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

\([\text{pyr}14][\text{TFSI}], [\text{pyr}13][\text{FSI}],\) and \([\text{EMIM}][\text{BF}_4]\)

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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)
  \[
    U^{RD} = \sum_{i<j} \left( A_{ij} \exp(-B_{ij}r_{ij}) - C_{ij}r_{ij}^{-6} \right)
  \]
  \[
    U^{ES} = \sum_{i<j} \left( \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} \right) - \frac{1}{2} \sum_i \bar{\mu} \cdot \bar{E}_i^0
  \]

• 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-prolylpyrrolidinium+

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

[TFSI]:   bis(trifluoromethylsulfonyl)imide

[FSI]:    bis(fluorosulfonyl)imide

[BF₄]:    boron tetrafluoride
Influence of Li$^+$-doping on anion distributions

Small anion separation around Li$^+$

- [pyr14][TFSI]
- 0.85[pyr14][TFSI] + 0.15Li[TFSI]
- 0.67[pyr14][TFSI] + 0.33Li[TFSI]

- [pyr13][FSI]
- 0.85[pyr13][FSI] + 0.15Li[FSI]
- 0.67[pyr13][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$^+$-Li$^+$ distributions

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

![Graphs showing Li$^+$-Li$^+$ distributions for different electrolytes.](image)
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), [BF₄] (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
Experimental comparison of ionic conductivity to that of Li-ion battery organic electrolytes

Mid-T ionic conductivity comparable to conventional electrolytes
Exchange of anions in the Li solvation shell

Li[BF₄] ↔ Li[TFSI]
**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_{Li^+}</th>
<th>[pyr14][TFSI]</th>
<th>[pyr13][FSI]</th>
<th>[EMIM][BF_4]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>D_{bax}^{Li^+}/D_{Li^+}^{Li^+} = 0.69</td>
<td>D_{bax}^{Li^+}/D_{Li^+}^{Li^+} = 0.81</td>
<td>D_{bax}^{Li^+}/D_{Li^+}^{Li^+} = 0.89</td>
</tr>
<tr>
<td>0.10</td>
<td>4.4</td>
<td>3.7</td>
<td>6.1</td>
</tr>
<tr>
<td>0.33</td>
<td>0.66</td>
<td>4.2</td>
<td>1.07</td>
</tr>
<tr>
<td>3.5</td>
<td>2.4</td>
<td>5.8</td>
<td></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

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Density

(a) Density as a function of temperature (T) for different mol fractions of Li-salt.

(b) Density as a function of mol fraction (x_{Li^+}) for different electrolyte solutions.
Viscosity

2.6 2.8 3 3.2 3.4

1000 \(/T (K^{-1})\)

\(\eta_{xy} (cP)\)

(a) [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)

(b) [EMIM][BF₄]
- \(x_{Li^+} = 0.10\)
- \(x_{Li^+} = 0.10\) (exp)
- \(x_{Li^+} = 0.00\)
- \(x_{Li^+} = 0.00\) (exp)

(c) [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][BF_4]

(d) 0.9[EMIM][BF_4] + 0.1Li[BF_4]

(e) [pyr13][FSI]

(f) 0.9[pyr13][FSI] + 0.1Li[FSI]

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\[ \frac{1000}{T} (K^{-1}) \]

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\[ \text{Diffusion/nor-marking/return} \]
Ionic conductivity

\[ \lambda (\text{mS/cm}) \]

- **[pyr14][TFSI]**
  - \( x_{Li^+} = 0.0 \)
  - \( x_{Li^+} = 0.0 \) (exp)
  - \( x_{Li^+} = 0.20 \)
  - \( x_{Li^+} = 0.18 \) (exp)

- **[EMIM][BF_4]**
  - \( x_{Li^+} = 0.0 \)
  - \( x_{Li^+} = 0.0 \) (exp)
  - \( x_{Li^+} = 0.10 \)
  - \( x_{Li^+} = 0.09 \) (exp)

- **[pyr13][FSI]**
  - \( x_{Li^+} = 0.0 \)
  - \( x_{Li^+} = 0.0 \) (exp)
  - \( x_{Li^+} = 0.15 \)
  - \( x_{Li^+} = 0.13 \) (exp)