Ionic Liquids at Electrified Interfaces

*From Double Layers to Decomposition*

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Ionic Liquids for Electrochemical Applications

• **Advanced electrodes**: help stabilize cycling against Li-metal

• **Li-ion batteries**: possible safer alternative to organic electrolytes

• **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)

NASA Electric Aircraft
Chosen for suppression of dendrites on Li⁺ metal anodes

1) Li⁺ Solvation and Transport

2) Behavior at Charged Interfaces

3) Behavior at Reactive Interfaces

Figure 1: Energetically favorable [Li(Anion)ₙ]ⁿ⁻ clusters from B3LYP/6-31+G** computations. Displayed are clusters having (a,d,g) n = 2, (b,e,h) n = 3, and (c,f,i) n = 4 anions for (a-c) [TFSI], (d-f) [FSI], and (g-i) [BF₄]. From DFT-MD simulations of liquids, solvation shells corresponding to clusters (a), (b), (d), (e), and (i) are found to be stable at 363 K.
Quantum Chemistry:
- Single Li\(^+\) solvation structures
- Electrochemical windows
- Reaction barriers

Polarizable Molecular Dynamics (MD):
- APPLE&P
- Large-scale Li\(^+\) solvation structures
- Physical properties

Constant Potential MD:
- Double layer structure
- Capacitance

Density Functional Theory MD:
- Electrochemical window
- Reactions
Figure 1: Energetically favorable \([\text{Li(Anion)}_n]_{(n-1)}\) clusters from B3LYP/6-31+G** computations. Displayed are clusters having (a,d,g) \(n=2\), (b,e,h) \(n=3\), and (c,f,i) \(n=4\) anions for (a-c) [TFSI], (d-f) [FSI], and (g-i) [BF\(_4\)]. From DFT-MD simulations of liquids, solvation shells corresponding to clusters (a), (b), (d), (e) and (i) are found to be stable at 363 K.

1) Li\(^+\) Transport and Solvation

2) Behavior at Charged Interfaces

3) Behavior at Reactive Interfaces
Ionic Conductivity

Conductivity decreases with anion size: TFSI < FSI < BF₄
Li-doping suppresses conductivity of all systems
Highly unfavorable configurations exchange anions
2 [TFSI] coordination dominant, 3 [TFSI] possible
Figure 1: Energetically favorable \([\text{Li(Anion)}_n]_n\) clusters from B3LYP/6-31+G** computations. Displayed are clusters having \((a,d,g)\), \((b,e,h)\), and \((c,f,i)\) \(n=2\), \(n=3\), and \(n=4\) anions for (a-c) \([\text{TFSI}]^-\), (d-f) \([\text{FSI}]^-\), and (g-i) \([\text{BF}_4^-]\). From DFT-MD simulations of liquids, solvation shells corresponding to clusters (a), (b), (d), (e) and (i) are found to be stable at 363 K.

2, 3 anion Li\(^+\) solvation shells for TFSI/FSI
4 anion Li\(^+\) solvation shell for BF\(_4^-\)
Li⁺…Li⁺ Networks

Networks of Li⁺ prevalent in ionic liquids
Figure 1: Energetically favorable \([\text{Li(Anion)}^n]^-(n + 1)\) clusters from B3LYP/6-31+G** computations. Displayed are clusters having (a,d,g) \(n = 2\), (b,e,h) \(n = 3\), and (c,f,i) \(n = 4\) anions for (a-c) [TFSI], (d-f) [FSI], and (g-i) [BF4]. From DFT-MD simulations of liquids, solvation shells corresponding to clusters (a), (b), (d), (e) and (i) are found to be stable at 363 K.

1) Li⁺ Transport and Solvation

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Ionic Liquids at Electrified Interfaces

Two electrode simulations performed as a function of electrode voltage drop

$L_z = 10 \text{ nm}$
Electric Double Layer (EDL)

Detailed picture of liquid structure at the interface
Polarization opposes formation of the EDL
Interface is enriched in cations or anions
Li$^+$ disrupts the EDL and accumulates near the surface
Li$^+$ Binding in the EDL

(a) 

(b) 

Li$^+$ accumulates in the second molecular layer
Free Energy Barrier to Li$^+$ Intercalation

Large energy to move Li$^+$ to the surface
Capacitance from Fluctuations

\[ C_{\Delta \Psi} = \frac{\partial \langle \sigma \rangle}{\partial \langle \Psi \rangle} = \left[ \beta A \langle |\sigma| \delta \sigma \rangle + \left\langle \frac{\partial \sigma}{\partial \Delta \Psi} \right\rangle \right] \left[ \beta A \langle |\sigma| \delta \Psi \rangle + \left\langle \frac{\partial \Psi}{\partial \Delta \Psi} \right\rangle \right]^{-1} \]

Validated fluctuation formulas for capacitance
Electrode surface subtly influences capacitance
Li$^+$ suppresses features in the capacitance profile
Electrochemical Windows

Occupied Molecular Level

Unoccupied Molecular Levels

<table>
<thead>
<tr>
<th></th>
<th>E-window</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[pyr14][TFSI]</td>
<td>4.6-6.5 eV</td>
<td>6 eV</td>
</tr>
<tr>
<td>[EMIM][BF₄]</td>
<td>3.9-5.4 eV</td>
<td>4.3 eV</td>
</tr>
<tr>
<td>[pyr13][FSI]</td>
<td>4.7-6.7 eV</td>
<td>4.3-6 eV</td>
</tr>
</tbody>
</table>

Bound the electrochemical window of liquids with pure and hybrid functionals
### Specific Energy Estimates

<table>
<thead>
<tr>
<th></th>
<th>E (Wh/m²)</th>
<th>E (Wh/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[pyr14][TFSI] Theory</td>
<td>0.7-1.3</td>
<td>0.8-1.4</td>
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<tr>
<td>Exp.</td>
<td>1.4-3.5</td>
<td>1.5-3.8</td>
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</tr>
<tr>
<td>Exp.</td>
<td>3.5-6.8</td>
<td>3.8-7.3</td>
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<tr>
<td>[EMIM][BF₄] Theory</td>
<td>0.5-0.9</td>
<td>0.5-1.0</td>
</tr>
<tr>
<td>Exp.</td>
<td>1.3-1.5</td>
<td>1.4-1.6</td>
</tr>
</tbody>
</table>

Assume specific surface area 1074 m²/g

[pyr13][FSI] highest energy from both experiment and theory
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Evaluation of Decomposition

Surface layers (mossy vs waxy) have dramatic effect on cycling performance
LUMO level is shared by both anions of the ionic liquid pair. Vacuum level alignment indicates the liquids are stable.
Ion levels mix with surface levels when near the surface.
Dynamics show that [TFSI]⁻ readily decomposes
[TFSI]- Decomposition Products

LiF, Li_2O, -CF_3, -SO_2, and –NSO_2CF_3 groups are generated.
XPS Analysis of Etched Surface Layer

LiF, Li₂O, -CF₃, -SO₂, and -NSO₂CF₃ products match XPS results

Bulk Interface Reactions

Bulk systems examined to examine other possible reactions
Bulk Interface Reactions

[pyr14][TFSI]

1. #1 - 9ps
2. #2 - 11.2ps

[EMIM][BF₄]

1. #1 - initial
2. #1 - 5ps

Product profile similar to single pair simulations
Cation Decomposition Barriers

All examined decompositions favorable except aromatic ring breaking in [EMIM]
Anion Decomposition Barriers

ΔG  = -87.4  
ΔG*= 10.1

ΔG  = -97.2  
ΔG*=  0.2

ΔG  = -5.3  
ΔG*= 18.0

ΔG  = -14.0  
ΔG*= 16.7

All reactions favorable, more Li⁺ reduce the reaction barrier
Conclusions

- Ionic conductivity a direct function of Li\(^+\) solvation structure and network formation
- Capacitor energetics governed primarily by voltage window
- Electric double layer impedes Li\(^+\) diffusion to the electrode surface
- All ions are found to decompose in the presence of Li-metal in reductive processes
- Differences in the solid electrolyte interphases can be traced to the reactants
  
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