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

[pyr14][TFSI], [pyr13][FSI], and [EMIM][BF₄]

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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: $\sim 10^4$ atoms
- Time scales: 50-200 ns


Ionic liquids of interest

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

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

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

[TFSI]$^-$  bis(trifluoromethylsulfonylimide

[FSI]$^-$  bis(fluorosulfonylimide

[BF$_4$]$^-$  boron tetrafluoride
Influence of Li\(^+\)-doping on anion distributions

Small anion separation around Li\(^+\)

[pjr14][TFSI]  
- 0.85[pjr14][TFSI] + 0.15Li[TFSI]  
- 0.67[pjr14][TFSI] + 0.33Li[TFSI]

[pjr13][FSI]  
- 0.85[pjr13][FSI] + 0.15Li[FSI]  
- 0.67[pjr13][FSI] + 0.33Li[FSI]

[EMIM][BF\(_4\)]  
- 0.85[EMIM][BF\(_4\)] + 0.15Li[BF\(_4\)]  
- 0.67[EMIM][BF\(_4\)] + 0.33Li[BF\(_4\)]
Li\textsuperscript{+}-Li\textsuperscript{+} distributions

Li\textsuperscript{+} .... Li\textsuperscript{+} clustering at low-r and high doping levels

[pyr14][TFSI] 
- \(x_{Li^+} = 0.05\)
- \(x_{Li^+} = 0.20\)
- \(x_{Li^+} = 0.33\)

[pyr13][FSI] 
- \(x_{Li^+} = 0.05\)
- \(x_{Li^+} = 0.20\)
- \(x_{Li^+} = 0.33\)

[EMIM][BF_4] 
- \(x_{Li^+} = 0.05\)
- \(x_{Li^+} = 0.20\)
- \(x_{Li^+} = 0.33\)
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⁺ ... 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

<table>
<thead>
<tr>
<th></th>
<th>[pyr14][TFSI]</th>
<th>[pyr13][FSI]</th>
<th>[EMIM][BF₄]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ρ</td>
<td>1421.5</td>
<td>1367.9</td>
<td>1296.9</td>
</tr>
<tr>
<td>D⁺</td>
<td>0.097</td>
<td>0.118</td>
<td>0.326</td>
</tr>
<tr>
<td>D⁻</td>
<td>0.081</td>
<td>0.121</td>
<td>0.228</td>
</tr>
<tr>
<td>D^{Li}</td>
<td>0.046</td>
<td>0.069</td>
<td>0.101</td>
</tr>
<tr>
<td>μ</td>
<td>150</td>
<td>89</td>
<td>107</td>
</tr>
<tr>
<td>λ</td>
<td>1.67</td>
<td>3.35</td>
<td>11.45</td>
</tr>
</tbody>
</table>

- 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

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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[TFSI] →

Li[BF₄] →
Li⁺/Anion residence times

- Longer residence times at higher Li-doping levels
- Times follow \([\text{TFSI}] > [\text{BF}_4] > [\text{FSI}]\)
## Contribution of anion exchange to diffusion

<table>
<thead>
<tr>
<th>$x_{\text{Li}^+}$</th>
<th>$\left[\text{pyr14}\right][\text{TFSI}]$</th>
<th>$\left[\text{pyr13}\right][\text{FSI}]$</th>
<th>$\left[\text{EMIM}\right][\text{BF}_4]$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$D_{\text{Li}^+}^{\text{bax}}/D_{\text{Li}^+}^{\text{Li}^+}$</td>
<td>$D_{\text{Li}^+}^{\text{bax}}/D_{\text{Li}^+}^{\text{Li}^+}$</td>
<td>$D_{\text{Li}^+}^{\text{bax}}/D_{\text{Li}^+}^{\text{Li}^+}$</td>
</tr>
<tr>
<td>0.05</td>
<td>0.69</td>
<td>0.81</td>
<td>0.89</td>
</tr>
<tr>
<td></td>
<td>4.4</td>
<td>3.7</td>
<td>6.1</td>
</tr>
<tr>
<td>0.10</td>
<td>0.66</td>
<td>0.85</td>
<td>1.07</td>
</tr>
<tr>
<td></td>
<td>4.2</td>
<td>2.4</td>
<td>5.8</td>
</tr>
<tr>
<td>0.33</td>
<td>0.59</td>
<td>0.73</td>
<td>0.91</td>
</tr>
<tr>
<td></td>
<td>3.5</td>
<td>2.0</td>
<td>3.9</td>
</tr>
</tbody>
</table>

- 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 $[\text{BF}_4] < [\text{FSI}] < [\text{TFSI}]$
  – lithium diffusion follows $[\text{BF}_4] > [\text{FSI}] > [\text{TFSI}]$

• Anion exchange secondary to net motion of lithium with the solvation shell
Acknowledgements
Density

![Graphs showing the relationship between density and temperature, and density and mol fraction Li-salt.](image)

- **Graph (a)**: Density as a function of temperature for different ionic liquid systems.
  - [pyr14][TFSI]
  - [pyr13][FSI]
  - [EMIM][BF₄]

- **Graph (b)**: Density as a function of mol fraction Li-salt for different ionic liquid systems.
  - [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)

[EMIM][BF$_4$]
- $x_{Li^+} = 0.10$
- $x_{Li^+} = 0.10$ (exp)
- $x_{Li^+} = 0.00$
- $x_{Li^+} = 0.00$ (exp)

[pyr13][FSI]
- $x_{Li^+} = 0.10$
- $x_{Li^+} = 0.00$
- $x_{Li^+} = 0.00$ (exp)
Diffusion

\[ D \times 10^{-10} \text{ (m}^2 \text{s}^{-1}) \]

(a) [pyr14][TFSI]
(b) 0.9[pyr14][TFSI] + 0.1Li[TFSI]
(c) [EMIM][BF₄]
(d) 0.9[EMIM][BF₄] + 0.1Li[BF₄]
(e) [pyr13][FSI]
(f) 0.9[pyr13][FSI] + 0.1Li[FSI]

Temperature (K): 2.6, 2.8, 3, 3.2, 3.4
Ionic conductivity

![Graphs showing ionic conductivity for different electrolytes.]

- [pyr14][TFSI]
- [EMIM][BF₄]
- [pyr13][FSI]

**Graph Legend:**
- Red circles: $x_{Li^+} = 0.0$
- Black squares: $x_{Li^+} = 0.20$
- Blue triangles: $x_{Li^+} = 0.18$ (exp)
- White circles: $x_{Li^+} = 0.0$ (exp)
- Black squares: $x_{Li^+} = 0.15$
- White circles: $x_{Li^+} = 0.13$ (exp)

**Equation:**

$$\lambda = \frac{1}{x_{Li^+}} \left( \frac{A}{T} \right)$$

**Values:**

<table>
<thead>
<tr>
<th>$x_{Li^+}$</th>
<th>[pyr14][TFSI]</th>
<th>[EMIM][BF₄]</th>
<th>[pyr13][FSI]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>$0.0$ (exp)</td>
<td>$0.0$ (exp)</td>
<td>$0.0$ (exp)</td>
</tr>
<tr>
<td>0.0</td>
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<td>$0.0$ (exp)</td>
<td>$0.0$ (exp)</td>
</tr>
<tr>
<td>0.20</td>
<td>$0.20$</td>
<td>$0.20$</td>
<td>$0.20$</td>
</tr>
<tr>
<td>0.18</td>
<td>$0.18$ (exp)</td>
<td>$0.18$ (exp)</td>
<td>$0.18$ (exp)</td>
</tr>
<tr>
<td>0.15</td>
<td></td>
<td>$0.15$</td>
<td>$0.15$</td>
</tr>
<tr>
<td>0.13</td>
<td></td>
<td>$0.13$</td>
<td>$0.13$</td>
</tr>
</tbody>
</table>

**Units:**

- $\lambda$ (mS/cm)
- $1000/T$ (K⁻¹)