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)
  \[ U^{RD} = \sum_{i<j} \left( A_{ij} \exp(-B_{ij}r_{ij}) - C_{ij}r_{ij}^{-6} \right) \]
  \[ U^{ES} = \sum_{i<j} \left( \frac{q_iq_j}{4\pi\varepsilon_0r_{ij}} \right) - \frac{1}{2} \sum_i \vec{\mu}_i \cdot \vec{E}_0^i \]
- 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(trifluoromethylsufonyl)imide

[FSI]- bis(fluorosufonyl)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
Li\textsuperscript{+}/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>Dᵋ</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 ion 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 [TFSI] > [BF₄] > [FSI]

\[ T = 298 \text{ K} \]

\[ x_{\text{Li}^+} \text{ (mole fraction Li-salt)} \]

\[ \tau_{\text{Li}^+} \text{ (ns)} \]

\[ x_{\text{Li}^+} = 0.10 \]

\[ T \text{ (K)} \]

\[ \tau_{\text{Li}^+} \text{ (ns)} \]
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></td>
<td>$D_{Li^+}/D_{Li^+}$</td>
<td>$N^{(R)}$</td>
<td>$D_{Li^+}/D_{Li^+}$</td>
</tr>
<tr>
<td>0.05</td>
<td>0.69</td>
<td>4.4</td>
<td>0.81</td>
</tr>
<tr>
<td>0.10</td>
<td>0.66</td>
<td>4.2</td>
<td>0.85</td>
</tr>
<tr>
<td>0.33</td>
<td>0.59</td>
<td>3.5</td>
<td>0.73</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

(a) Density vs. temperature for various Li-salt concentrations.

(b) Density vs. mol fraction Li-salt concentration for different ionic liquids.
Viscosity

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

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

\[ \text{[pyr14][TFSI]} \]

\[ \text{[EMIM][BF}_4\text{]} \]

\[ \text{[pyr13][FSI]} \]

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

\[ \text{[pyr13]}^+ \]

\[ \text{[TFSI]}^- \]

\[ \text{Li}^+ \]

\[ \text{Li}^+ \text{ (luc)} \]

\[ \text{[pyr14]}^+ \text{ (exp)} \]

\[ \text{[TFSI]}^- \text{ (exp)} \]

\[ \text{Li}^+ \text{ (exp)} \]

\[ \text{[EMIM]}^+ \]

\[ \text{[BF}_4\text{]}^- \]

\[ \text{Li}^+ \]

\[ \text{[EMIM]}^+ \text{ (exp)} \]

\[ \text{[BF}_4\text{]}^- \text{ (exp)} \]

\[ \text{Li}^+ \text{ (exp)} \]

\[ \text{Li}^+ \text{ (exp)} \]

\[ \text{Li}^+ \text{ (exp)} \]

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Ionic conductivity

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

- [EMIM][BF$_4$]
  - $x_{\text{Li}^+} = 0.0$
  - $x_{\text{Li}^+} = 0.0$ (exp)
  - $x_{\text{Li}^+} = 0.10$
  - $x_{\text{Li}^+} = 0.09$ (exp)

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