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)
  $$ U^{RD} = \sum_{i<j} \left( A_{ij} \exp(-B_{ij} r_{ij}) - C_{ij} r_{ij}^{-6} \right) $$
  $$ U^{ES} = \sum_{i<j} \left( \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} \right) - \frac{1}{2} \sum_i \bar{\mu} \cdot \vec{E}_i^0 $$
- 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-prolylpyrrolidinium\(^+\)
- [EMIM]\(^+\) 1-methyl-3-ethylimidazolium\(^+\)
- [TFSI]\(^-\) bis(trifluoromethylsulfonyl)imide
- [FSI]\(^-\) bis(fluorosulfonyl)imide
- [BF$_4$]\(^-\) boron tetrafluoride
Influence of Li$^+$-doping on anion distributions

Small anion separation around Li$^+$
Li\(^+\)-Li\(^+\) distributions

Li\(^+\) .... Li\(^+\) clustering at low-r and high doping levels
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

Density: $\rho$ (kg/m$^3$) | Diffusion: D (1e-10 m$^2$/s) | Viscosity: $\mu$ (cP) | Conductivity: $\lambda$ (mS/cm)

<table>
<thead>
<tr>
<th></th>
<th>[pyr14][TFSI]</th>
<th>[pyr13][FSI]</th>
<th>[EMIM][BF$_4$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho$</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>$\mu$</td>
<td>150</td>
<td>89</td>
<td>107</td>
</tr>
<tr>
<td>$\lambda$</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

![Graph showing ionic conductivity comparison](image)

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>$x_{Li^+}$</th>
<th>([\text{pyr14}]\text{TFSI} )</th>
<th>([\text{pyr13}]\text{FSI} )</th>
<th>([\text{EMIM}]\text{BF}_4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{Li^+}^{bax}/D_{Li^+}$</td>
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<td>$D_{Li^+}^{bax}/D_{Li^+}$</td>
</tr>
<tr>
<td>$N_{\langle R \rangle}$</td>
<td>$N_{\langle R \rangle}$</td>
<td>$N_{\langle R \rangle}$</td>
<td>$N_{\langle R \rangle}$</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

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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 [BF$_4$] < [FSI] < [TFSI]
  – lithium diffusion follows [BF$_4$] > [FSI] > [TFSI]

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

(a) $\rho (\text{kg} \cdot \text{m}^{-3})$ vs. $T (\text{K})$

(b) $\rho (\text{kg} \cdot \text{m}^{-3})$ vs. $x_{\text{Li}}$ (mol fraction Li-salt)

- [pyr14][TFSI]
- [pyr13][FSI]
- [EMIM][BF$_4$]
- [pyr14][TFSI] (exp)
- [pyr13][FSI] (exp)
- [EMIM][BF$_4$] (exp)
Viscosity

[pyr14][TFSI]
- $x_\text{Li}^+ = 0.10$
- $x_\text{Li}^+ = 0.10$ (luc)
- $x_\text{Li}^+ = 0.10$ (exp)
- $x_\text{Li}^+ = 0.00$
- $x_\text{Li}^+ = 0.00$ (exp)

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

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

(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]

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Ionic conductivity

![Graphs showing ionic conductivity for different electrolytes.](image)

(a) [pyr14][TFSI]

(b) [EMIM][BF₄]

(c) [pyr13][FSI]