Investigation of structure and transport in Li-doped ionic liquid electrolytes

[pyr14][TFSI], [pyr13][FSI], and *[EMIM][BF_4]*

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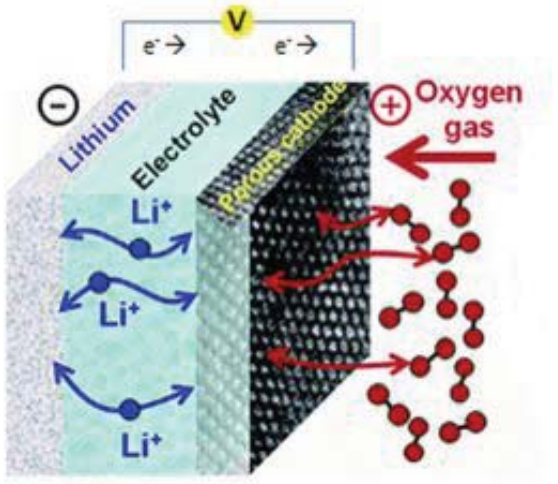
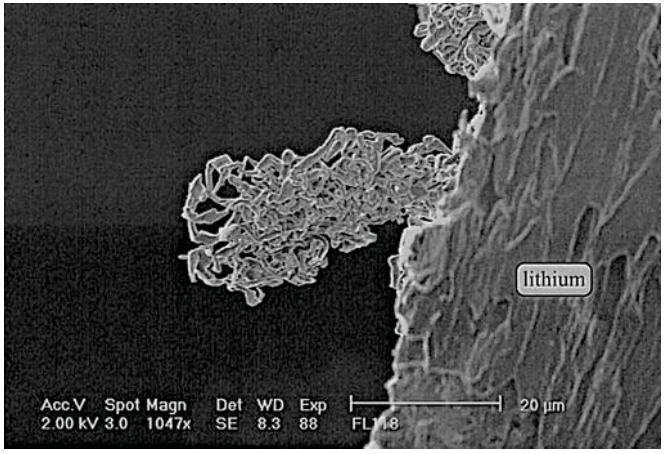
Outline

- Li-doped ionic liquids for electrochemical applications
- Atomistic computational modeling of ionic liquids
- Influence of Li^+ on ionic liquid structure
  - Li^+/Anion binding and solvation
  - Li^+ … Li^+ network statistics
- Transport properties of Li-doped ionic liquids
- Kinetics of Li^+ transport in ionic liquids
  - Li^+/Anion residence times
  - contribution of anion exchange to diffusion

Ionic liquids for electrochemical applications

- **Li-ion batteries**: possible safer alternative to organic electrolytes
- **Advanced electrodes**: helps stabilize cycling against Li-metal
- **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)

Computational models and molecular dynamics (MD)

- Newton's law *F=ma* for atoms

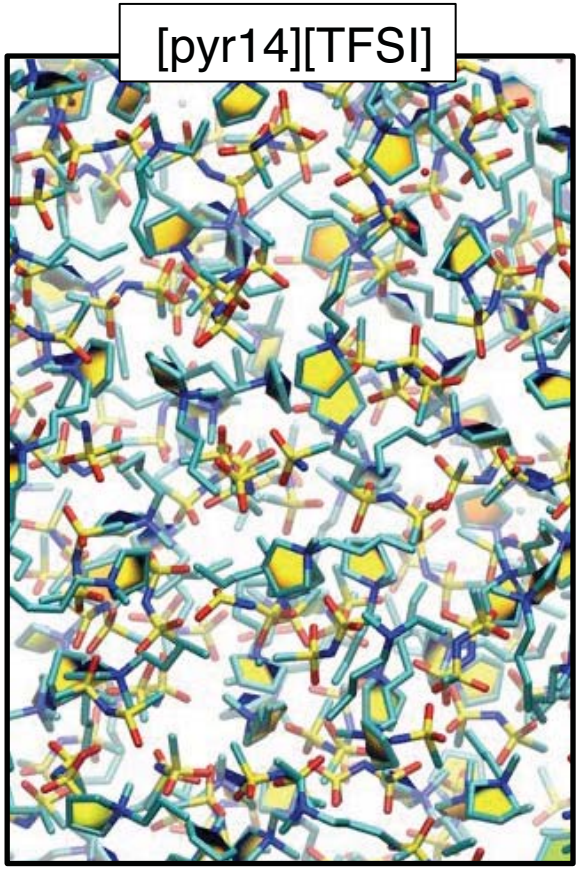
$$F = -\nabla U$$

- Atomistic polarizable potential for liquids, electrolytes and polymers (APPLE&P)

$$U^{RD} = \sum_{i<j} \left(A_{ij} \exp(-B_{ij} r_{ij}) - C_{ij} r_{ij}^{-6} \right)$$

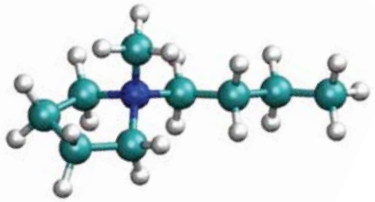
$$U^{ES} = \sum_{i<j} \left(\frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} \right) - \frac{1}{2} \sum_i \vec{\mu} \cdot \vec{E}_i^0$$

- Includes many body polarization
- System sizes: ~10^4 atoms
- Time scales: 50-200 ns

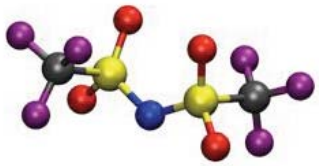


O. Borodin, *J. Phys. Chem. B* **113**, 11463 (2009)
O. Borodin, et al., *J. Phys. Chem. B* **110**, 6279-6292 (2006)
O. Borodin, et al., *J. Phys. Chem. B* **110**, 6293-6299 (2006)

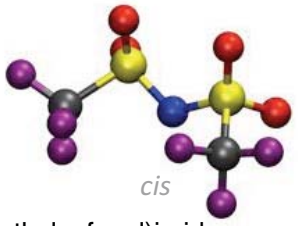
Ionic liquids of interest



[pyr14]$^+$ N-methyl-N-butylpyrrolidinium$^+$

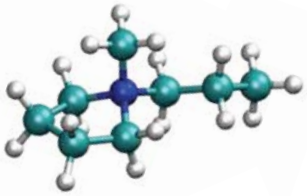


trans

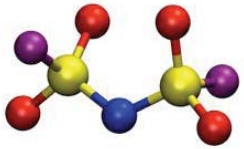


cis

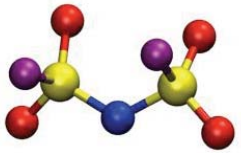
[TFSI]$^-$ bis(trifluoromethylsufonyl)imide



[pyr13]$^+$ N-methyl-N-proylpyrrolidinium$^+$

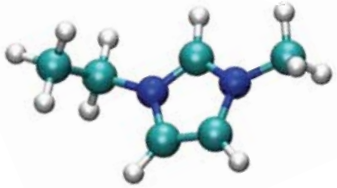


trans

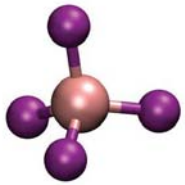


cis

[FSI]$^-$ bis(fluorosufonyl)imide



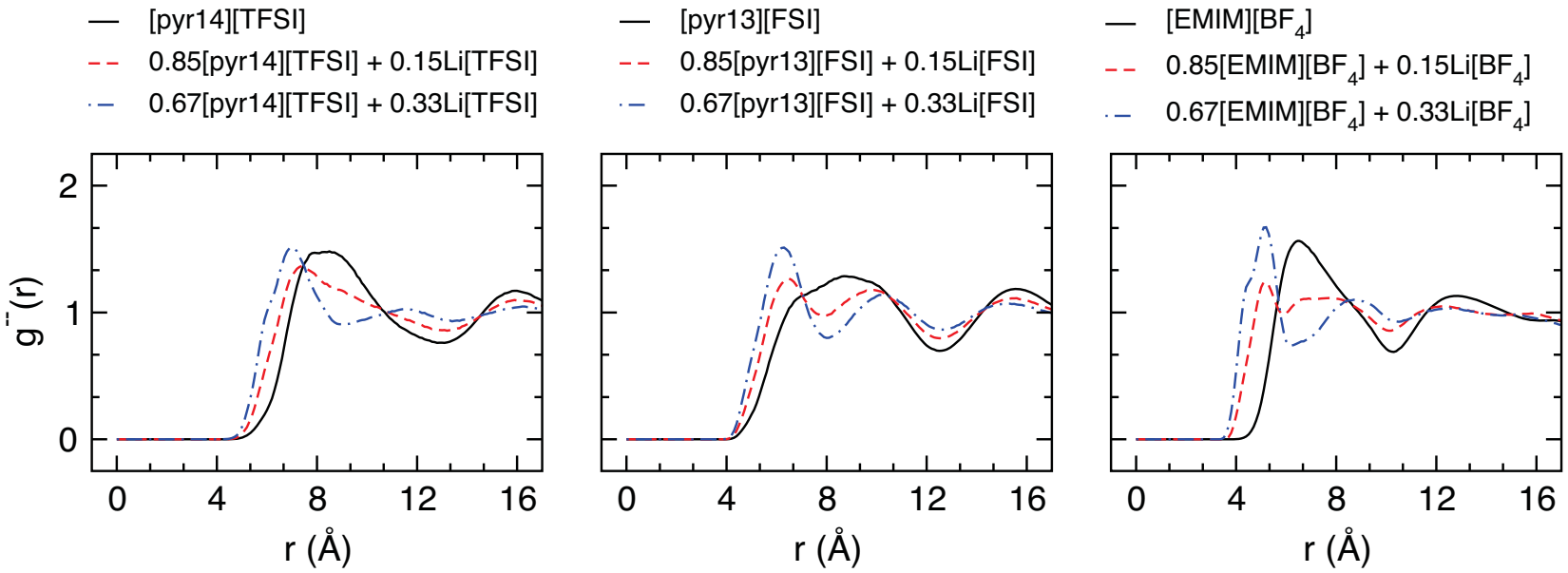
[EMIM]$^+$ 1-methyl-3-ethylimidazolium$^+$



[BF_4]$^-$ boron tetrafluoride

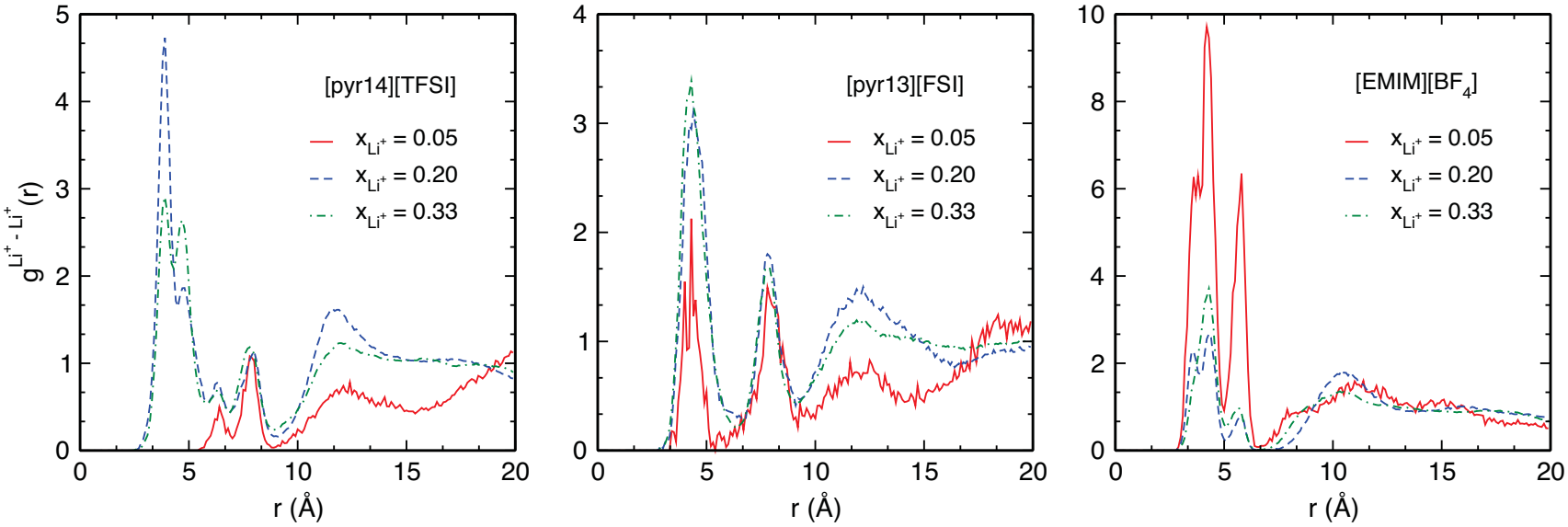
Influence of Li^+-doping on anion distributions

Small anion separation around Li^+

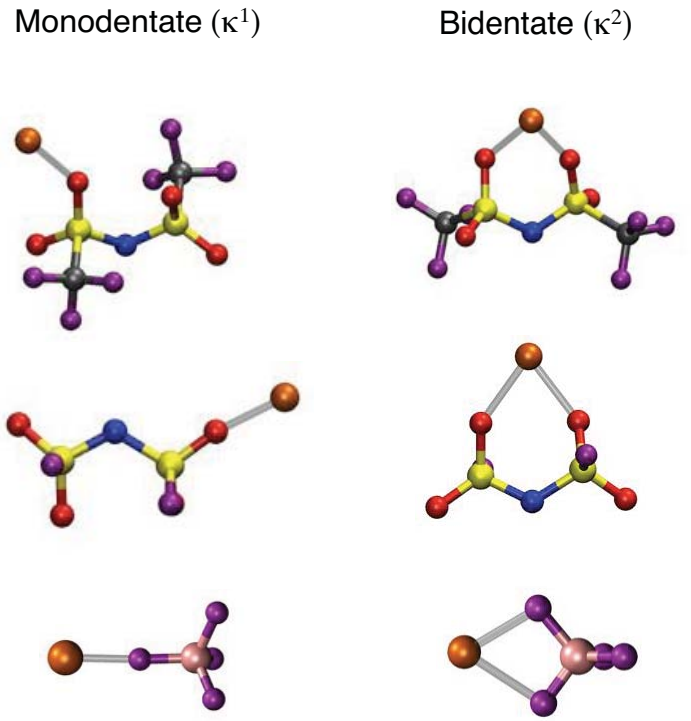


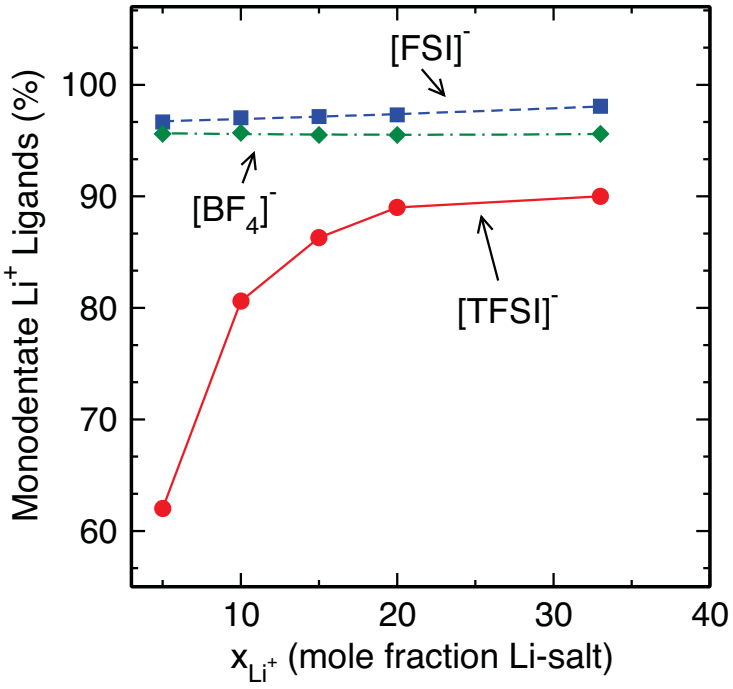
Li^+-Li^+ distributions

Li^+ …. Li^+ clustering at low-r and high doping levels



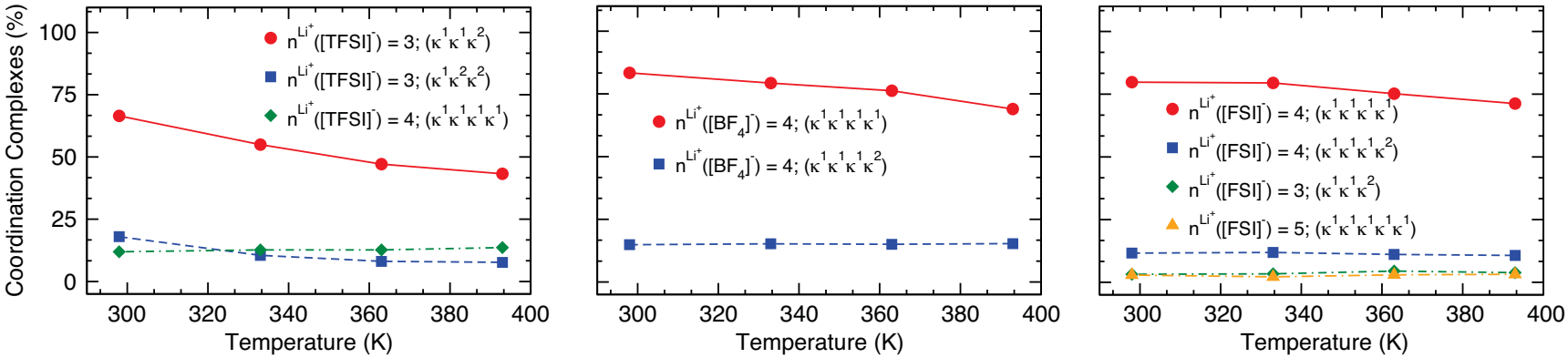
Li^+/Anion bonding structures





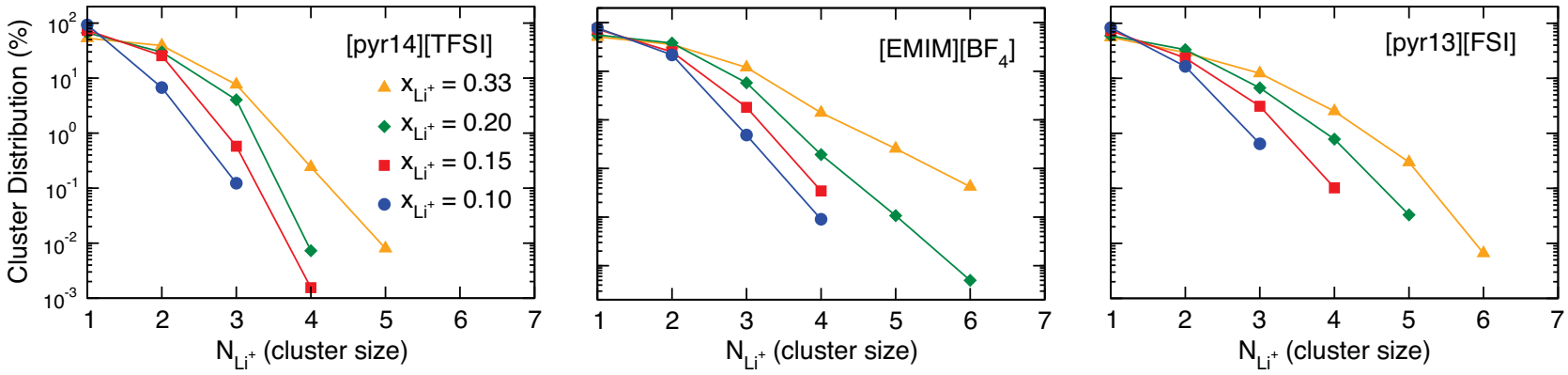
- Li-[TFSI] bonding dependence on Li-doping level
- More monodentate at high doping levels

Li^+/Anion solvation shells

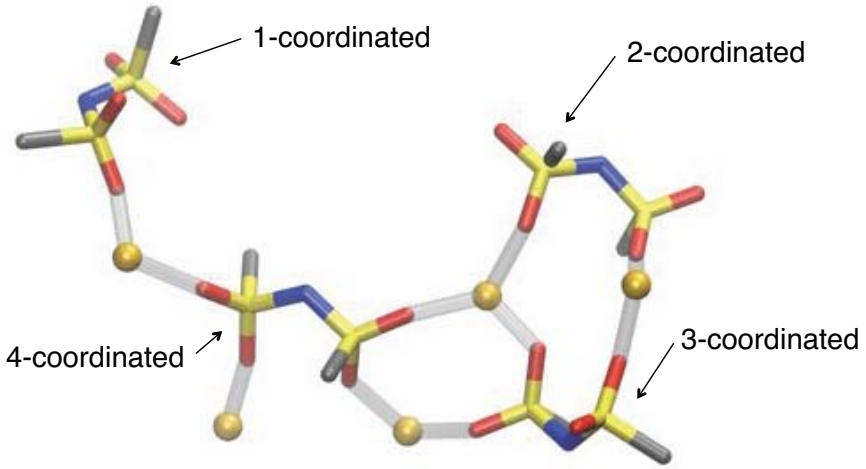


- 4-5 anion neighbors in Li^+ solvation shell: [TFSI] (3-4), [BF_4] (4), [FSI] (3-5)
- $[Li(TFSI)_2]^-$ and $[Li(FSI)_3]^{-2}$ from expeiment (J.C. Lassegues, et al., *J. Phys. Chem. A* **113**, 305 (2009) and K. Fujii, et al., *J. Phys. Chem. C* **117**, 19314 (2013))

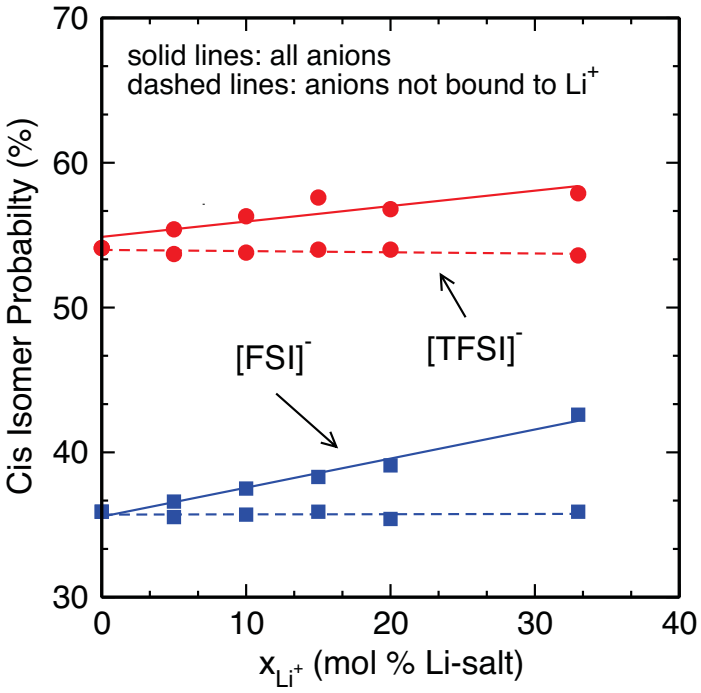
Li^+ … Li^+ networks

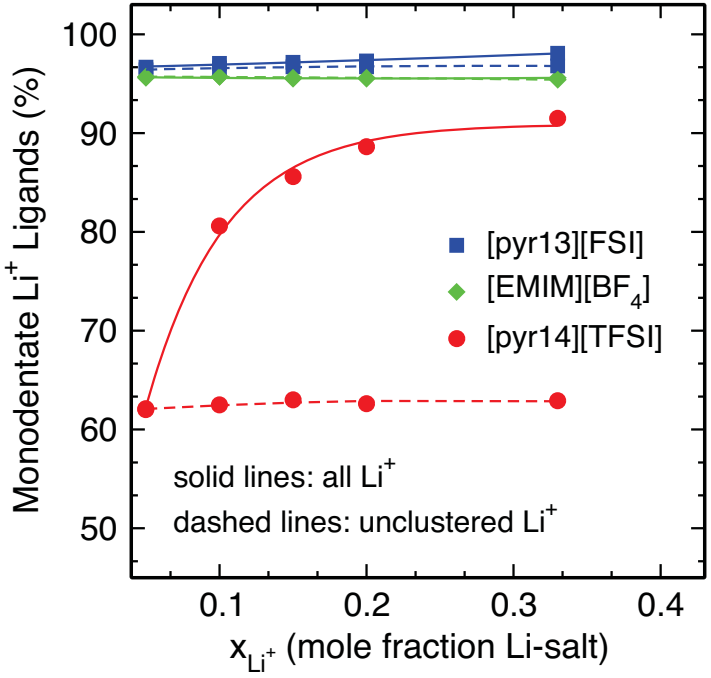


- Networks at all levels of Li-doping
- 5-6 Li-ions in largest networks
- Structural impact on anions



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





- cis-[TFSI] and cis-[FSI] conformers in Li^+ solvation shell
- Monodentate binding in [TFSI] networks

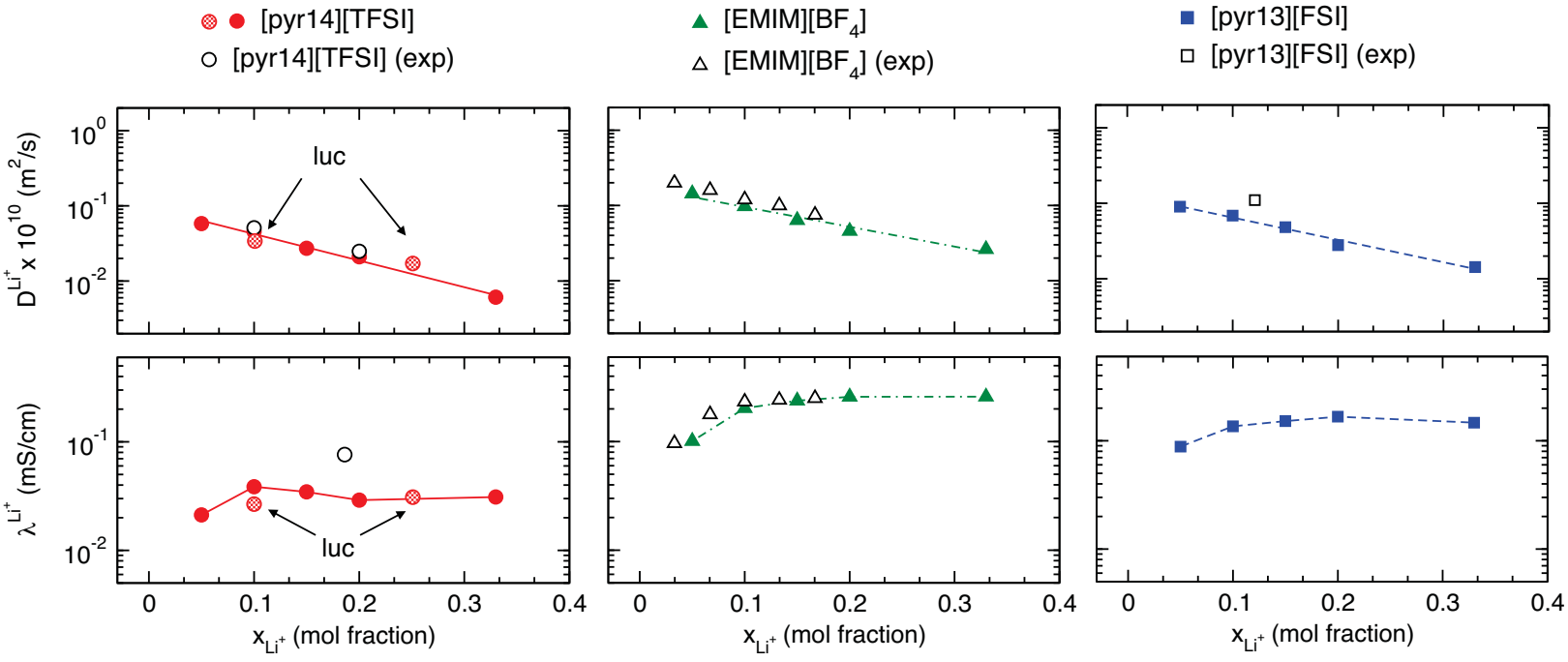
Computational measures of thermodynamics and transport

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

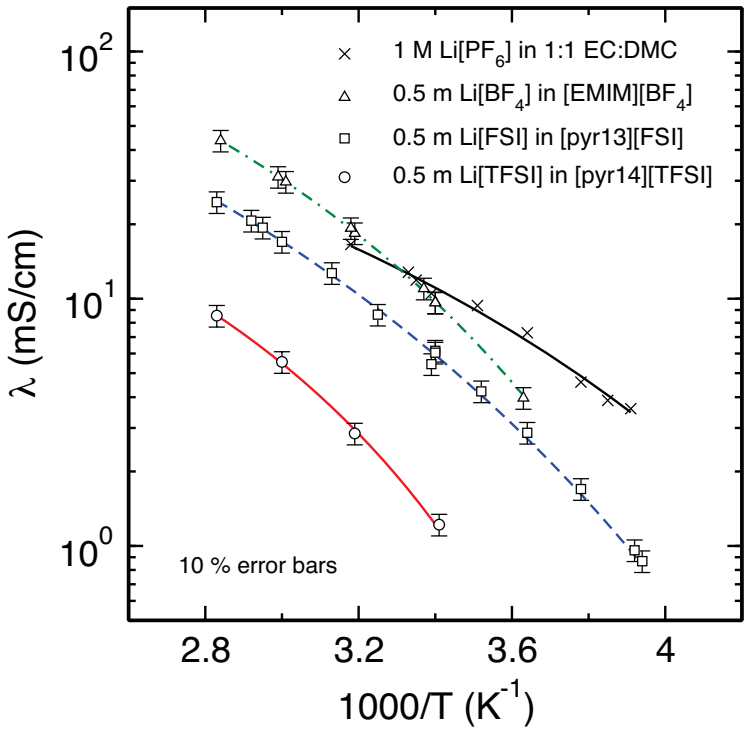
- Greater ion mobility with decreasing density and ion size
- High accuracy of predicted properties:
  - density within ~1%
  - diffusion within 10-25%
  - conductivity within 10-20%

Comparison of room-T Li transport



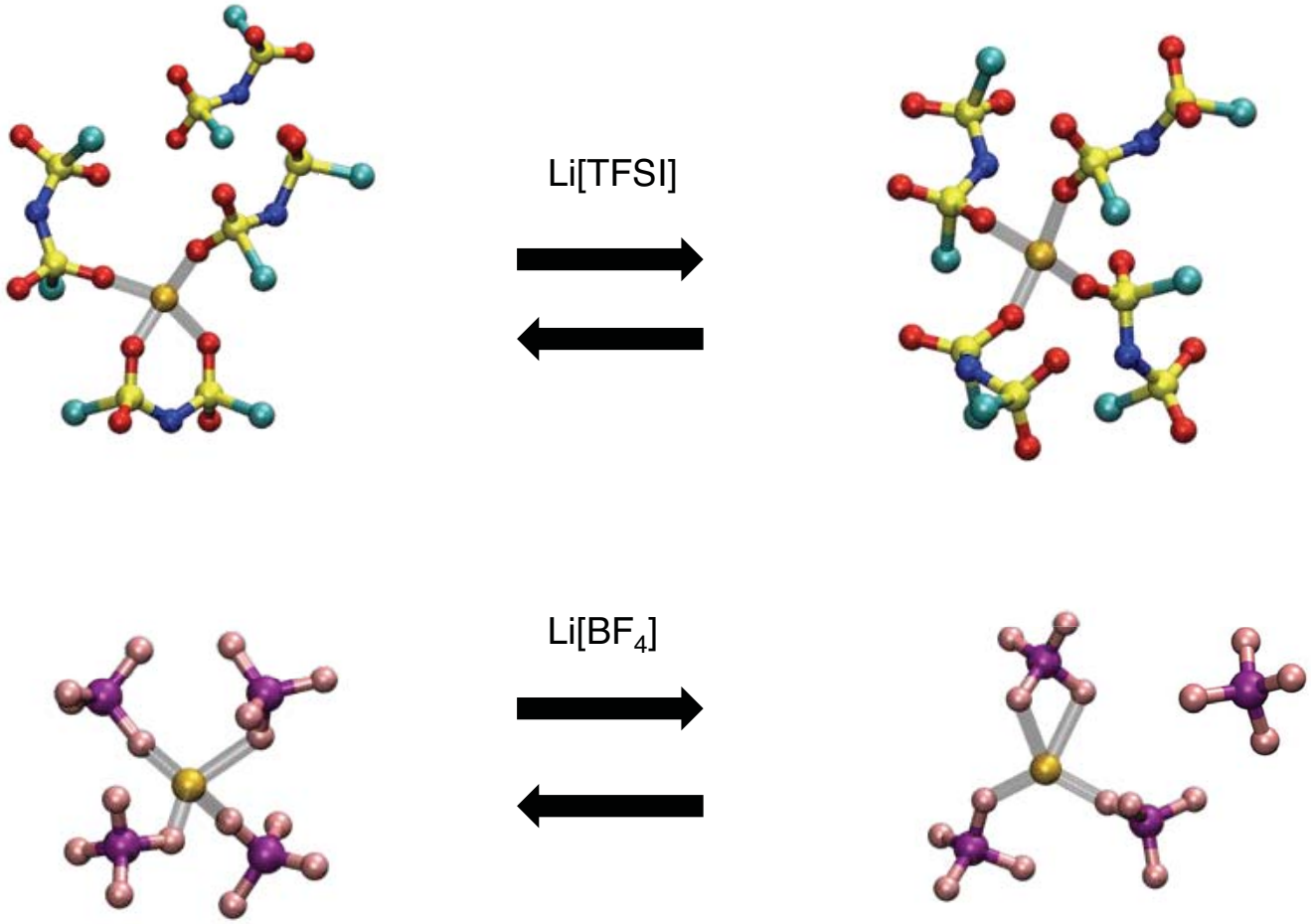
- *T* = 298 K properties computationally expensive (~200 ns)
- Li^+ ionic conduction order of magnitude lower in [pyr14][TFSI]
- Plateau in ionic conduction at high Li-doping

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

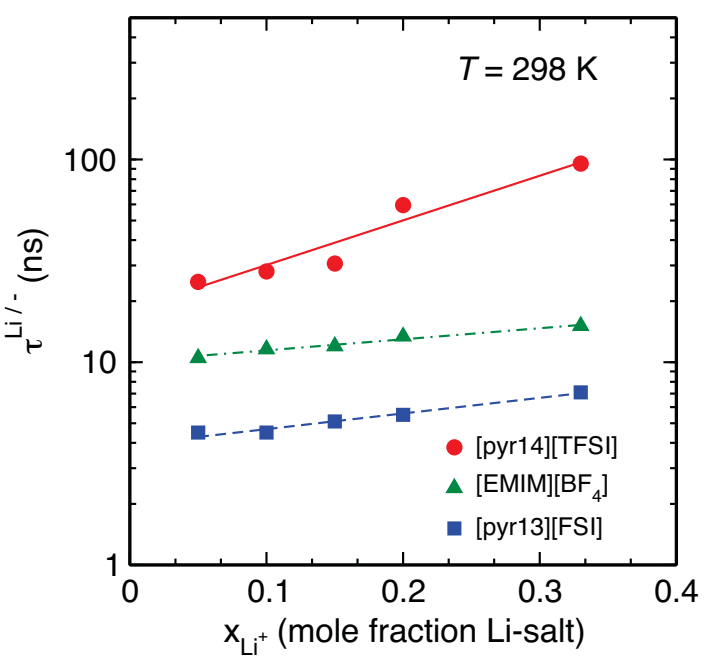


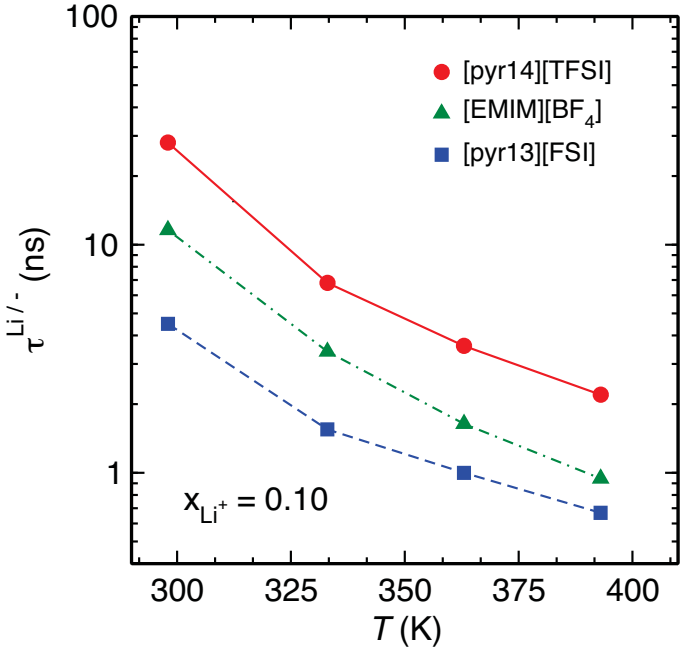
Mid-T ion conductivity comparable to conventional electrolytes

Exchange of anions in the Li solvation shell



Li^+/Anion residence times



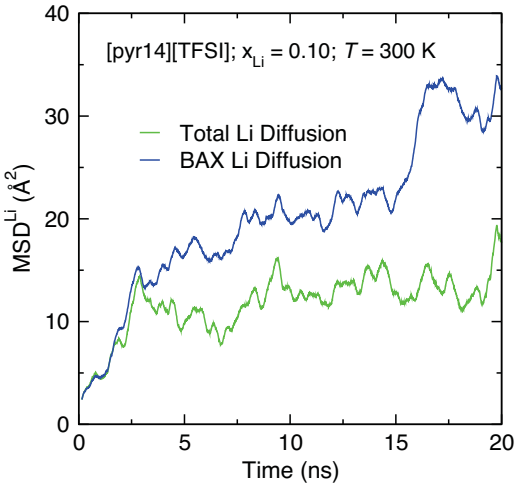


- Longer residence times at higher Li-doping levels
- Times follow [TFSI] > [BF_4] > [FSI]

Contribution of anion exchange to diffusion

	[pyr14][TFSI]		[pyr13][FSI]		[EMIM][BF_4]	
x_{Li^+}	$D^{Li^+}_{bax}/D^{Li^+}$	$N^{\langle R\rangle}$	$D^{Li^+}_{bax}/D^{Li^+}$	$N^{\langle R\rangle}$	$D^{Li^+}_{bax}/D^{Li^+}$	$N^{\langle R\rangle}$
0.05	0.69	4.4	0.81	3.7	0.89	6.1
0.10	0.66	4.2	0.85	2.4	1.07	5.8
0.33	0.59	3.5	0.73	2.0	0.91	3.9

- Anion exchange a secondary factor in Li^+ diffusion
- Anion exchange more important with larger anions and higher Li-doping



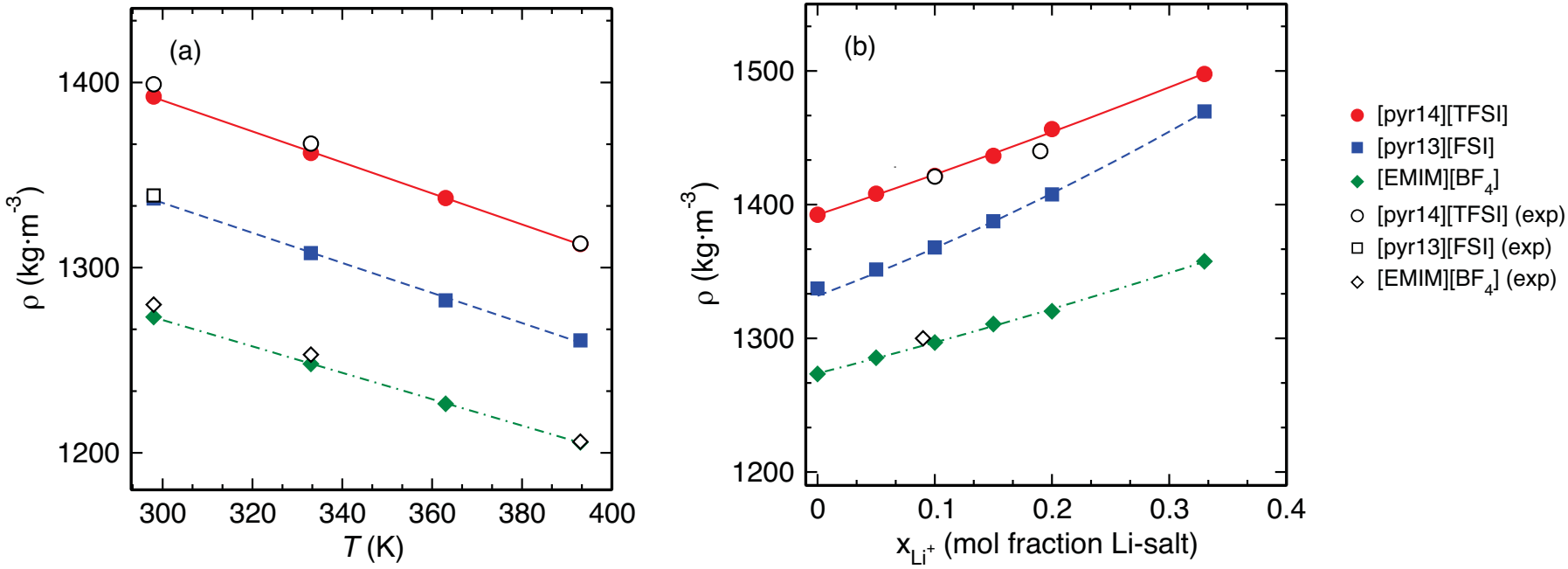
Conclusions

- Lithium networks present at all levels of doping
- Li/anion binding tends to prefer monodentate at all high levels of doping
- Transport properties in good agreement with experiment
  - density follows $[BF_4] < [FSI] < [TFSI]$
  - lithium diffusion follows $[BF_4] > [FSI] > [TFSI]$
- Anion exchange secondary to net motion of lithium with the solvation shell

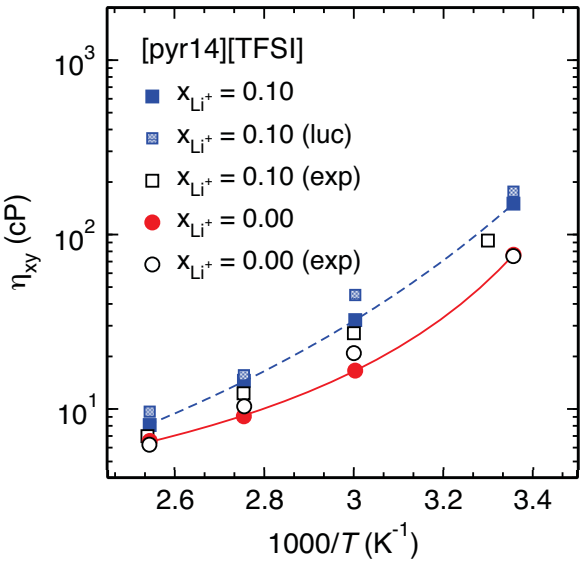
Acknowledgements

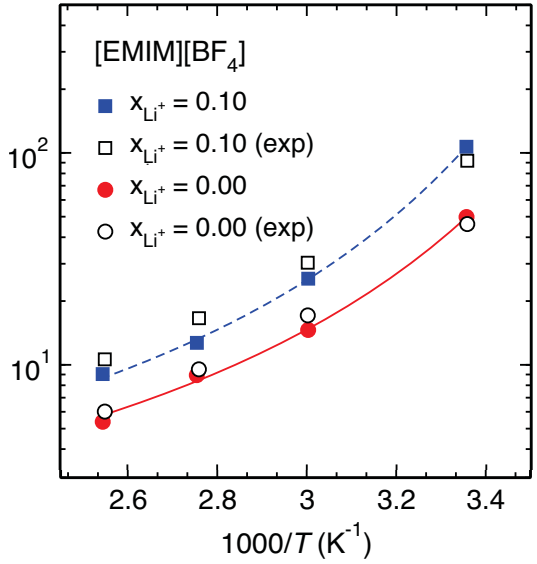
Miscellaneous slides

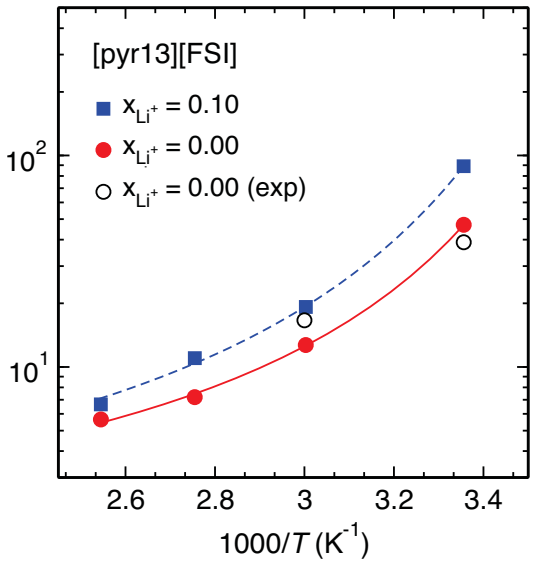
Density


(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
x Li+ (mol fraction Li-salt)
[pyr14][TFSI]
[pyr13][FSI]
[EMIM][BF4]
[pyr14][TFSI] (exp)
[pyr13][FSI] (exp)
[EMIM][BF4] (exp)

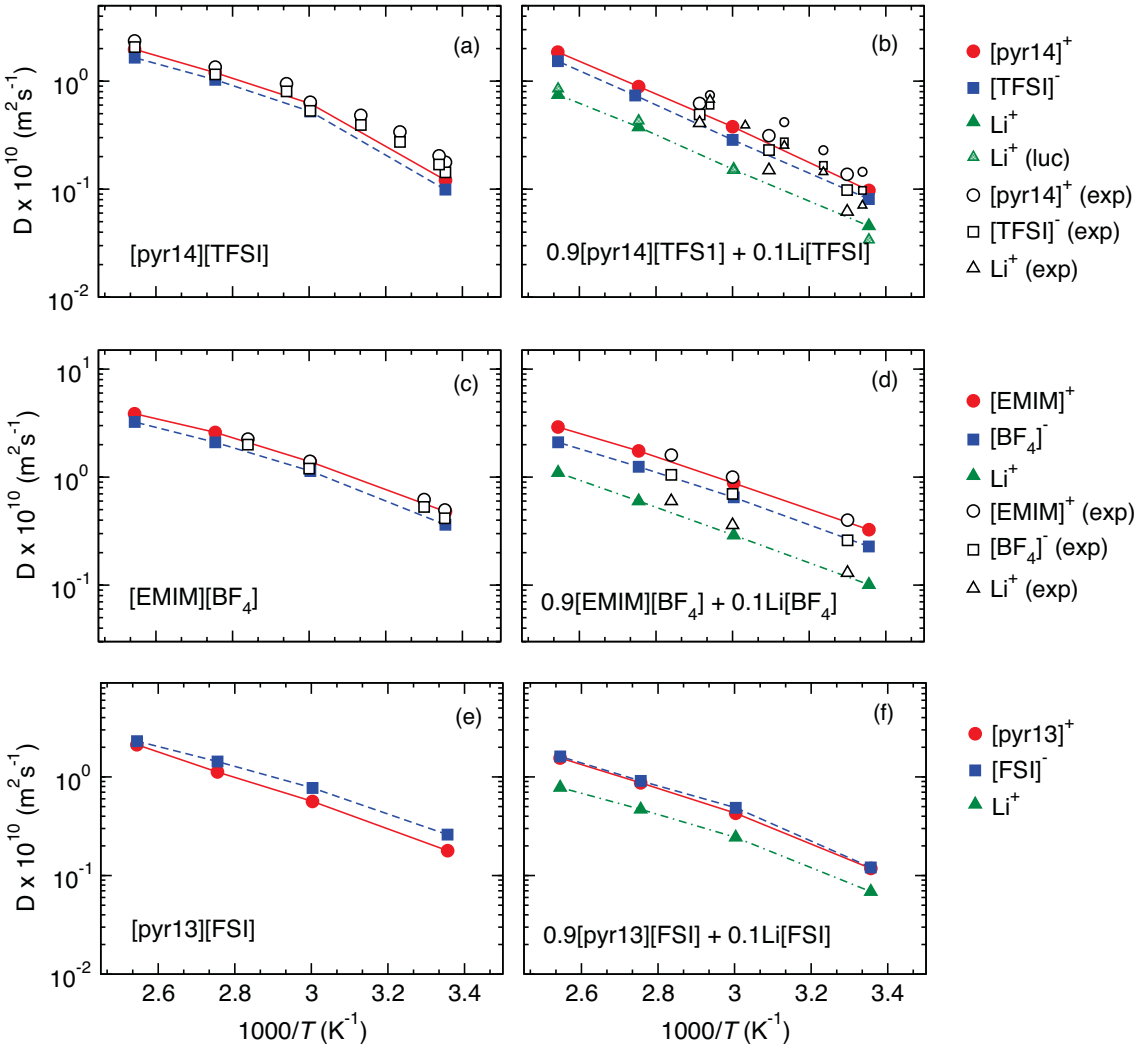
Viscosity


[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})

Diffusion


(a)
(b)
(c)
(d)
(e)
(f)
D x 10^10 (m^2 s^-1)
[pyr14][TFSI]
0.9[pyr14][TFS1] + 0.1Li[TFSI]
[EMIM][BF4]
0.9[EMIM][BF4] + 0.1Li[BF4]
[pyr13][FSI]
0.9[pyr13][FSI] + 0.1Li[FSI]
1000/T (K^-1)
[pyr14]+
[TFSI]-
Li+
Li+ (luc)
[pyr14]+ (exp)
[TFSI]- (exp)
Li+ (exp)
[EMIM]+
[BF4]-
Li+
[EMIM]+ (exp)
[BF4]- (exp)
Li+ (exp)
[pyr13]+
[FSI]-
Li+

Ionic conductivity