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

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

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

![Graphs showing anion distributions](image-url)
Li⁺-Li⁺ distributions

Li⁺ …. Li⁺ 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][BF₄]
- $x_{Li^+} = 0.05$
- $x_{Li^+} = 0.20$
- $x_{Li^+} = 0.33$
Li$^+/\text{Anion bonding structures}$

- 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)

248th ACS National Meeting | August 10-14, 2014 | San Francisco, CA
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>$\rho$ (kg/m$^3$)</td>
<td>1421.5</td>
<td>1367.9</td>
<td>1296.9</td>
</tr>
<tr>
<td>$D^+$ (m/s)</td>
<td>0.097</td>
<td>0.118</td>
<td>0.326</td>
</tr>
<tr>
<td>$D^-$ (m/s)</td>
<td>0.081</td>
<td>0.121</td>
<td>0.228</td>
</tr>
<tr>
<td>$D^{Li}$ (m/s)</td>
<td>0.046</td>
<td>0.069</td>
<td>0.101</td>
</tr>
<tr>
<td>$\mu$ (cP)</td>
<td>150</td>
<td>89</td>
<td>107</td>
</tr>
<tr>
<td>$\lambda$ (mS/cm)</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 $\sim$1%
  - diffusion within 10-25%
  - conductivity within 10-20%
Comparison of room-T Li transport

- $T = 298$ K properties computationally expensive ($\sim 200$ 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[BF$_4$]

Li[TFSI]
Li⁺/Anion residence times

- Longer residence times at higher Li-doping levels
- Times follow [TFSI] > [BF₄] > [FSI]
Contribution of anion exchange to diffusion

<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>$D_{\text{bax}}^{\text{Li}^+}/D_{\text{Li}^+}^{\text{Li}^+}$</td>
<td>$D_{\text{bax}}^{\text{Li}^+}/D_{\text{Li}^+}^{\text{Li}^+}$</td>
<td>$D_{\text{bax}}^{\text{Li}^+}/D_{\text{Li}^+}^{\text{Li}^+}$</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

(a) Density as a function of temperature ($T$) for various lithium salts.

(b) Density as a function of mol fraction of lithium salts ($x_{Li^+}$).
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][BF₄]
- $x_{Li^+} = 0.10$
- $x_{Li^+} = 0.10$ (exp)
- $x_{Li^+} = 0.00$
- $x_{Li^+} = 0.00$ (exp)

[pyr3][FSI]
- $x_{Li^+} = 0.10$
- $x_{Li^+} = 0.00$
- $x_{Li^+} = 0.00$ (exp)
Ionic conductivity

[pyr14][TFSI]

[EMIM][BF₄]

[pyr13][FSI]