Low-flammable electrolytes with Fluoroethylene carbonate based solvents and LiTFSI for safer Li-ion batteries

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Motivation
Battery explosion

„at a crossroads burns a Tesla Model S“
2013, Washington, USA
The fire had arisen in the damaged battery module in this e-car.

„explosion of E-Bike-accu triggered parking garage fire“
2017, Hannover, Deutschland
The reason of the fierce fire was an exploded electric bike battery.

„worldwide sales stop and exchange recall for Samsung Galaxy Note 7“
2016
An ambitious design of the battery modules in the phone, led to the short circuit.
Motivation
Battery explosion

- Safety during production, transport and storage
- Balance of safety & performance under usage conditions
- Risk under control (cooling system, flame retardant)

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Strategies @ electrolyte
low-/non-flammable and fire-extinguisher

- Low-/non-flammable electrolytes achieved...
  - By changing chemicals:
    substitution by solvents of high boiling/flash point and thermal stabil.
    → Fluorinated linear/cycling carbonates [1, 2]
    → high thermal stabil linear carbonates [1],
    → non-carbonate organic solvents (e.g. sulfone [3,4], adiponitril [5])
    → Water-based electrolytes [6]
  - By changing phase state:
    low-volatile, low-flammable gels or solid states
    → anorganic fillers (e.g. Al$_2$O$_3$, SiO$_2$ etc.)
    → ionic liquids
    → glass electrolyte [7]

[1] Z. Wang, A. Hofmann, T. Hanemann., Low-flammable electrolytes with fluoroethylene carbonate based solvent mixtures and lithium bis(trifluoromethanesulfonyl) imide for lithium-ion batteries, in review progress
Strategies @ electrolyte
low-/non-flammable and fire-extinguisher

- Fire-extinguishing achieved…
  - By adding flame retardant (FR):
    thermal shielding, evolution of gas phase, radical quenching

  ➔ Additives [8]
  e.g. tris(2,2,2-trifluoroethyl)phosphate (TFP), tris(2,2,2-trifluoroethyl)phosphite (TTFPi),
  bis(2,2,2 trifluoroethyl)methylphosphonate (TFMP),
  (ethoxy)pentafluorocyclotriphosphazene (PFPN) and
  (phenoxy)pentafluoro-cyclotriphosphazene (FPPN)

  ➔ FR-based electrolytes [9, 10]
  ➔ Intergration of FR with separator [11]

- By Battery System Management (BMS): thermal management, thermal runaway

[10] Z. Zeng et al., Non-flammable electrolytes with high salt-to-solvent ratios for Li-ion and Li-metal batteries, Nature Energy 3, 2018: 674-681
Composition

ELECTROLYTES

Lithium salt, solvent
„Salt-in-solvent“ Electrolyte
Salt, solvent

- Thermal stable Li-salt dissolved in carbonate-based high boiling solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>EC</th>
<th>PC</th>
<th>1,2-BC</th>
<th>FEC</th>
<th>DBC</th>
<th>DPrC</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>EM-0</th>
<th>EM-1</th>
<th>EM-2</th>
<th>EM-3</th>
<th>EM-4</th>
<th>EM-5</th>
<th>EM-6</th>
</tr>
</thead>
<tbody>
<tr>
<td>solvents (1:1 molar ratio)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EC</td>
<td></td>
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<tr>
<td>DMC</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>conducting salt</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiPF₆</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Concentration, [mol kg⁻¹]</td>
<td>0.771</td>
<td>0.75</td>
<td>0.75</td>
<td>0.75</td>
<td>0.75</td>
<td>0.75</td>
<td>0.75</td>
</tr>
</tbody>
</table>

reference Sample: LP30

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Physicochemical analysis

ELECTROLYTES

Density, phase transition, viscosity, ionic conductivity
Physicochemical Properties

**thermal, density, rheological, ion-conductive**

- Sufficient boiling point and High flash point $T_f/°C$

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Flash point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EM-0</td>
<td>25</td>
</tr>
<tr>
<td>EM-1</td>
<td></td>
</tr>
<tr>
<td>EM-2</td>
<td></td>
</tr>
<tr>
<td>EM-3</td>
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<td>EM-4</td>
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<td>EM-5</td>
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<tr>
<td>EM-6</td>
<td></td>
</tr>
</tbody>
</table>

- The flash point $T_f$ correlated with the temperature when the electrolyte burns on, after contact to a flame source (e.g. electrical spark, hot surface and external flame)
- Influenced by boiling point and flammability
- Safety improvement

aim at "prevention" rather than "rescue" (e.g. by flame retardants)
Physicochemical Properties

**thermal, density, rheological, ion-conductive**

**Balance between safety issue and the basic properties**

**Viscosity \( \eta \)**
- \( \eta = \eta_0 \times \exp \left[ \frac{B}{(T - T_0)} \right] \)
  Fitted by VFTH equation
- \( \eta = \eta_0 \times \exp \left[ \frac{E_a}{RT} \right] \)
  Arrhenius-like equation
- Activation energy \( E_a \) : potential barrier for molecule-ion movement
- „Strong“ and „fragile“ *
  Structured coordination

**DSC**
- Glass-forming ability and lower \( T_g \)
- Large polarizable anion \( \text{TFSI}^- \) and flexible \( S-N-S \) bond

**Ionic conductivity \( \Lambda \)**
- \( \Lambda = \Lambda_0 \times \exp \left[ \frac{C}{(T - T_2)} \right] \)
  Fitted by VFTH equation
- \( \text{Li}^+ \) diffusion across electrolyte

**Melting point \( T_m \)**
- Application temperature-range

**Relationship between structure and ion transport**
- by Walden rule
  \( \Lambda \times \eta^\alpha = C \)

* C.A. Angell, Formation of glasses from liquids and biopolymers

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Electrochemical aspects

ELECTROLYTES

Li vs. Pt, Li vs. Al, Li vs. NMC, Graphite vs. NMC (coin and pouchbag cells)
Electrochemical stability
Li vs. Pt (cyclovoltammetry)

- Gentle / sharp rise of current density (kinetic) Electrolyte degradation;
  Different oxidative stability of components (e.g. benzyl in EM-5);

- sufficient potential $E_{\text{ox}} \geq 4.2 \, \text{V}$ versus Li/Li$^+$
  electrochemical windows;

- Peak-current (at 6 V)
  lower value
  $\Rightarrow$ Plating of resistive interface layer at inactive Pt surface;

Higher value (e.g. EM-1)
  $\Rightarrow$ insufficient decomposition when only FEC included

Periodical cycling
- 3 – 6 V
- Scan rate: $\pm 1 \, \text{mV/s}$
- $@ 25^\circ \text{C}$
- Current density $j / \text{mA cm}^{-2}$ vs. $E / \text{V}$

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<td>solvents</td>
<td>EC</td>
<td>FEC</td>
<td>FEC EC</td>
<td>FEC PC</td>
<td>FEC 1,2-BC</td>
<td>FEC DBC</td>
<td>FEC DPrC</td>
</tr>
<tr>
<td>$E_{\text{ox}}$, Li</td>
<td>Pt [V] $^*$</td>
<td>4.7</td>
<td>5.0</td>
<td>5.1</td>
<td>4.7</td>
<td>4.8</td>
<td>4.2</td>
</tr>
</tbody>
</table>

$^*$ The oxidative potentials are taken at a maximum anodic current density value of $j = 0.4 \, \text{mA cm}^{-2}$ in case of first half scan from 3-6V.
Anodic dissolution

**Li vs. Al**

- Aluminum (Al) as current collector of cathode materials
- Periodical cycling (**100 cycles**)
  - 2.5 – 4.5 V
  - Scan rate: ± 1 mV/s
  - @ 25°C
  - j/mA cm$^{-2}$ vs. E /V

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**Al-corrosion process**

absorption of **TFSI- anions** on surface of Al foil and depletion of native passivated Al$_2$O$_3$

- Distributed corrosion pits of Al foils after cycling
- Post-cycling examination of cycled Al foils

- **re-passivation** at Al surface
- suppression of corrosion

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**Post-cycling examination of cycled Al foils**

- Al-Folie
- Li
- Separator

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Half-cell cycling

\( \text{Li} \) vs. \( \text{NMC111} \) (\( \text{LiN}_{\frac{1}{3}}\text{Mn}_{\frac{1}{3}}\text{Co}_{\frac{1}{3}}\text{O}_2 \))

**Periodical cycling**

- Coin cell (CR2032)
- \( 3 – 4.3 \) V
- Current: \( 0.2 \) C up to \( 3 \) C
- \( @ 25°C \)
- Discharge capacity /m\( \text{Ah g}^{-1} \) vs. Cycle numbers

**Discharge capacity fading**

- C-rate dependent
  - \( >1\text{C} \): capacity significantly smaller than \( \text{EM-0} \)
- Capacity retention
  - \textit{Influence of electrolyte on the cathode}

**Influence of electrolyte on the cathode**

- \( \text{EM-1 (FEC)} \): stable and uniform LiF-rich SEI film and less dead Li
- \( \text{EM-2 (EC/FEC) & EM-3 (PC/FEC)} \): aluminum dissolution
- \( \text{EM-5 (DBC/FEC)} \): higher viscosity destruction of cathode (peeling off from collector)

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Selection criteria of better electrolyte balance between different properties

- EM-1 (FEC)
- EM-2 (FEC/EC)
- EM-3 (FEC/PC)
- EM-4 (FEC/1,2-BC)
- EM-5 (FEC/DBC)
- EM-6 (FEC/DPrC)
- EM-0 (reference sample)

- flash point
- electrochemical stability
- Anodic Korrosion
- Half-cell performance
- viscosity, ionic conductivity

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Full-cell cycling

Graphite vs. NMC (coin cell)

Additive (SEI-layer „enabler“, Al „protector“)
- LiBOB (1wt.%)  
- LiDFOB (1wt.%)  
- VC (1wt.%)  

Periodical cycling (CR2032)
- 3 – 4.2 V  
- Current: 0.1 C up to 4 C  
- @ 25°C  
- Discharge capacity /mA cm⁻² vs. Cycle numbers

- Capacity retention (from 0.2 C to 0.5C)
  EM-0: 91.8%  
  EM-4: 93.5%  

- Capacity retention (from 0.5 C to 1C)
  EM-0: 93.1%  
  EM-4: 86.2%  
  ⇒ the absence of sufficient lithium ions supplied to the electrode surface, related to the metallic lithium deposition on the anode

- Capacity retention (cycling history)
  Decreased slightly (<1%)  
  ⇒ Growth of resistive layers, thus clogged graphite pores consumed some Li

- sealing of the coin cell
  water and O₂ content
Full-cell cycling

Graphite vs. NMC (pouch-bag cell)

- Capacity retention (after 200 cycles)
  - Middle-high range (10 Hz ~ 50 kHz)

Two semicircles:
1. resistance of SEI layer
   ⇒ EM-0: lower; slighter/fewer growth of interface layer
2. electronic conductivity of electrode components
   ⇒ EM-4: slower increasing of real part

Middle range (< 50 mHz ~ 10 Hz):
Li+ ions transfer resistance at the interface
⇒ EM-0: lower,
⇒ EM-4: plating of metallic Li

Electrolyte degradation
⇒ Resistive layer on/within graphite electrode blocking the re-fresh pores for Li-intercalation
Lithium depletion
⇒ Growth of SEI layer

Frequency-dependent impedance
- Measured every 25 or 100 cycles of pouch-bag cells
- Interface evolution
- Influence of cycled (de)insertion and electrochemical processes

Capacity / mAh g⁻¹

Cycle number

EM-0: 92.0 %
EM-4: 94.5 %

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London
17 11.09.2018
Conclusion

Outlook

- **Safe carbonate-based electrolyte**
  - High boiling point and significantly higher flash point (than reference LP30)

- **Systematic measurement and analysis**
  - Physicochemical: Density, DSC, viscosity, ionic conductivity
  - Electrochemical: cyclovoltammetry, anodic dissolution
  - Ion-molecule interaction
  - Influence of carbonate structures on properties
  - Anti-corrosion protection by using simply additive

- **Cell performance**
  - Half-cell (Li vs. NMC) and full-cell (Graphite vs. NMC)
  - Influence of components on the C-rate dependence and capacity retention

- **Outlook**
  - Other novel salts and solvents of different structures
  - Analysis of resistive interface layer
Thank you for your attention!

Acknowledgement
Dr. Andreas Hofmann, Prof. Dr. Thomas Hanemann