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

\([\text{pyr14}][\text{TFSI}], \ [\text{pyr13}][\text{FSI}], \text{ and } [\text{EMIM}][\text{BF}_4]\)

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AIChE Annual Meeting | November 16-21, 2014 | Atlanta, GA
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)
Computational modeling of Li-doped ionic liquid electrolytes

- Comprehensive analysis of structure, thermodynamics, and transport
- Three distinct ionic liquid systems
- Six Li-doping levels ($x_{Li} = 0 - 0.33$)
- Four temperatures ($T = 298 - 393$ K)
- Polarizable force field
- Long simulation times (200 ns)
- Cross-checked with different codes

Outline

1. Li⁺ solvation structure
2. Transport properties
3. Li⁺ transport mechanism
Ionic liquids

Chosen for supression of dendrites on Li⁺ metal anodes*

Radial distribution functions

<table>
<thead>
<tr>
<th>Cation-Cation</th>
<th>Cation-Anion</th>
<th>Anion-Anion</th>
</tr>
</thead>
<tbody>
<tr>
<td>[pyr14][TFSI]</td>
<td>[pyr13][FSI]</td>
<td>[EMIM][BF₄]</td>
</tr>
<tr>
<td>0.85[pyr14][TFSI] + 0.15Li[TFSI]</td>
<td>0.85[pyr13][FSI] + 0.15Li[FSI]</td>
<td>0.85[EMIM][BF₄] + 0.15Li[BF₄]</td>
</tr>
<tr>
<td>0.67[pyr14][TFSI] + 0.33Li[TFSI]</td>
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</tr>
</tbody>
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Figure 2: T = 298 K radial distribution functions for ionic liquid ions as a function of Li-salt doping. Distributions are provided for cations with other cations \(g^{++}(r)\), cations with anions \(g^{+}(r)\), and anions with anions \(g^{-}(r)\) for (a,d,e) [pyr14][TFSI], (b,e,h) [pyr13][FSI], and (c,f,i) [EMIM][BF₄].
Radial distribution functions

Figure 2: \( T = 298 \text{ K} \) radial distribution functions for ionic liquid ions as a function of Li-salt doping. Distributions are provided for cations with other cations (\( g^{++} \)), cations with anions (\( g^{+} \)), and anions with anions (\( g^{-} \)) for (a,d,e) [pyr14][TFSI], (b,e,h) [pyr13][FSI], and (c,f,i) [EMIM][BF\(_4\)].
Solvation shells of Li$^+$

3 anion coordination for [TFSI] and 4 for [FSI] and [BF$_4$]
Li⁺/Anion bonding

Monodentate (κ¹)

Bidentate (κ²)

Monodentate bonding preferred at high Li-doping
Li⁺ ... Li⁺ networks

Network Li⁺ share bridging anions
Li⁺ … Li⁺ networks present at all levels of doping
Li-doping suppresses diffusion of all ions
Ionic conductivity

Li-doping suppresses conductivity of all systems
Room-T Li transport

Li⁺ contribution to conduction plateaus at high salt doping
What is the mechanism for Li-diffusion?
What is the mechanism for Li-diffusion?

Hopping of Li$^+$ through exchange of anions

Anion Exchange
What is the mechanism for Li-diffusion?

Vehicular

Net motion of Li\(^+\) with the solvation shell
Li$^+$/Anion residence times

![Graph of Li$^+$/Anion residence times with data points and lines indicating the trend as a function of mole fraction Li-salt and temperature.](image)

[TFSI] has longer residence times than other anions

Note: residence time of [TFSI] 30 ns at room-T
## Room-T diffusion kinetics

<table>
<thead>
<tr>
<th>$x_{\text{Li}}$</th>
<th>[pyr14][TFSI]</th>
<th>[pyr13][FSI]</th>
<th>[EMIM][BF$_4$]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$%D_{\text{veh}}$</td>
<td>$%D_{\text{veh}}$</td>
<td>$%D_{\text{veh}}$</td>
</tr>
<tr>
<td>0.05</td>
<td>69</td>
<td>81</td>
<td>89</td>
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<tr>
<td>0.10</td>
<td>66</td>
<td>85</td>
<td>107</td>
</tr>
<tr>
<td>0.33</td>
<td>59</td>
<td>73</td>
<td>91</td>
</tr>
</tbody>
</table>

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

• High Li-doping induces monodentate bonds

• Networks present at even low-levels of doping

• Transport properties in good agreement with experiment
  – Li$^+$ diffusion follows [BF$_4$] > [FSI] > [TFSI]
  – Li$^+$ conduction contribution plateaus at high doping levels

• Li$^+$ transport by anion exchange secondary to the vehicular mechanism

• Future work: properties at electrified interfaces


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