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

[pyr14][TFSI], [pyr13][FSI], and [EMIM][BF$_4$]

Justin B. Haskins,$^1$ William R. Bennett,$^2$ James J. Wu,$^2$
Dionne M. Hernández,$^2$ Oleg Borodin,$^3$ Joshua D. Monk,$^1$
Charles W. Bauschlicher Jr.,$^4$ John W. Lawson$^5$

$^1$ERC, Inc., NASA Ames Research Center, Moffett Field, CA 94035
$^2$Electrochemistry Branch, NASA Glenn Research Center, Cleveland, OH 44135
$^3$Electrochemistry Branch, U.S. Army Research Laboratory, Adelphi, MD 20783
$^4$Entry Systems and Technology Division, NASA Ames Research Center, Moffett Field, CA 94035
$^5$Thermal Protection Materials Branch, NASA Ames Research Center, Moffett Field, CA 94035
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)
  \[ U^{RD} = \sum_{i<j} \left( A_{ij} \exp(-B_{ij}r_{ij}) - C_{ij}r_{ij}^{-6} \right) \]
  \[ U^{ES} = \sum_{i<j} \left( \frac{q_iq_j}{4\pi\varepsilon_0r_{ij}} \right) - \frac{1}{2} \sum_i \bar{\mu} \cdot \bar{E}_i^0 \]
- 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-proylpyrrolidinium$^+$

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

[TFSI]$^-$  bis(trifluoromethylsufonyl)imide

[FSI]$^-$  bis(fluorosufonyl)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

![Graphs showing Li$^+$ clustering at low-r and high doping levels for different electrolytes: (a) [pyr13][FSI], (b) [pyr14][TFSI], and (c) [EMIM][BF$_4$].]
Li\(^+\)/Anion bonding structures

- Li-[TFSI] bonding dependence on Li-doping level
- More monodentate at high doping levels
Li\textsuperscript{+}/Anion solvation shells

- 4-5 anion neighbors in Li\textsuperscript{+} solvation shell: [TFSI] (3-4), [BF\textsubscript{4}] (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>Density: $\rho$ (kg/m$^3$)</th>
<th>Diffusion: $D$ (1e-10 m$^2$/s)</th>
<th>Viscosity: $\mu$ (cP)</th>
<th>Conductivity: $\lambda$ (mS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[pyr14][TFSI]</td>
<td>[pyr13][FSI]</td>
<td>[EMIM][BF$_4$]</td>
<td></td>
</tr>
<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>$D^\text{Li}$</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 ~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[BF$_4$]  \[\rightarrow\]  Li[TFSI]  \[\rightarrow\]  Li[BF$_4$]  \[\leftarrow\]  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>$D^{\text{Li}^+}_{\text{bax}}/D^{\text{Li}^+}$</td>
<td>$D^{\text{Li}^+}_{\text{bax}}/D^{\text{Li}^+}$</td>
<td>$D^{\text{Li}^+}_{\text{bax}}/D^{\text{Li}^+}$</td>
</tr>
<tr>
<td>0.05</td>
<td>0.69</td>
<td>0.81</td>
<td>0.89</td>
</tr>
<tr>
<td>0.10</td>
<td>0.66</td>
<td>0.85</td>
<td>1.07</td>
</tr>
<tr>
<td>0.33</td>
<td>0.59</td>
<td>0.73</td>
<td>0.91</td>
</tr>
<tr>
<td></td>
<td>4.4</td>
<td>3.7</td>
<td>6.1</td>
</tr>
<tr>
<td></td>
<td>4.2</td>
<td>2.4</td>
<td>5.8</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
Miscellaneous slides
Density

(a) Density $\rho$ in kg/m$^3$ as a function of temperature $T$ (K).
(b) Density $\rho$ in kg/m$^3$ as a function of mole fraction $x_{Li^+}$ of Li-salt.
Viscosity
Diffusion

![Graphs showing diffusion coefficients for different electrolyte solutions](image)

- [pyr14]^-  [TFSI]^-  Li^+  Li^+ (luc)
- [pyr14]^+  [TFSI]^-  0.9[pyr14][TFSI] + 0.1Li[TFSI]
- [EMIM]^+  [BF_4]^-  Li^+  Li^+ (exp)
- [EMIM]^+  [BF_4]^-  0.9[EMIM][BF_4] + 0.1Li[BF_4]
- [pyr13]^+  [FSI]^-  Li^+  0.9[pyr13][FSI] + 0.1Li[FSI]
Ionic conductivity

[Graphs showing ionic conductivity for different electrolytes as a function of temperature (1000/T in K⁻¹). Three plots are shown for different electrolytes: [pyr14][TFSI], [EMIM][BF₄], and [pyr13][FSI]. Each plot includes data points for different Li⁺ concentrations: x_{Li⁺} = 0.0, x_{Li⁺} = 0.0 (exp), x_{Li⁺} = 0.20, x_{Li⁺} = 0.18 (exp).]