Interfacial Structure and Capacitance of Li-doped Ionic Liquid Electrolytes from Molecular Simulation

Justin B. Haskins\textsuperscript{1} and John W. Lawson\textsuperscript{2}

\textsuperscript{1}AMA, Inc., NASA Ames Research Center
\textsuperscript{2}NASA Ames Research Center
Collaborators

NASA Ames Research Center
John W. Lawson
Charles W. Bauschlicher
Justin B. Haskins
Josh D. Monk

NASA Glenn Research Center
James J. Wu
Dionne M. Hernandez
William R. Bennett
Vadim Lvovich

Army Research Center
Oleg Borodin
Green Aviation at NASA

Efficient Aircraft: NASA LEAPTech

UAVs: NASA “Greased-Lightning”

Solar-Battery Hybrid: NASA “Pathfinder”

Battery-Gas Hybrid: Boeing “SUGAR Volt”
Other requirements are rechargeable, safety, power, recharge time, cost, etc.

Major requirement is: High Energy Density
Li metal | Electrolyte | V | Li₂O₂ + ?
2Li + O₂ ↔ Li₂O₂ + ?

Li-Air Battery Chemistry

Electrolytes for Li-metal

Structural Electrolytes

Hybrid Battery/Supercapacitors
Ionic Liquid Electrolytes for Supercapacitors

Figure 1: Representation of the cations (a) and anions (b) of the three ionic liquids considered in this work: (a) N-methyl-N-butylpyrrolidinium [pyr14][TFSI], (b) N-methyl-N-proylpyrrolidinium [pyr13][FSI], and (c) 1-ethyl-3-methylimidazolium [EMIM][BF$_4$].

C (green)  
N (blue)  
S (yellow)  
O (red)  
F (purple)  
B (pink)  
H (white)

Chosen for potential use in both batteries and supercapacitors

Computational Study of Ionic liquids Electrolytes

• Classical Polarizable-MD (APPLE&P) simulation for capacitance:
  – large systems
  – constant potential electrodes
  – structural origin of capacitance
  – influence of Li-salt

• Quantum simulations for electrochemical window:
  – small liquid systems
  – density functional theory molecular dynamics simulation
  – influence of Li-salt

First all-simulation approach to supercapacitors: capacitance, operation range, and energy density

Electric Double Layer (EDL)

Two electrode simulations performed as a function of electrode voltage drop.
Ion accumulation at the surface: [pyr14][TFSI]

Figure 7: Composition of the surface ion layer, $N$, (a, c, and e) as $N$ increases in surface ion density, (b, d, and f) for ionic liquids having $x_{Li}$ values of 0.0 and 0.2. Potential is referenced to the potential of zero charge found at $\Psi = 0$ V. Data in (e) is reproduced from a previous work.

Ion depletion at high voltage

Li⁺ Influence on the EDL

Li⁺ disrupts the EDL and accumulates in 2nd layer

Li$^+$ binding at the interface: [pyr14][TFSI]

Figure 10: Representative binding of Li$^+$ with anions in the double layer at (a) negative electrode potential and (b) positive electrode potential. The red and blue bars indicate the (x,y) plane of the anode and cathode surfaces, respectively.

Li$^+$ accumulates in the second molecular layer.
Li$^+$ binding at the interface: [pyr14][TFSI]

Li$^+$ accumulates in the second molecular layer
Free energy barrier to Li$^+$ intercalation: [pyr14][TFSI]

\[ F^s = -101.6 \text{ kcal/mol} \]

Solvation free energy concurs with Li-density

Influence of Li$^+$ on capacitance

Figure 3: Differential capacitance as a function of surface potential of our three ionic liquid systems having $x_{Li}$ values of 0.0 (a,c,e) and 0.2 (b,d,f). Data in (e) is reproduced from a previous work.

Electrochemical windows (DFT-MD Liquid)

Electrochemical Windows (eV)

<table>
<thead>
<tr>
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<th>DFT (PBE)</th>
<th>DFT (HSE06)</th>
<th>Exp.</th>
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</thead>
<tbody>
<tr>
<td>[pyr14][TFSI]</td>
<td>4.6</td>
<td>6.5</td>
<td>6</td>
</tr>
<tr>
<td>[pyr13][FSI]</td>
<td>4.7</td>
<td>6.7</td>
<td>6</td>
</tr>
<tr>
<td>[EMIM][BF₄]</td>
<td>3.9</td>
<td>5.4</td>
<td>4.3</td>
</tr>
</tbody>
</table>

10 PFF-MD configurations; 24 pairs; T = 298 K

Specific energy estimate

<table>
<thead>
<tr>
<th></th>
<th>E (Wh/m²)</th>
<th>E (Wh/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[pyr14][TFSI]</td>
<td>Theory</td>
<td>0.7-1.3</td>
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<tr>
<td></td>
<td>Exp.</td>
<td>1.4-3.5</td>
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<tr>
<td>[pyr13][FSI]</td>
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<td>Exp.</td>
<td>3.5-6.8</td>
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<tr>
<td>[EMIM][BF₄]</td>
<td>Theory</td>
<td>0.5-0.9</td>
</tr>
<tr>
<td></td>
<td>Exp.</td>
<td>1.3-1.5</td>
</tr>
</tbody>
</table>

Assume specific surface area 1074 m²/g
Specific Energy = 0.5C_{sl}(EW)^2

Specific energy estimates predict experimental trends

Conclusions

- Li$^+$ disruption of the electric double layer
- Magnitude of capacitance is a weak function of Li-doping
- Capacitance profile shows variation with Li-doping
- Electrochemical stability a weak function of Li-doping
- Computed specific energy in good agreement with experiment