Ionic Liquids as Electrolytes
Ionic Liquids as Electrolytes

What do IL’s offer as Electrolytes?

„being an electrically conductive liquid without any solvents !“

- non-flammable liquid with broad liquid range
- no vapour pressure
- high electric conductivity
- high electrochemical stability
- good compatibility with electrode materials
Ionic Liquids as Electrolytes

Options for Ionic Liquid as Electrolytes

- **BF$_4^-$**
- **PF$_6^-$**
- **SCN**
- **DCA**
- **N$_3$C-CN$^-$**
- **TCM**
- **RMIM**
- **F$_3$C-SO$_2$-N-SO$_2$-CF$_3$**
- **FSI** (SOLVIONIC)
- **F-SO$_2$-N-SO$_2$-F** (SOLVIONIC)
- **RM PYR**
- **RM PIP**
# Ionic Liquids as Electrolytes

## Conductivity vs. Electrochemical Stability

<table>
<thead>
<tr>
<th>Ionic Liquid</th>
<th>Conductivity (mS/cm)</th>
<th>E (V)</th>
<th>E&lt;sub&gt;ox&lt;/sub&gt; (V)</th>
<th>E&lt;sub&gt;red&lt;/sub&gt; (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EMIM PF6</td>
<td>5</td>
<td>4,2</td>
<td>-2,2</td>
<td>2,0</td>
</tr>
<tr>
<td>EMIM BF4</td>
<td>11</td>
<td>4,3</td>
<td>-2,2</td>
<td>2,1</td>
</tr>
<tr>
<td>EMIM SCN</td>
<td>22</td>
<td>3,2</td>
<td>-2,2</td>
<td>0,9</td>
</tr>
<tr>
<td>EMIM DCA</td>
<td>28</td>
<td>3,2</td>
<td>-2,2</td>
<td>1,0</td>
</tr>
<tr>
<td>EMIM TCM</td>
<td>15</td>
<td>3,0</td>
<td>-2,2</td>
<td>0,8</td>
</tr>
<tr>
<td>EMIM TCB *)</td>
<td>13</td>
<td>4,5</td>
<td>-2,2</td>
<td>2,3</td>
</tr>
<tr>
<td>EMIM TFSI</td>
<td>9</td>
<td>4,7</td>
<td>-2,2</td>
<td>2,5</td>
</tr>
<tr>
<td>EMIM OTf</td>
<td>8</td>
<td>4,1</td>
<td>-2,2</td>
<td>1,9</td>
</tr>
<tr>
<td>EMIM FSI **)</td>
<td>18</td>
<td>4,4</td>
<td>-2,2</td>
<td>2,2</td>
</tr>
<tr>
<td>EMIM FAP *)</td>
<td>4</td>
<td>5,2</td>
<td>-2,2</td>
<td>3,0</td>
</tr>
<tr>
<td>MP PYR TFSI **)</td>
<td>4</td>
<td>5,5</td>
<td>-3,4</td>
<td>2,1</td>
</tr>
<tr>
<td>MP PIP TFSI **)</td>
<td>1,5</td>
<td>5,5</td>
<td>-3,4</td>
<td>2,1</td>
</tr>
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<td>MP PYR FSI **)</td>
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<td>MP PIP FSI **)</td>
<td>4</td>
<td>5,5</td>
<td>-3,3</td>
<td>2,2</td>
</tr>
</tbody>
</table>

*) product of MERCK  
**) product of SOLVIONIC
**Ionic Liquids as Electrolytes**

**BASIONICS™: BASF's Standard IL-Portfolio**

These products are regularly produced @ BASF in high quality and 100 kg's to tons quantities.

<table>
<thead>
<tr>
<th>Ionic Liquid</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>EMIM Chloride x AlCl₃</td>
<td>Aluminium Plating processes</td>
</tr>
<tr>
<td>EMIM Tetrafluoroborate</td>
<td>SuperCapacitors</td>
</tr>
<tr>
<td>ETA Tetrafluoroborate</td>
<td>SuperCapacitors</td>
</tr>
<tr>
<td>RMIM Iodides</td>
<td>Dye Sensitized Solar Cells</td>
</tr>
<tr>
<td>EMIM Triflate</td>
<td>all electrochemical applications</td>
</tr>
<tr>
<td>EMIM Thiocyanate</td>
<td>all electrochemical applications</td>
</tr>
<tr>
<td>EMIM TFSI *)</td>
<td>low viscosity, hydrophobic</td>
</tr>
</tbody>
</table>

*) TFSI = bis(trifluoromethanesulfonyl)imide
Ionic Liquids as Electrolytes

Li⁺ Batteries

**major components**
- anode (e.g. graphite)
- cathode (e.g. LiCoO₂)
- separator
- electrolyte (e.g. LiPF₆, IL)
- solvent (e.g. carbonates, IL)

**advantages**
- high energy density
- high voltage (3.6-3.8 V)
- high efficiency
Ionic Liquids as Electrolytes

Ionic Liquids for Li⁺ Batteries

$\text{RMIM X}$

$X = \begin{align*}
\text{TFSI} & \quad \text{bis(trifluoromethanesulfonyl)imide} \\
\text{FSI} & \quad \text{bis(fluorosulfonyl)imide} \\
\text{TCB} & \quad \text{tetracyanoborate}
\end{align*}$

$R = \text{Me, Et, Pr, Bu}$
Ionic Liquids as Electrolytes

Ionic Liquids for Li⁺ Batteries

pro‘s & con‘s

- non-flammable
- high electrochem. stability
- cost / performance ratio
- limited Li⁺ transport efficiency

Trends in R&D

- new electrode materials
  (esp. lithium cathode)
- new solvents
  (esp. carbonates)
**Ionic Liquids as Electrolytes**

**Dye Solar Cells ("Graetzel-Cells")**

**major components**

- TiO$_2$
- dye
- IL-based electrolyte
- counter electrode (e.g. PEN with ITO layer)

*M. Grätzel et al., Nature 1991, 353, 737 – 740*
Ionic Liquids as Electrolytes

Dye Solar Cells (“Graetzel-Cells”)

**Major components**
- TiO₂
- dye
- IL-based electrolyte
- counter electrode (e.g. PEN with ITO layer)

**Advantages**
- lower costs (target <0.50$/Wp)
- higher efficiency @ low light
- colour (decorative appl.)
Ionic Liquids as Electrolytes

Ionic Liquids for Dye Solar Cells

\[ \text{RMIM I} \]

\[ \text{RMIM X} \]

\[ R = \text{Me, Et, Pr, Bu} \]

\[ X = \text{e.g. TFSI, FSI, TCB} \]
Ionic Liquids as Electrolytes

Ionic Liquids in Dye Solar Cells

pro’s & con’s

+ enabling technology

? longevity

- potential risk for leakages

trends in R&D

new dyes
polymer electrolytes
alternative Redox systems
cheaper electrode materials
Ionic Liquids as Electrolytes

SuperCapacitors

EDLC = Electric Double Layer Capacitor

**major components**
- nanoporous electrodes (e.g. activated charcoal)
- separator
- electrolyte (NH$_4^+$, IL, BF$_4^-$)
- solvent (e.g. carbonates, acrylonitrile)

**advantages**
- high power density
- small volume
- high rates of charge/discharge
Ionic Liquids as Electrolytes

Ionic Liquids for SuperCapacitors

EDLC = Electric Double Layer Capacitor

ETA BF₄

with solvents (e.g. carbonates)

RMIM BF₄

R = Me, Et, Pr, Bu

without solvents
Ionic Liquids as Electrolytes

Ionic Liquids for SuperCapacitors

EDLC = Electric Double Layer Capacitor

pro’s & con’s

- high thermal stability
- low temperature performance
- operating voltage
- cost / performance ratio

EDLC = Electric Double Layer Capacitor

new electrode materials
(e.g. carbon nanotubes)

new solvents
(esp. carbonates)

Trends in R&D
Ionic Liquids as Electrolytes

Aluminium Plating

major components
- Aluminium anode
- inert cathode + substrate
- electrolyte (RMIM X & AlCl₃)
- additives

advantages
- non flammable electrolyte
- higher deposition rate
- overall lower costs
**Ionic Liquids as Electrolytes**

**Effect of additives on the deposition process**

**EMIMCl \times 1.5 \text{AlCl}_3**

- dendritic, not dense Al-deposits
- poor adhesion
- poor finish

**EMIMCl \times 1.5 \text{AlCl}_3 \text{ plus additive}**

- dendrite-free, dense Al-layer
- excellent adhesion
- bright finish
Ionic Liquids as Electrolytes

Process scheme – Alu Plating from IL’s

- [Image of process diagram]

- Low loss of IL!
Ionic Liquids as Electrolytes: How to get there?

IL’s are very valuable tools in developing electrolytes for electrochemical processes "being solid and liquid at the same time and additionally offering conductivity"

-the properties of IL’s are a strong function of the ions "design of properties by structural variation"

each electrochemical device needs customized electrolytes (esp. for the optimization of processes at the electroldes) "application specific IL electrolytes"