MetILs: New Ionic Liquids for Flow Batteries

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Ionic Liquids (ILs) for Flow Batteries

- Higher energy density
- Negligible vapor pressure
- Non-corrosive

Ionic Liquids with Metal Cations (MetILs)

Ferrocenyl-Functionalized Imidazoliums

Zinc- and Silver-Amine Complexes


Initial Strategy to MetILs

Modify the surface of the coordination sphere with new functional groups

\[(\text{CF}_3\text{SO}_2)_2\text{N}^-\quad 2+ \quad \text{N(}\text{CF}_3\text{SO}_2)_2\]

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FY09 Activities

\[(\text{CH}_3\text{(CH}_2\text{)}_3\text{CH(C}_2\text{H}_5\text{)CO}_2\text{)}_2\text{Cu} + 6 \text{NH}_2\text{CH}_2\text{CH}_2\text{OH} \rightarrow 115^\circ\text{C, 5 min} \]

Amine Coordination

Synthesis Properties

- Scalable
- Large Versatility
- Low Cost

FY10: Synthesis of an iron ionic liquid

\[
(CF_3SO_3)_3Fe + 6 \text{NH}(CH_2CH_2OH)_2 \xrightarrow{\Delta} +3 (CF_3SO_3)^- \]

\[\sigma = 0.207 \text{ mS cm}^{-1} \]
\[\mu = 4482 \text{ cP} \]

Hydroxyl (↑) and amine bands (↑) of Fe IL are blue shifted 200 and 30 cm\(^{-1}\) relative to diethanolamine.

FY10: MetILs Family

Versatile synthesis allows one to tailor material and electrochemical properties

<table>
<thead>
<tr>
<th></th>
<th>Mn-1</th>
<th>Mn-2</th>
<th>Fe-1</th>
<th>Fe-2</th>
<th>Zn-1</th>
<th>Zn-2</th>
<th>Zn-3</th>
<th>Cu-1</th>
<th>Cu-2</th>
<th>Cu-3</th>
<th>Cu-4</th>
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<tbody>
<tr>
<td>μ [cP]</td>
<td>11671</td>
<td>760</td>
<td>6413</td>
<td>4482</td>
<td>2533</td>
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<td>σ [mS cm⁻¹]</td>
<td>624</td>
<td>0.45</td>
<td>466</td>
<td>0.21</td>
<td>0.34</td>
<td>0.10</td>
<td>439</td>
<td>0.05</td>
<td>0.01</td>
<td>0.07</td>
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<tr>
<td>Tg [°C]</td>
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<td>−82</td>
<td>−70</td>
<td>−64</td>
<td>−84</td>
<td>−55</td>
<td>−52</td>
<td>−63</td>
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<td>−53</td>
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<tr>
<td>Td [°C]</td>
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<td>290</td>
<td>260</td>
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<td>200</td>
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<td>NH</td>
<td>OH</td>
<td>OH</td>
<td>OH</td>
<td>OH</td>
<td>**</td>
<td>NH</td>
<td>OH</td>
<td>NH</td>
<td>NH</td>
</tr>
</tbody>
</table>

*OH, hydroxyl coordination, NH amine coordination **no preference
Recent work with cerium has yielded a “spider” IL with significantly lower viscosity and higher conductivity.

Experiment with new metals (Ce, V, and Co), new ligands (Im), and new anions (NTf$_2$)

Build flow battery tester designed to accommodate ILs
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