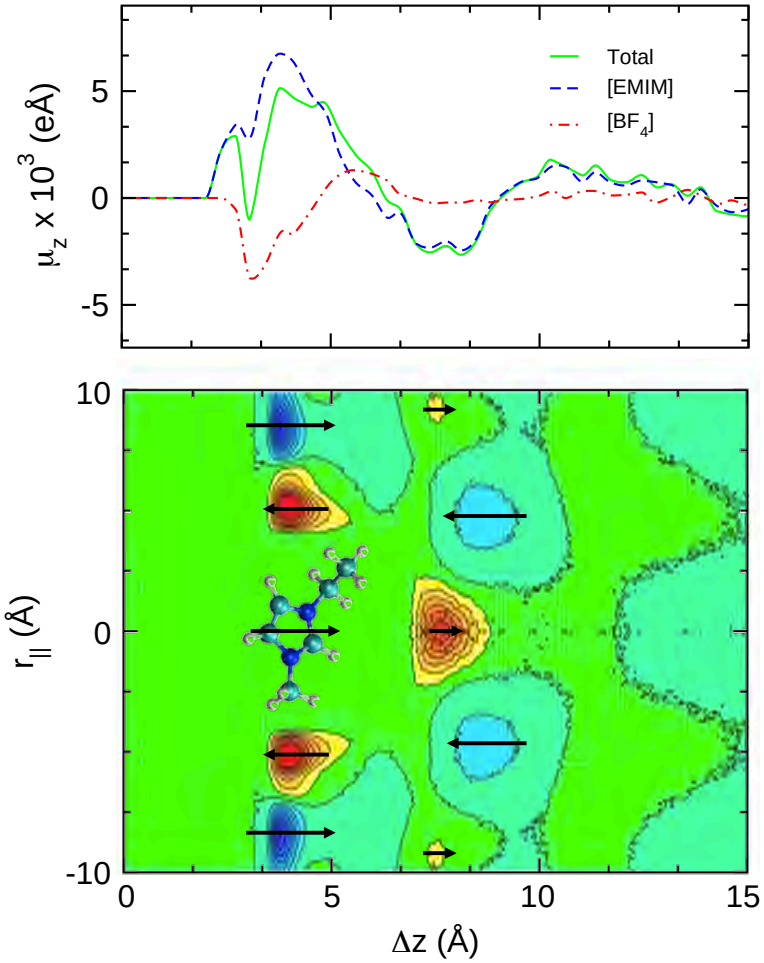
Two electrode simulations performed as a function of electrode voltage drop!

Electric Double Layer (EDL)



Two electrode simulations performed as a function of electrode voltage drop!

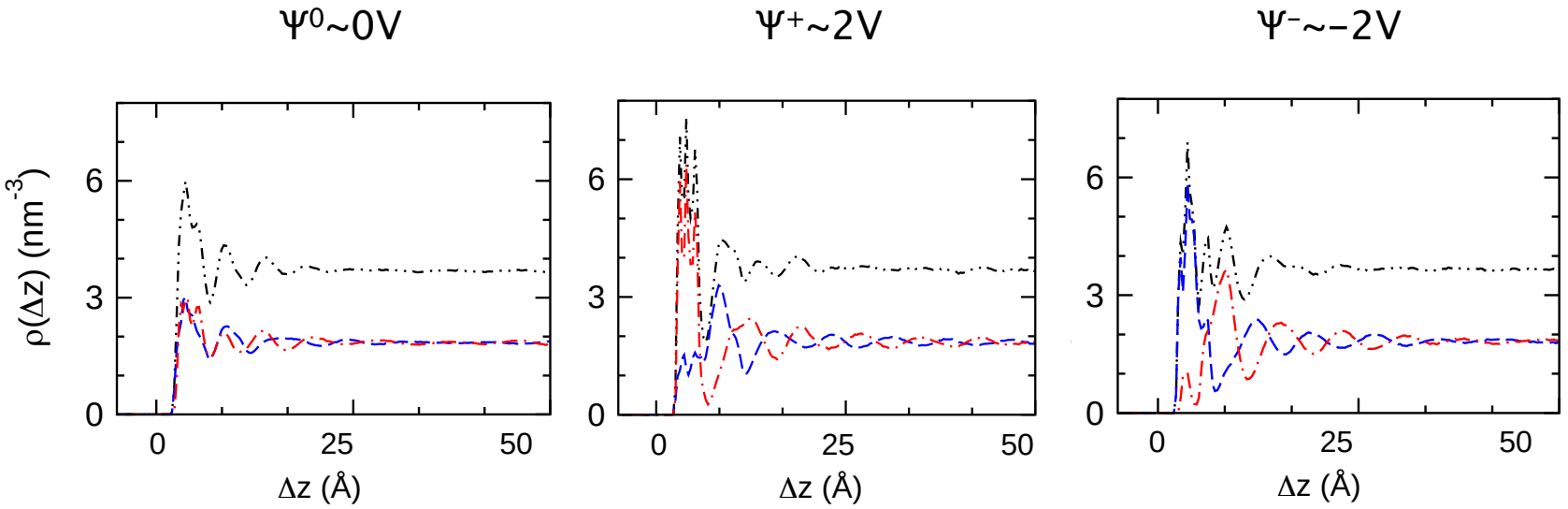
Polarization influence on the EDL



Polarization opposes formation of the EDL!

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

Ion density profiles: [pyr14][TFSI]

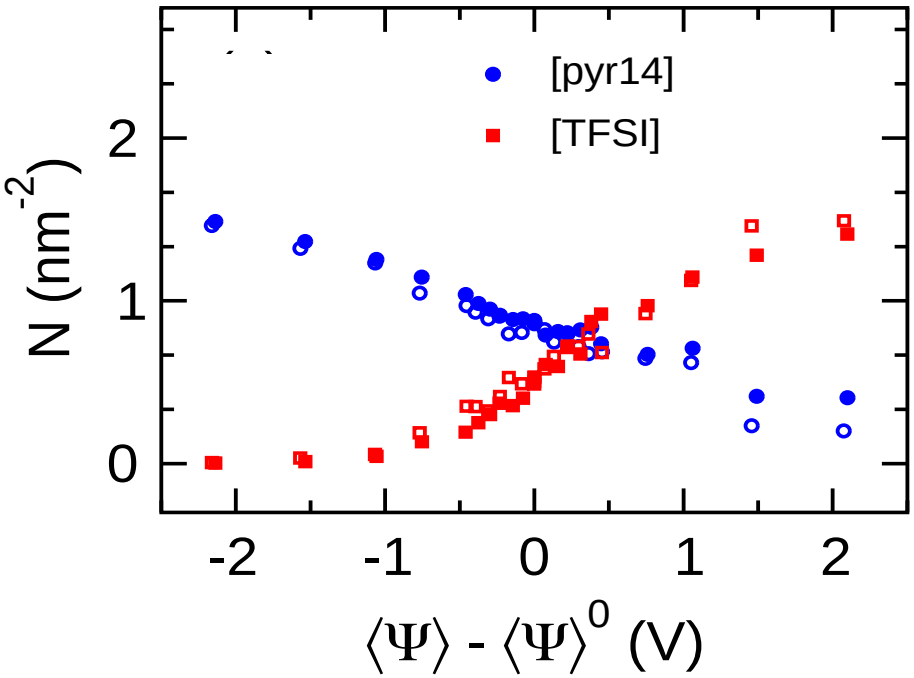


Black – total; Red – anion; Blue – cation

Complex layered structure at neutral and charged electrodes !

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

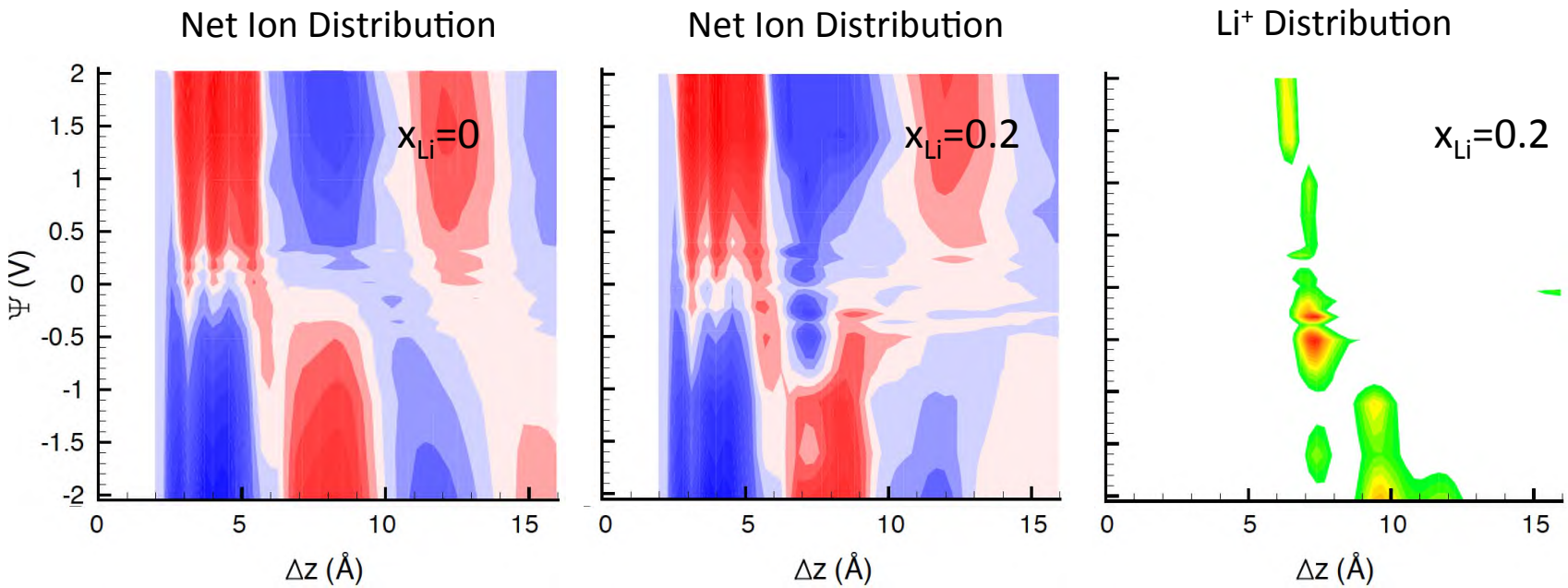
Ion accumulation at the surface: [pyr14][TFSI]



Ion depletion at high voltage!

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

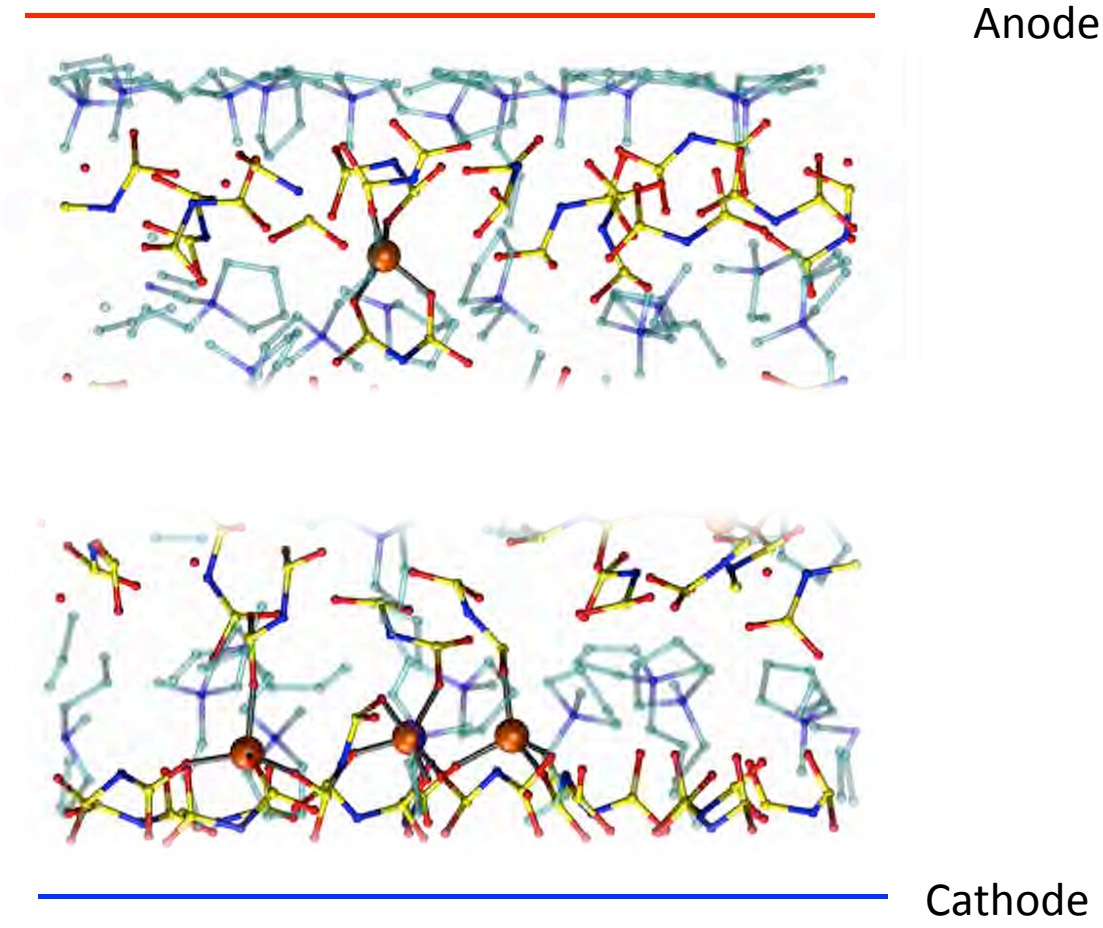
Li^+ influence on the EDL: [pyr14][TFSI]



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

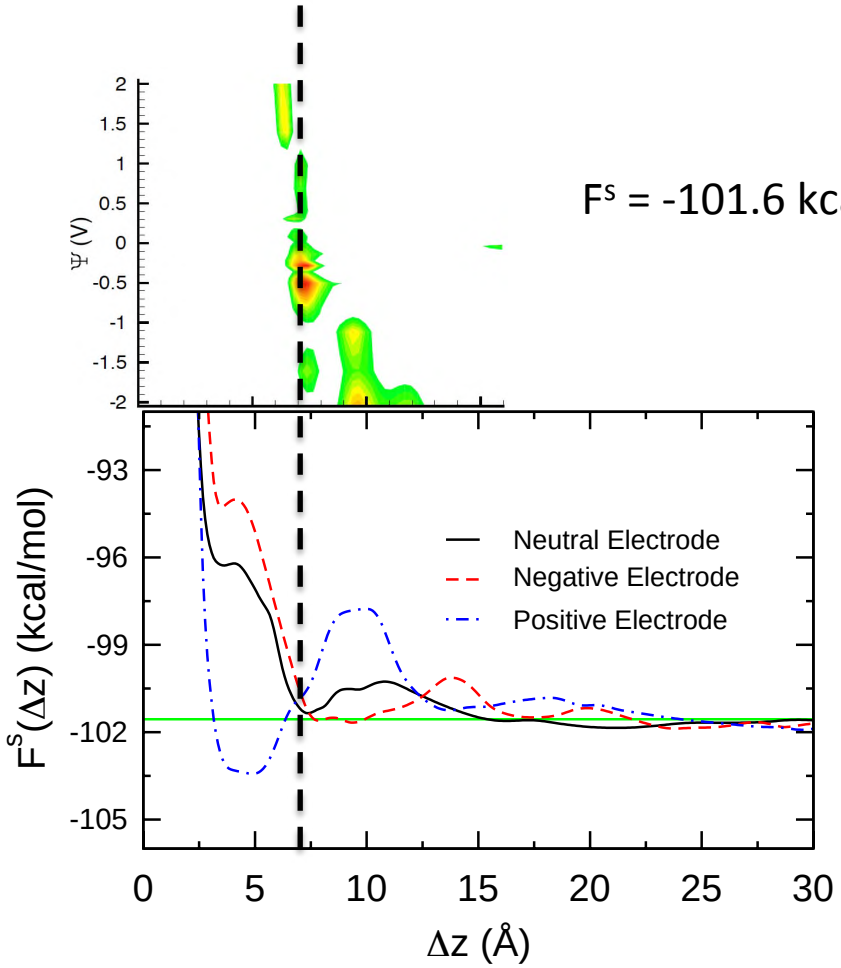
J.B. Haskins, et al., *J. Phys. Chem. C* (submitted)

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



Li^+ accumulates in the second molecular layer!

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



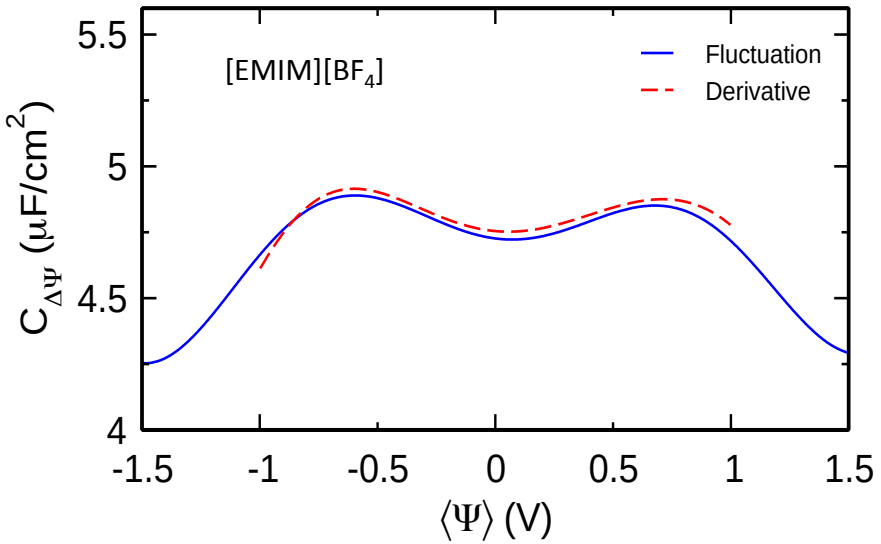
F^s = -101.6 kcal/mol

Solvation free energy concurs with Li-density!

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

Capacitance fluctuation formulas and electrode effects

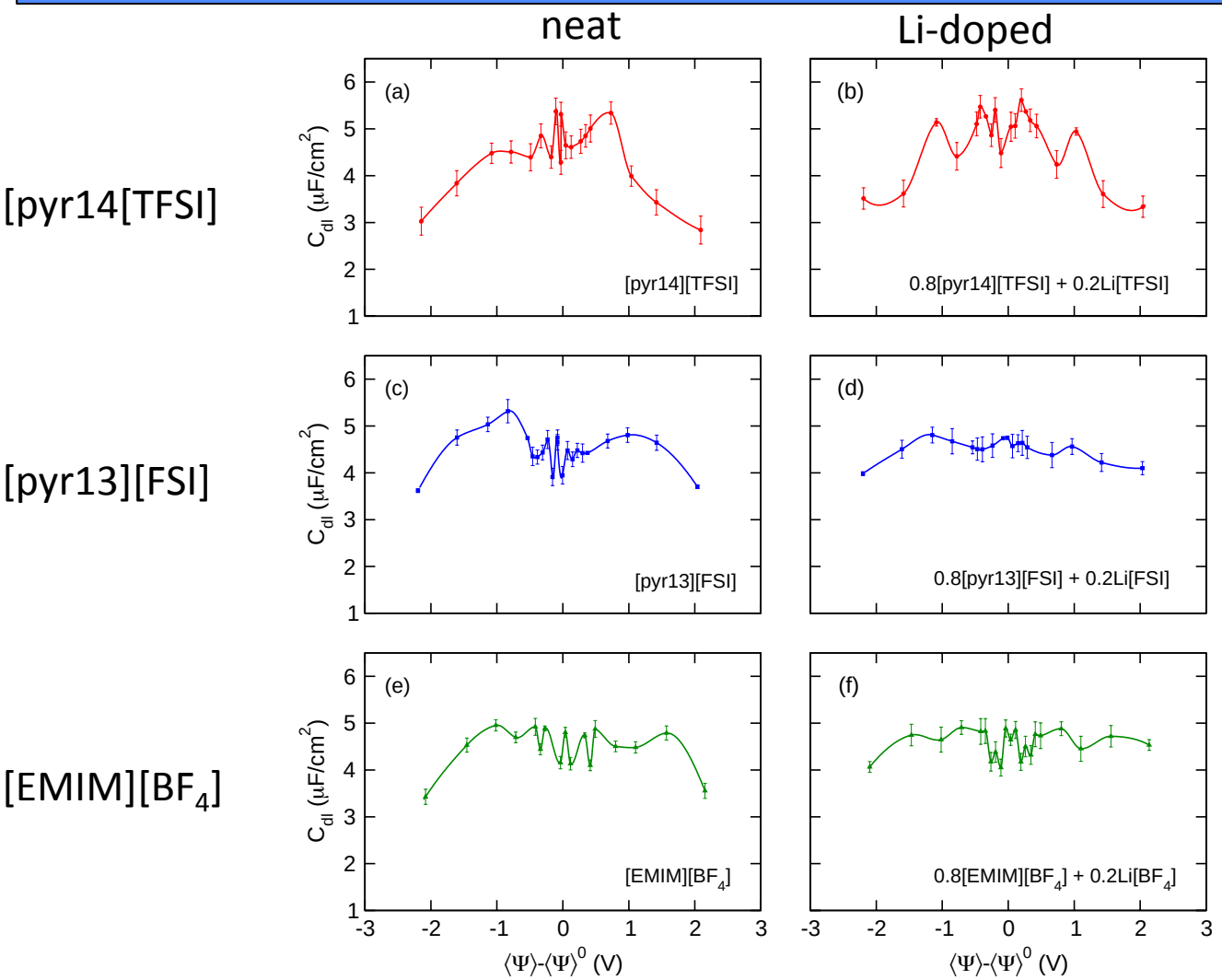
$$C_{\Delta\Psi} = \frac{\partial\langle\sigma\rangle}{\partial\langle\Psi\rangle} = \left[\beta A\left\langle|\sigma|\delta\sigma\right\rangle + \left\langle\frac{\partial\sigma}{\partial\Delta\Psi}\right\rangle\right]\left[\beta A\left\langle|\sigma|\delta\Psi\right\rangle + \left\langle\frac{\partial\Psi}{\partial\Delta\Psi}\right\rangle\right]^{-1}$$



Validated fluctuation formulas for capacitance!

J.B. Haskins, et al., *J. Chem. Phys.* (submitted)
C. Merlet, et al., *J. Phys. Chem. C*, **118**, 18291 (2014)

Influence of Li^+ on capacitance



Computations performed on ideal graphite electrodes!

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

J. Vatamanu, et al., *J. Am. Chem. Soc.* **132**, 14825 (2010)

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

[pyr13][FSI] highest energy from both experiment and theory!

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

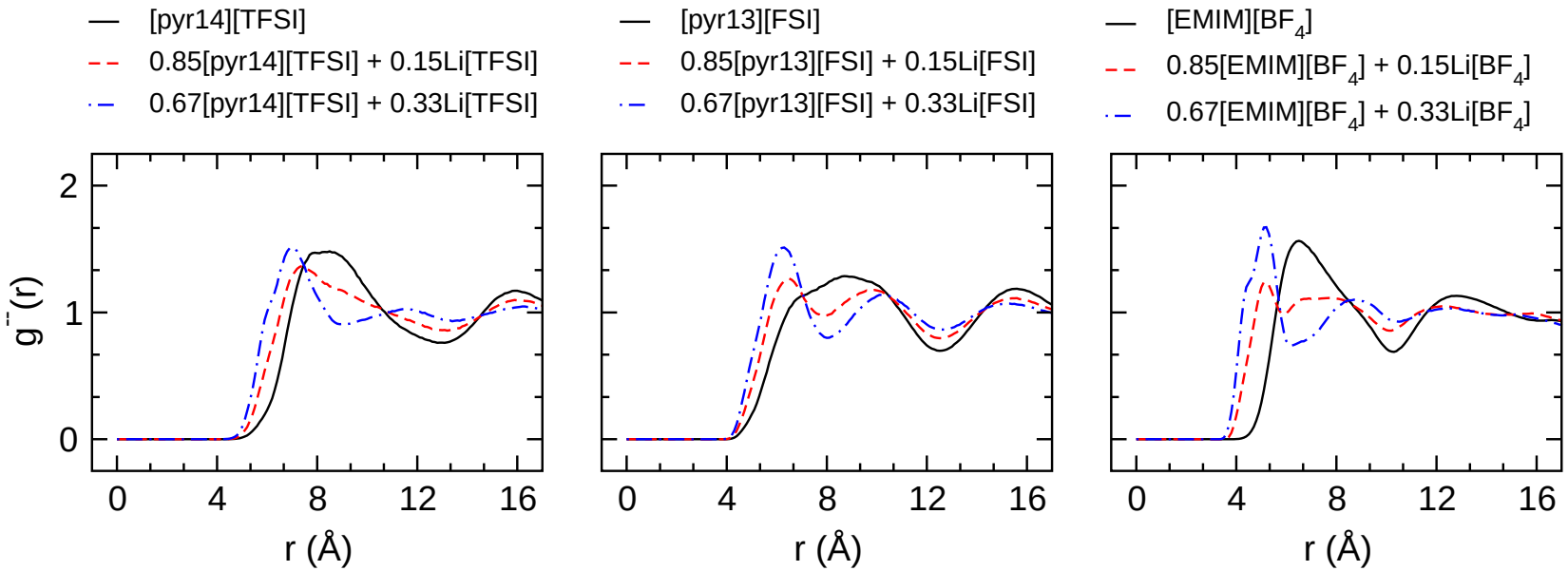
Conclusions

- 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
- Li^+ disruption of the electric double layer
- Fluctuation formulas and camel-type shape of capacitance
- Future work: inclusion of more realistic interfacial effects to refine capacitance

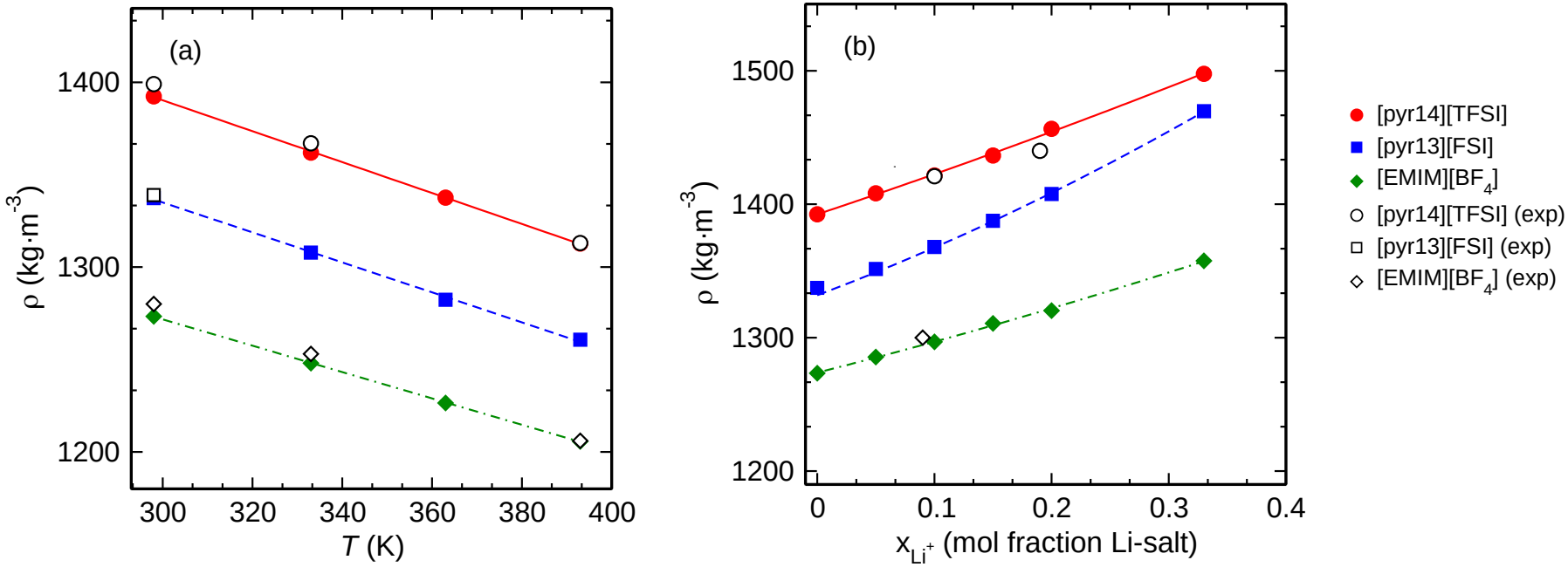
Additional Slides

Influence of Li^+-doping on anion distributions

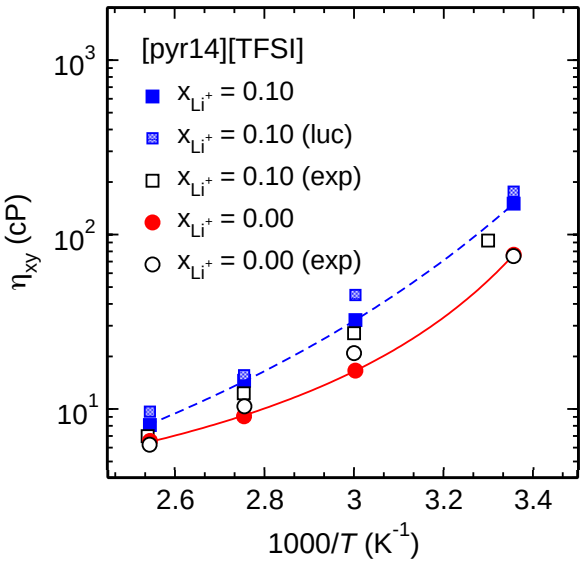
Small anion separation around Li^+!

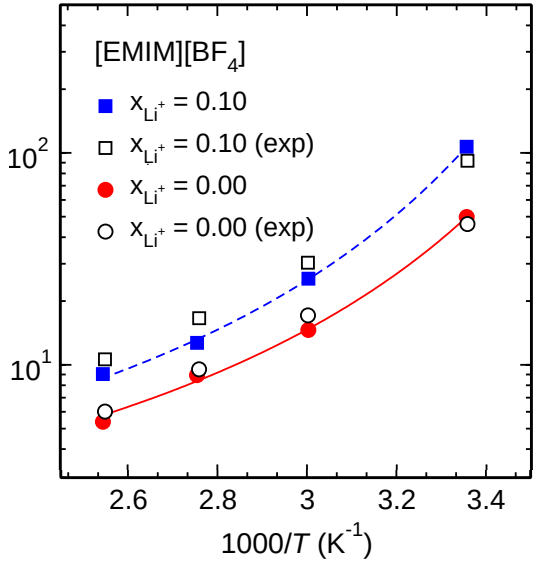


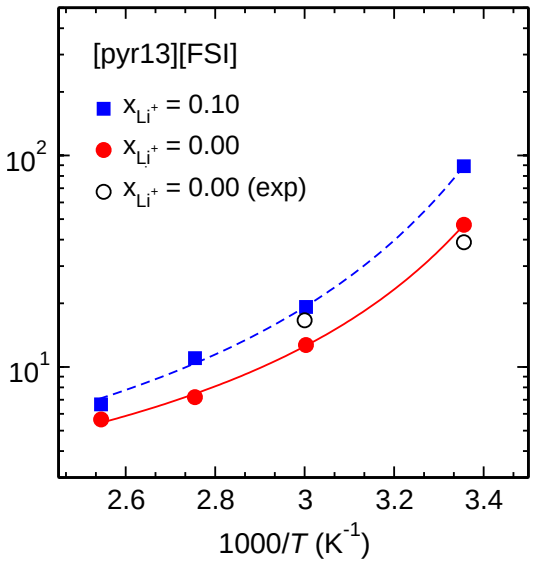
Density


(a)
1400
1300
1200
ρ (kg·m-3)
300
320
340
360
380
400
T (K)
(b)
1500
1400
1300
1200
ρ (kg·m-3)
0
0.1
0.2
0.3
0.4
xLi+ (mol fraction Li-salt)
[pyr14][TFSI]
[pyr13][FSI]
[EMIM][BF4]
[pyr14][TFSI] (exp)
[pyr13][FSI] (exp)
[EMIM][BF4] (exp)

Viscosity


[pyr14][TFSI]
x_{Li^+} = 0.10
x_{Li^+} = 0.10 (luc)
x_{Li^+} = 0.10 (exp)
x_{Li^+} = 0.00
x_{Li^+} = 0.00 (exp)
η_{xy} (cP)
10^3
10^2
10^1
2.6
2.8
3
3.2
3.4
1000/T (K^{-1})


[EMIM][BF_4]
x_{Li^+} = 0.10
x_{Li^+} = 0.10 (exp)
x_{Li^+} = 0.00
x_{Li^+} = 0.00 (exp)
10^2
10^1
2.6
2.8
3
3.2
3.4
1000/T (K^{-1})


[pyr13][FSI]
x_{Li^+} = 0.10
x_{Li^+} = 0.00
x_{Li^+} = 0.00 (exp)
10^2
10^1
2.6
2.8
3
3.2
3.4
1000/T (K^{-1})

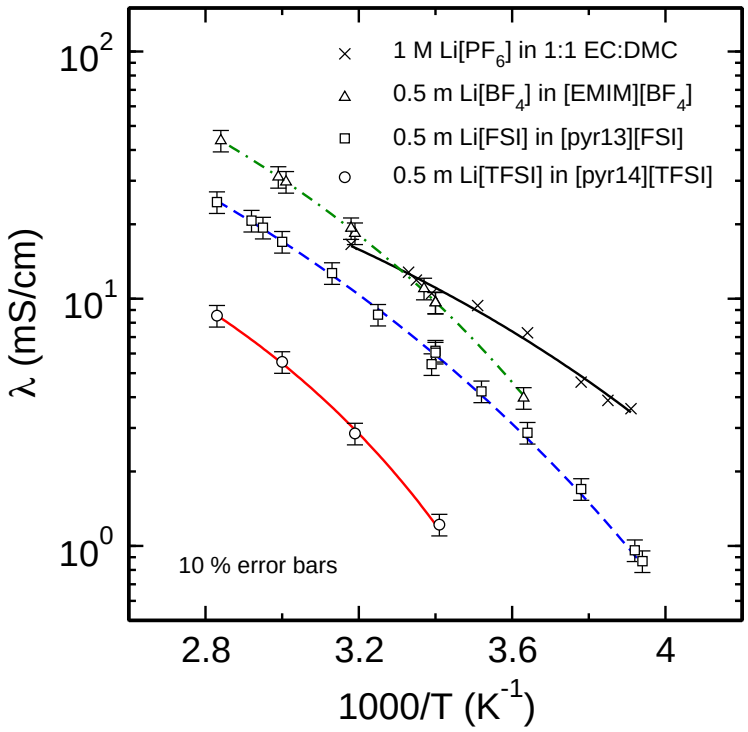
Computational measures of thermodynamics and transport

Density: ρ (kg/m^3) | Diffusion: D (1e-10 m^2/s) | Viscosity: μ (cP) | Conductivity: λ (mS/cm)

	[pyr14][TFSI]	[pyr13][FSI]	[EMIM][BF_4]
ρ	1421.5	1367.9	1296.9
D^+	0.097	0.118	0.326
D^-	0.081	0.121	0.228
D^{Li}	0.046	0.069	0.101
μ	150	89	107
λ	1.67	3.35	11.45

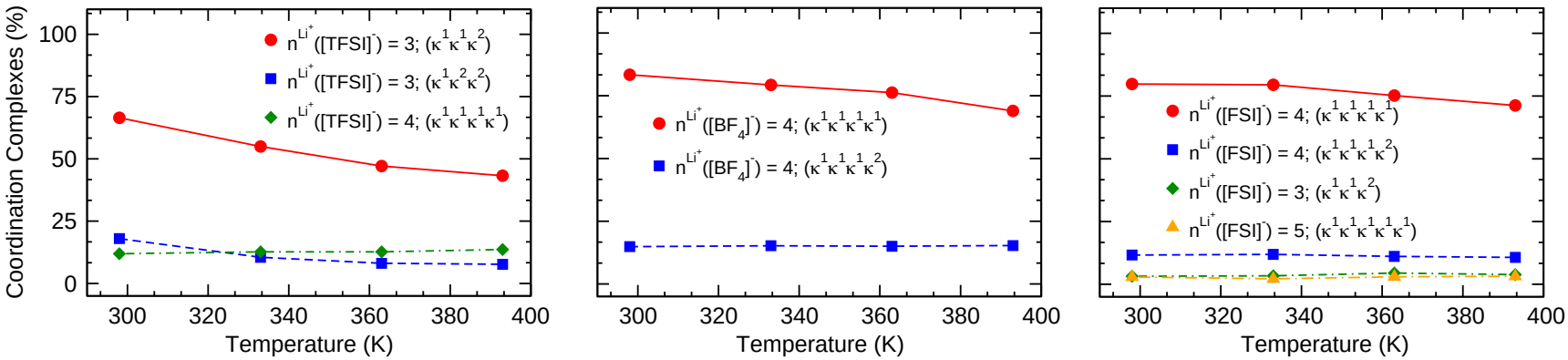
- Greater ion mobility with decreasing density and ion size
- High accuracy of predicted properties:
  - density within ~1%
  - diffusion within 10-25%
  - conductivity within 10-20%

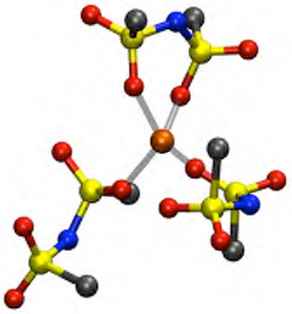
Experimental comparison of ionic conductivity to that of Li-ion battery organic electrolytes

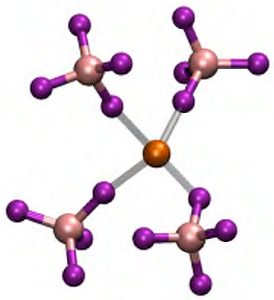


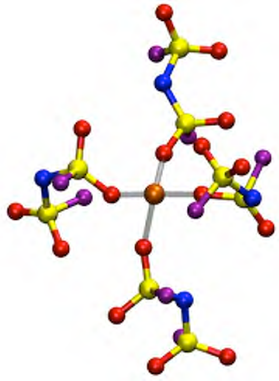
Mid-T ion conductivity comparable to conventional electrolytes!

Prevalent Li^+/Anion solvation shells





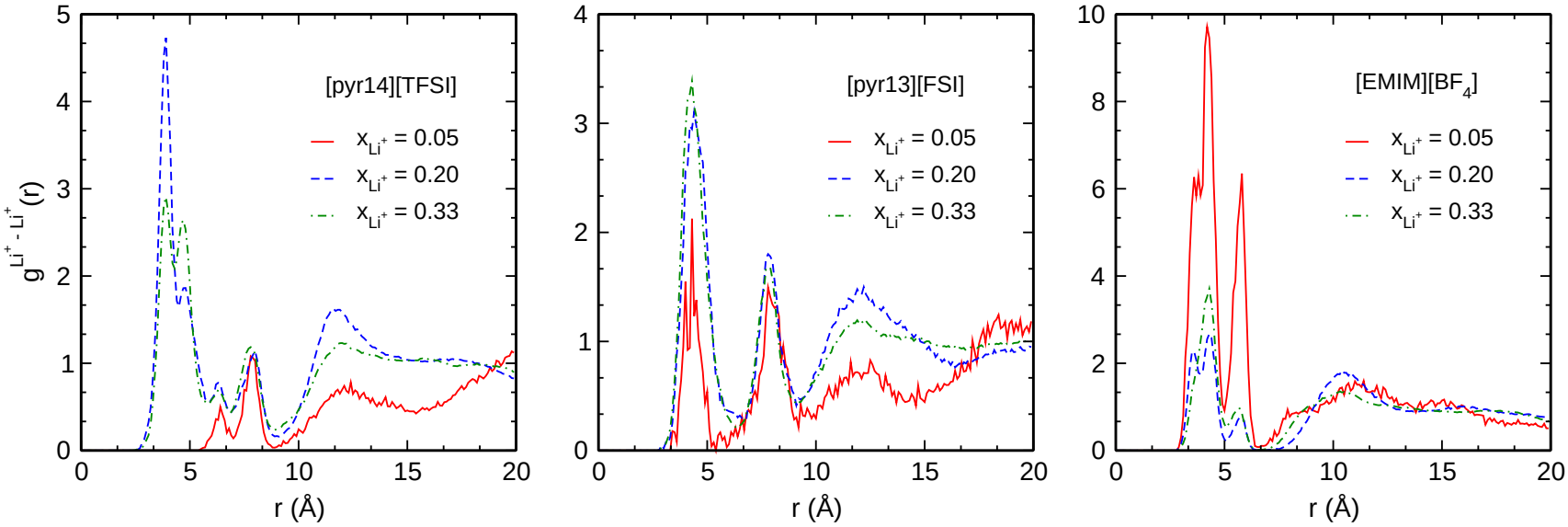




- 4-5 anion neighbors in Li^+ solvation shell: [TFSI] (3-4), [BF_4] (4), [FSI] (3-5)!
- $[Li(TFSI)_2]^-$ and $[Li(FSI)_3]^{-2}$ from experiment (J.C. Lassegues, et al., *J. Phys. Chem. A* **113**, 305 (2009) and K. Fujii, et al., *J. Phys. Chem. C* **117**, 19314 (2013))!

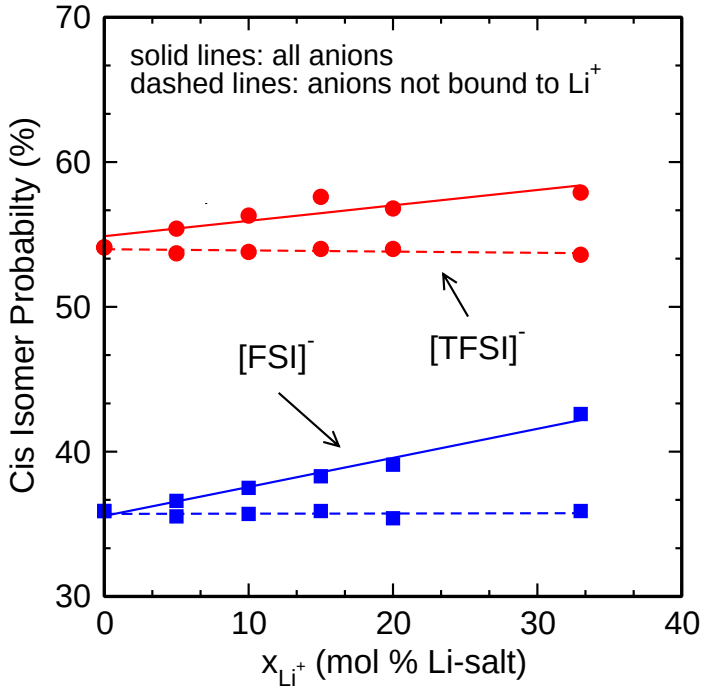
Li^+-Li^+ distributions

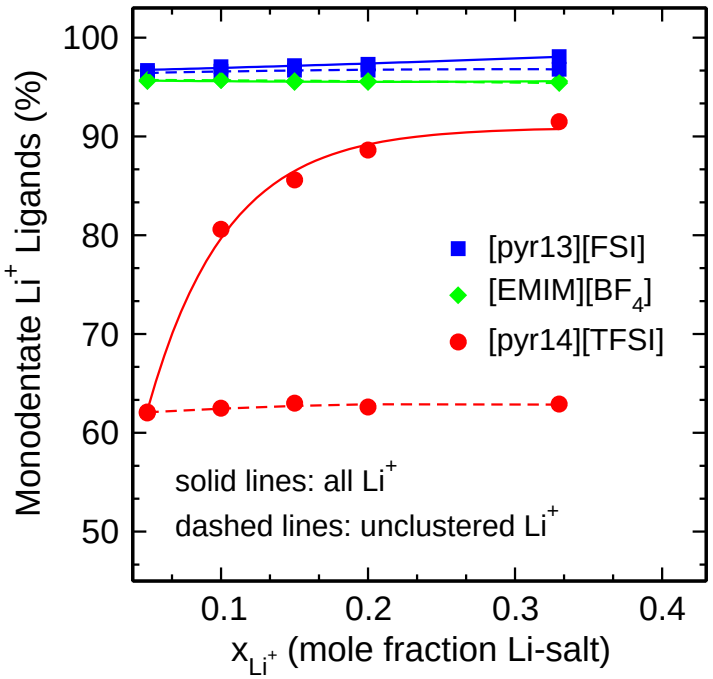
Li^+ …. Li^+ networks at most doping levels!



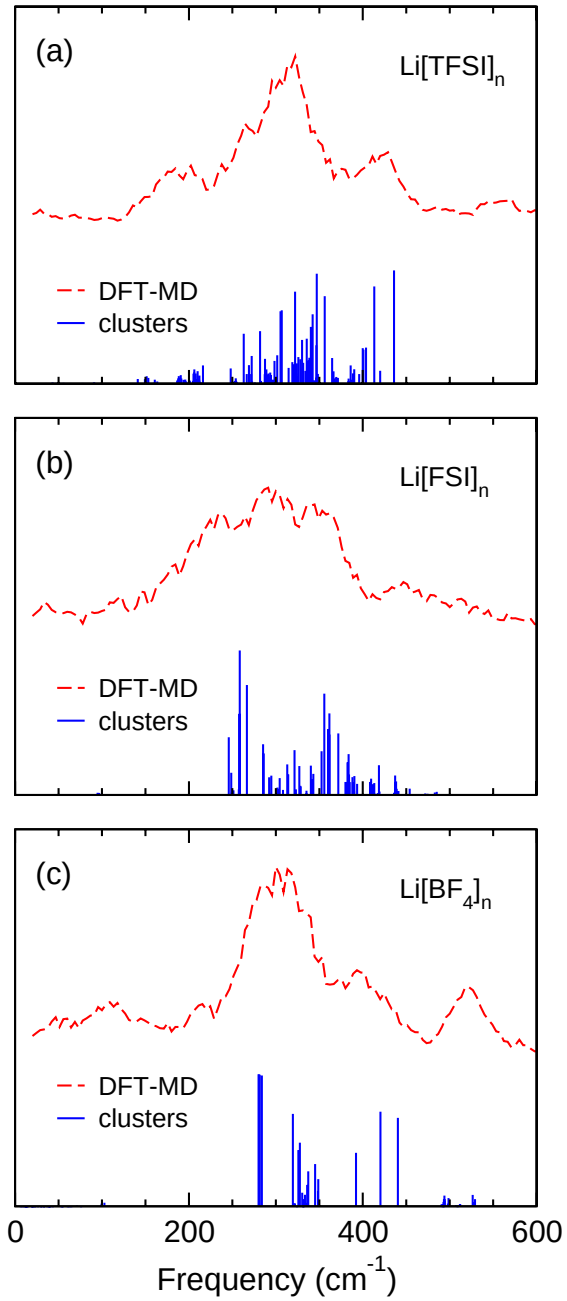
Influence of Li^+ … Li^+ networks on structure

Li^+ …. Li^+ networks induce cis-conformers and monodentate bonds!



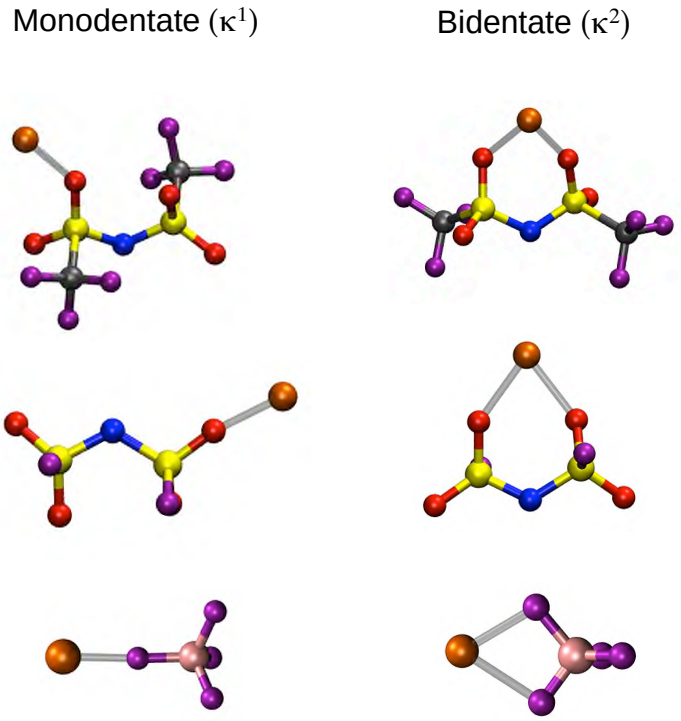


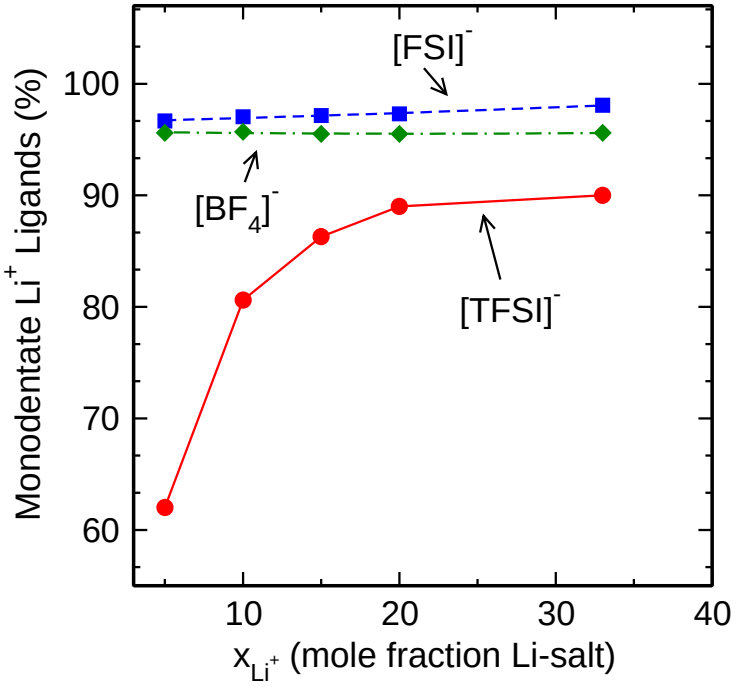
Solvation shells of L



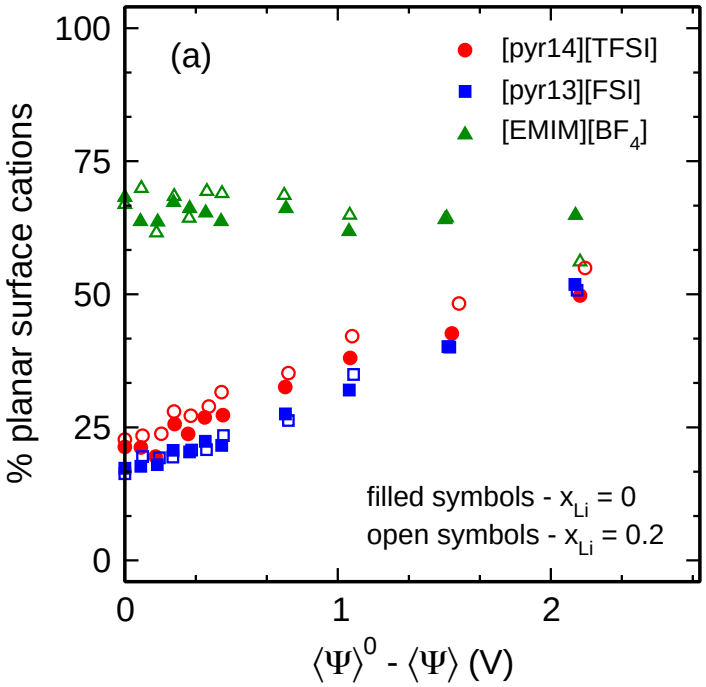
3 anion coord SI] and [BF_4]!

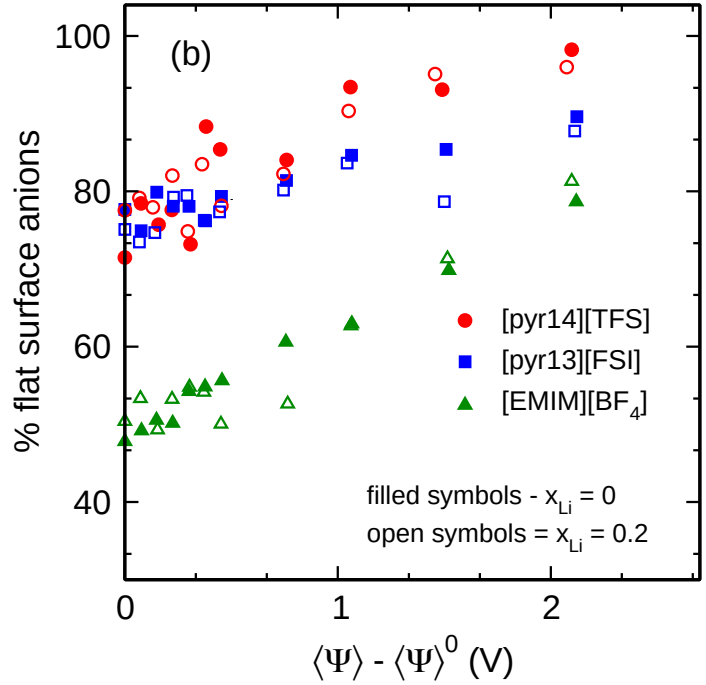
Li^+/Anion bonding

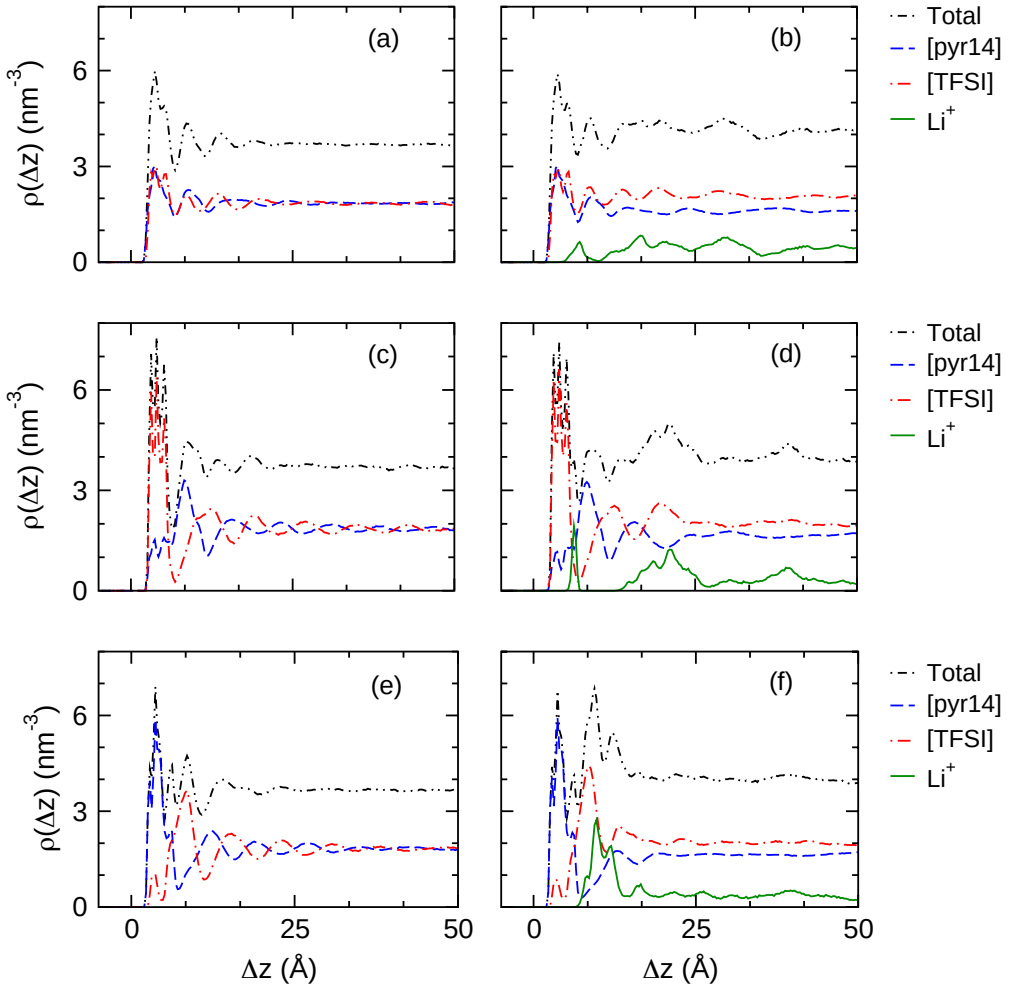




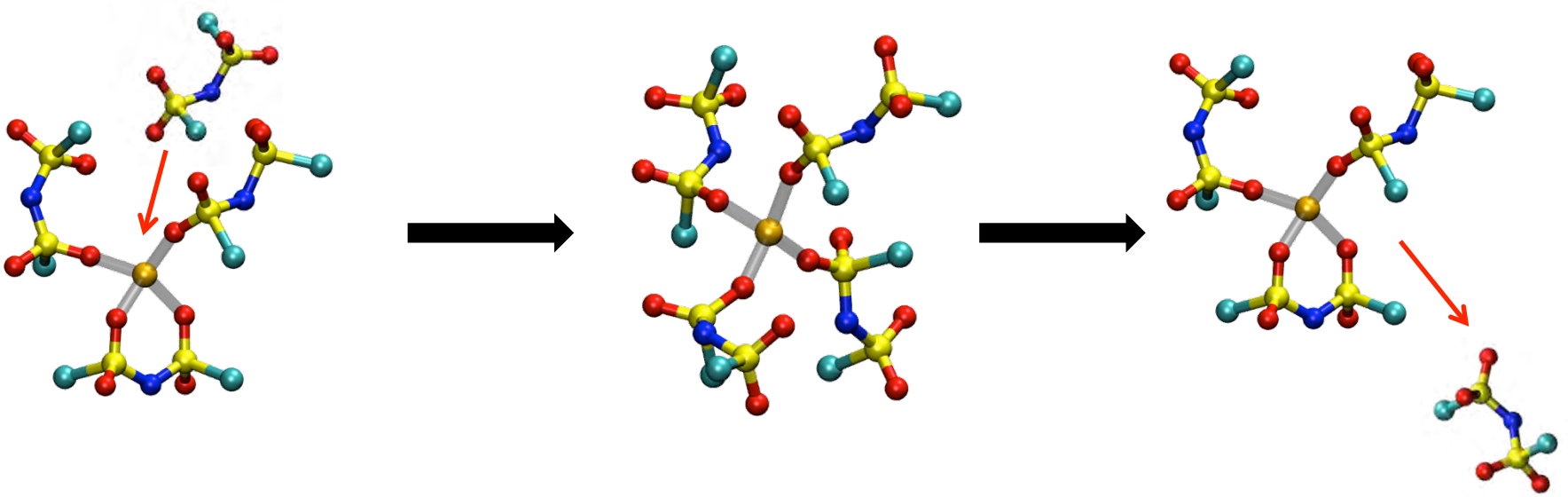
Monodentate bonding preferred at high Li-doping!


(a)
[pyr14][TFSI]
[pyr13][FSI]
[EMIM][BF4]
filled symbols - xLi = 0
open symbols - xLi = 0.2
% planar surface cations
⟨Ψ⟩0 - ⟨Ψ⟩ (V)


(b)
[pyr14][TFS]
[pyr13][FSI]
[EMIM][BF4]
filled symbols - xLi = 0
open symbols = xLi = 0.2
% flat surface anions
⟨Ψ⟩ - ⟨Ψ⟩0 (V)


(a)
(b)
(c)
(d)
(e)
(f)
Total
[pyr14]
[TFSI]
Li+
ρ(Δz) (nm-3)
Δz (Å)

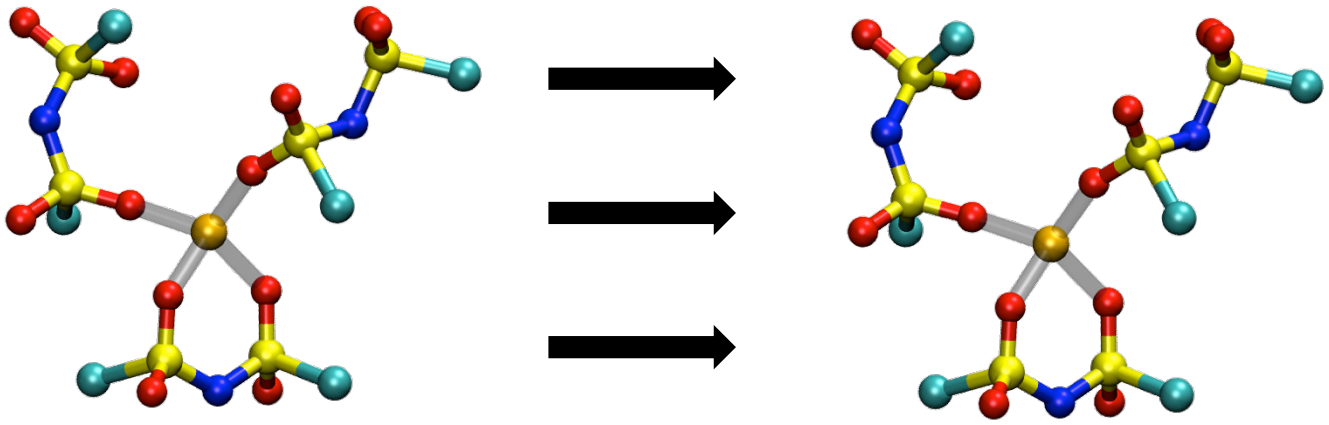
What is the mechanism for Li-diffusion?



Anion Exchange

Hopping of Li^+ through exchange of anions!

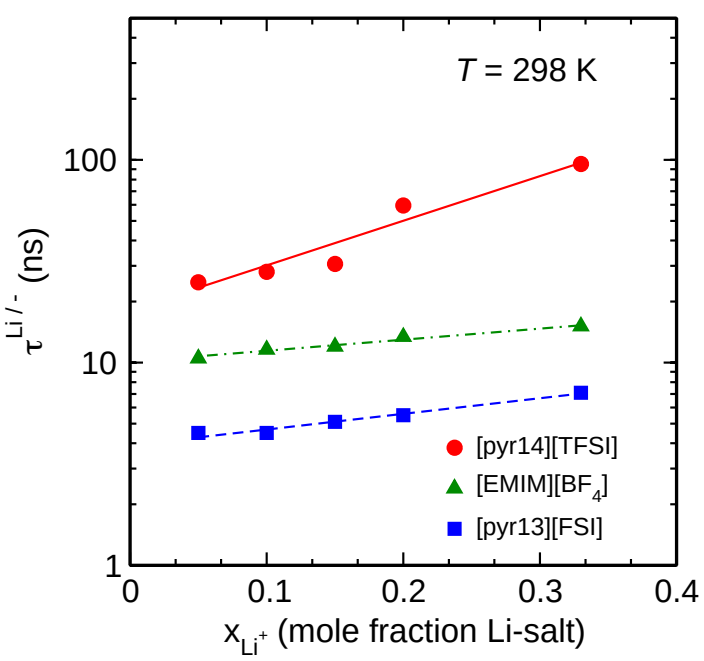
What is the mechanism for Li-diffusion?

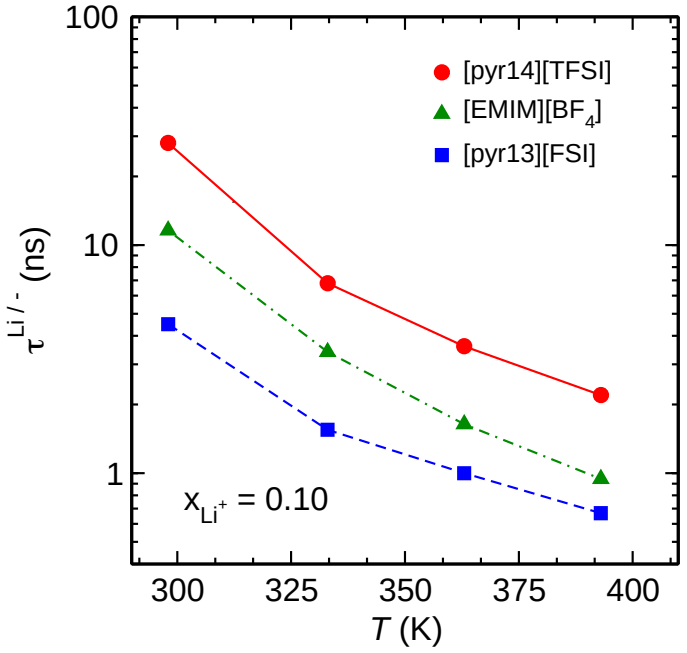


Vehicular

Net motion of Li^+ with the solvation shell!

Li^+/Anion residence times





[TFSI] has longer residence times than other anions!
!
Note: residence time of [TFSI] 30 ns at room-T!

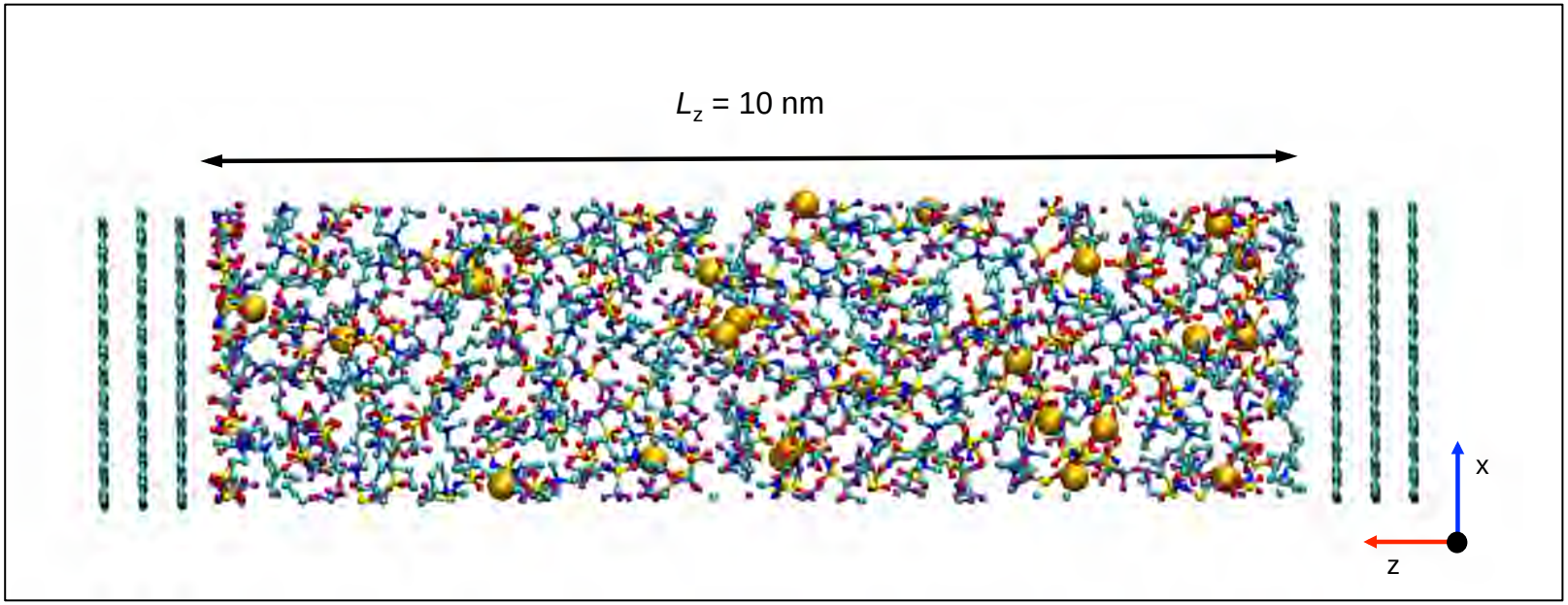
J.B. Haskins, et al., *J. Phys. Chem. B* **118**, 11295 (2014)

Room-T diffusion kinetics

x_{Li}	[pyr14][TFSI] D_{veh}/D_{tot}	[pyr13][FSI] D_{veh}/D_{tot}	[EMIM][BF_4] D_{veh}/D_{tot}
0.05	0.69	0.81	0.89
0.10	0.66	0.85	1.07
0.33	0.59	0.73	0.91

Vehicular mechanism dominates the diffusion and increases in importance with decreasing anion size !

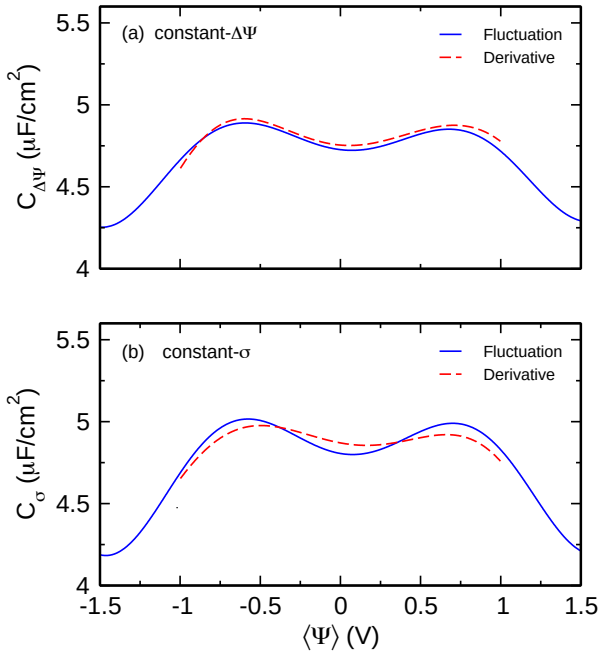
Interfacial Structure Simulations

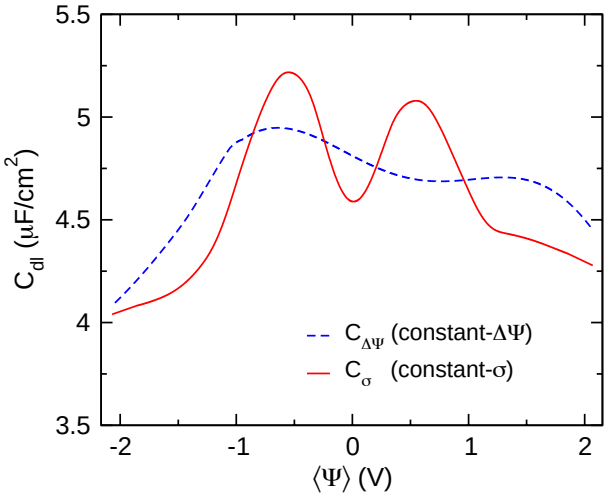


Two electrode simulations performed as a function of electrode voltage drop!

Capacitance fluctuation formulas and electrode effects

$$C_{\Delta\Psi} = \frac{\partial\langle\sigma\rangle}{\partial\langle\Psi\rangle} = \left[\beta A\left\langle|\sigma|\delta\sigma\right\rangle + \left\langle\frac{\partial\sigma}{\partial\Delta\Psi}\right\rangle\right]\left[\beta A\left\langle|\sigma|\delta\Psi\right\rangle + \left\langle\frac{\partial\Psi}{\partial\Delta\Psi}\right\rangle\right]^{-1}$$





Validated fluctuation formulas for capacitance!
Electrode surface subtly influences capacitance!

Diffusion

		t^{sim}	N_{pairs}	t	$D^{+,app}(t)$	$D^{-,app}(t)$	$D^{Li,app}(t)$
[pyr14][TFSI]	DFT-MD	0.1	8	0.05	6.47 (3.2)	6.10 (2.4)	1.91 (0.6)
	PFF-MD	6.0	8	0.05	4.23	3.17	0.75
		6.0	8	$t \to \infty$	1.40	0.89	0.28
		6.0	144	$t \to \infty$	0.80	0.66	0.34
[pyr13][FSI]	DFT-MD	0.1	8	0.05	4.78 (2.3)	4.27 (2.4)	1.64 (0.5)
	PFF-MD	6.0	8	0.05	4.85	3.85	0.92
		6.0	8	$t \to \infty$	1.41	1.29	0.44
		6.0	216	$t \to \infty$	0.89	0.91	0.47
[EMIM][BF_4]	DFT-MD	0.1	8	0.05	7.77 (3.6)	3.78 (2.2)	1.03 (0.3)
	PFF-MD	6.0	8	0.05	4.77	2.97	0.97
		6.0	8	$t \to \infty$	1.97	1.48	0.75
		6.0	216	$t \to \infty$	1.93	1.38	0.65

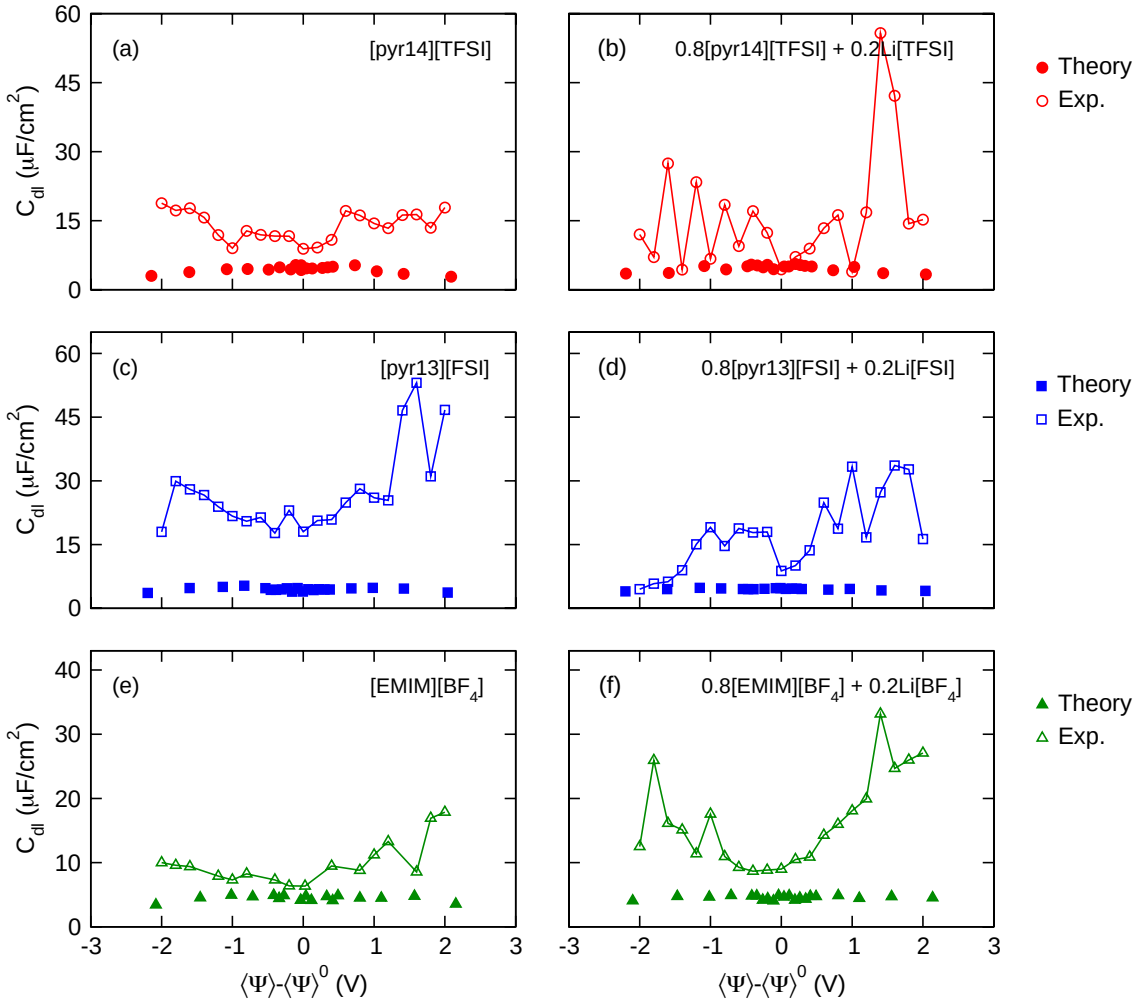
Adjusting for time-scale and size effects brings DFT measure close to polarizable MD and experiment!

Surface energy estimate

		Elec. Window (eV)	C_{dl} (F/m^2)	E (Wh/m^2)
[pyr14][TFSI]	Theory	4.6-6.53	4.4	0.7-1.3
	Exp.	3.8-6	13.9	1.4-3.5
[pyr13][FSI]	Theory	4.7-6.4	4.5	0.7-1.4
	Exp.	4.3-6	27.2	3.5-6.8
[EMIM][BF_4]	Theory	3.9-5.5	4.5	0.5-0.9
	Exp.	4.3-4.6	9.9	1.3-1.5

Experiments performed on glassy carbon!

Experimental analysis of capacitance



Experiments performed on glassy carbon!

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