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Institut für Angewandte Materialien

Novel electrolytes for lithium-ion cells with improved safety characteristics

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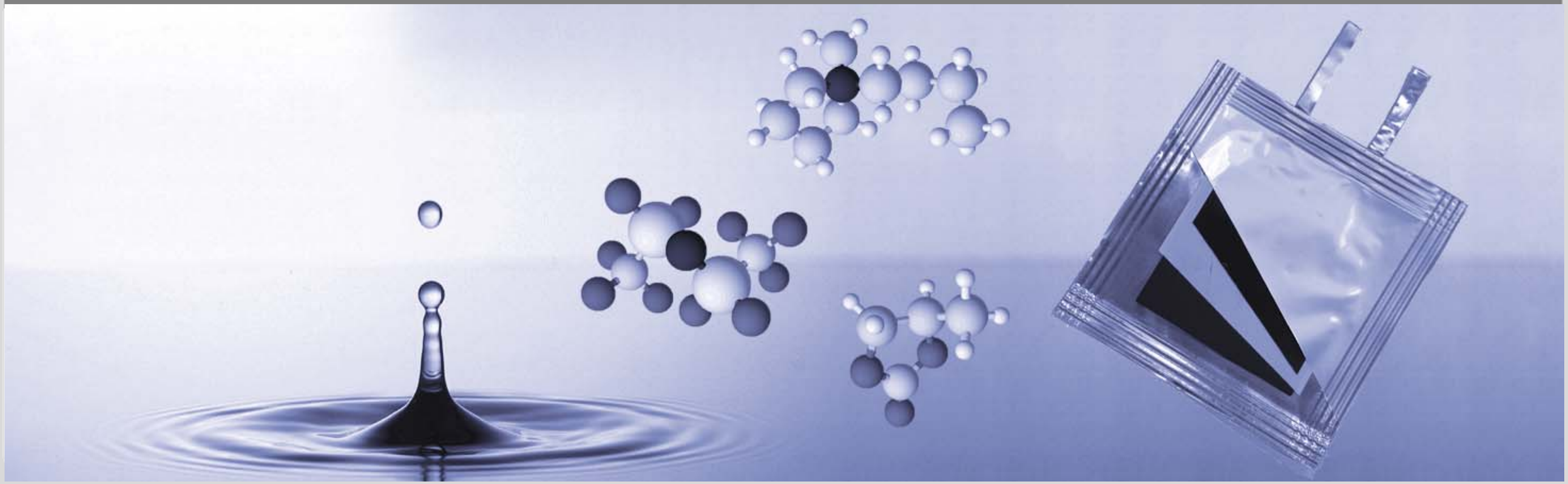


Outline

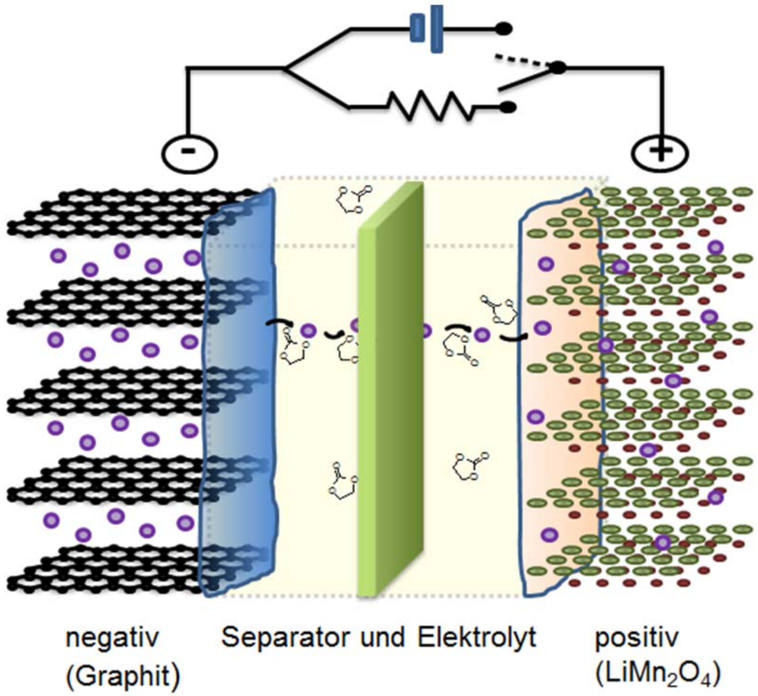
- Electrolytes in Li-ion cells
- Development of electrolyte with high flash points
- Cell tests against commercial electrode materials

Electrolytes for Li-ion cells: basics

"*Chemical compounds which are able to form ionic crystals in solid state and are composed of ions under liquid or molten conditions or when dissolved in a solvent.*

lithium salt + matrix + additives

- Enable the lithium transport through the cell
- Basis for the current flow
- Solid electrolyte interface
- Interact with all parts inside the cell



Electrolytes for Li-ion cells: requirements

- Nonflammable liquid electrolytes with adequate Li ion conductivity
- Inherent safety
- Infinite cycling
- Low cost
- Non-toxic salts and solvents
- Improved low-temperature performance
- Effective redox shuttles for overcharge protection
- Electrolyte additives for effective SEI layer formation
- Stable ionic liquids and solid polymer electrolytes with acceptable conductivity

Electrolytes in Li-ion cells: state of the art

State of the art:

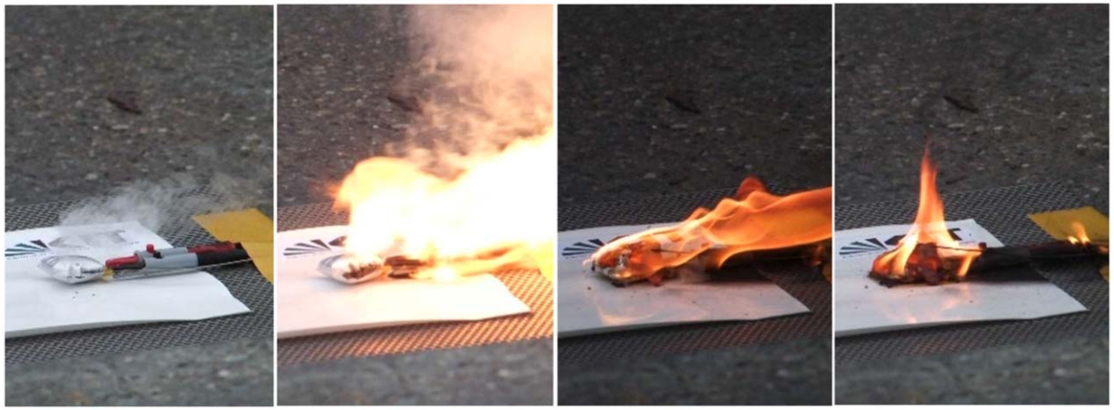
- Carbonate-based electrolytes (z.B. EC/DMC + 1M $LiPF_6$)
- Gel polymer electrolytes with liquids (carbonate based)

Composition:

- Mixture of organic carbonates
- $LiPF_6$ (1 mol/l)
- Additives

Properties:

- Stable up to 4.2 V vs. Li/Li^+
- Highly flammable (flash point EC/DMC: 24°C)
- Temperatures up to 60 °C



Electrolytes for Li-ion cells: research

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- Replacement of $LiPF_6$
- Use of electrolytes
  - New electrolytes for new electrode materials
  - Electrolyte uptake
  - Range of temperature
  - Intercalation of solvents (graphite)
- Electrolytes for high voltage applications
  - New solvents at $E > 4.2 – 4.5$ V vs. Li/Li^+
  - Electrolyte decomposition, gas formation
- Safety issues
  - High toxicity of $LiPF_6$
  - Intrinsic fire safety
  - Reduce of leakage

$LiPF_6$

Dimethylcarbonat

Interaction of the electrolyte with all parts inside the cell

Li-ion cell improvement by additives (≤ 5 wt.-%)

- Possibility to improve the lithium cell properties with only few percentage of material:
  - Forming and protection of the solid electrolyte interface (SEI)
  - Overcharging protection by redox shuttle additives
  - Additives as flame retardants
  - Improve of the wetting characteristics and electrolyte filling
  - Increase of battery performance and lifetime
  - Water protection of the electrolyte
- Difficult to increase the lithium mobility in liquid electrolytes based on limiting factors caused by the solvent mixture (viscosity)
- Under development:
  - Replacement of toxic additives
  - Novel concepts for cell safety


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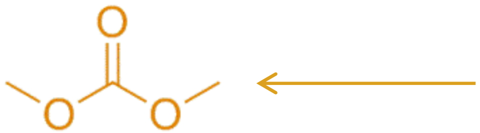
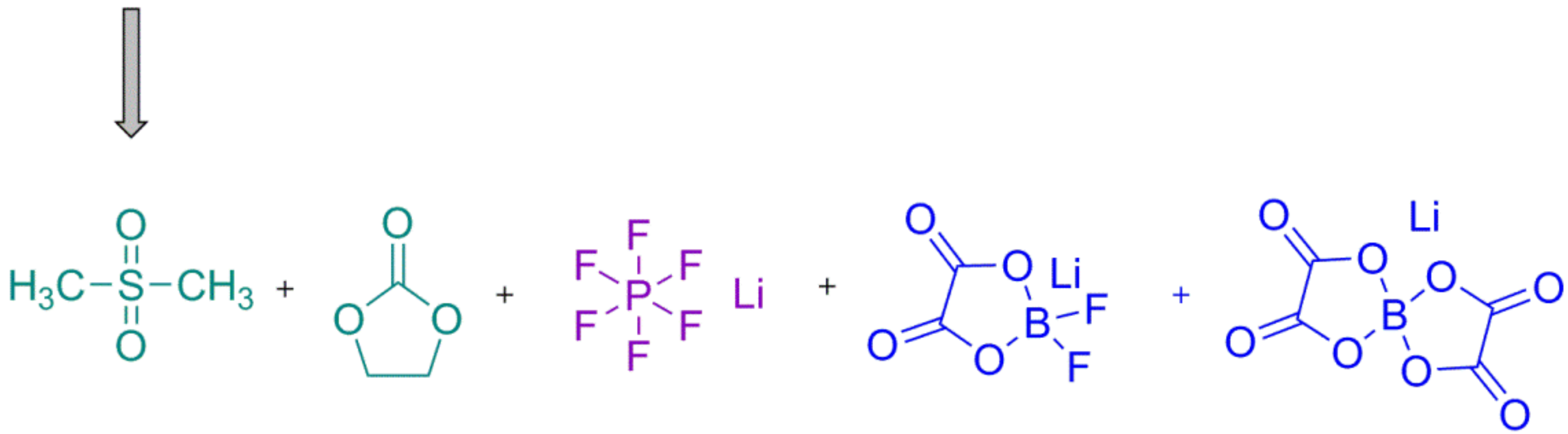
* http://www.ecta-gmbh.de/images/masterbatches.png

Electrolyte formulation

- **Solvent composition**:
  Ethylene carbonate, Dimethyl sulfone
- **Conducting salt**:
  $LiPF_6$, $LiBF_4$, Lithium bis(trifluoromethanesulfonyl)azanide (LiTFSA)
- **Additives**:
  Lithium bis(oxalato)borate (LiBOB), Lithium difluoro(oxalato)borate (LiDFOB)



Replacement of volatile dimethyl carbonate



Physicochemical properties of the electrolytes

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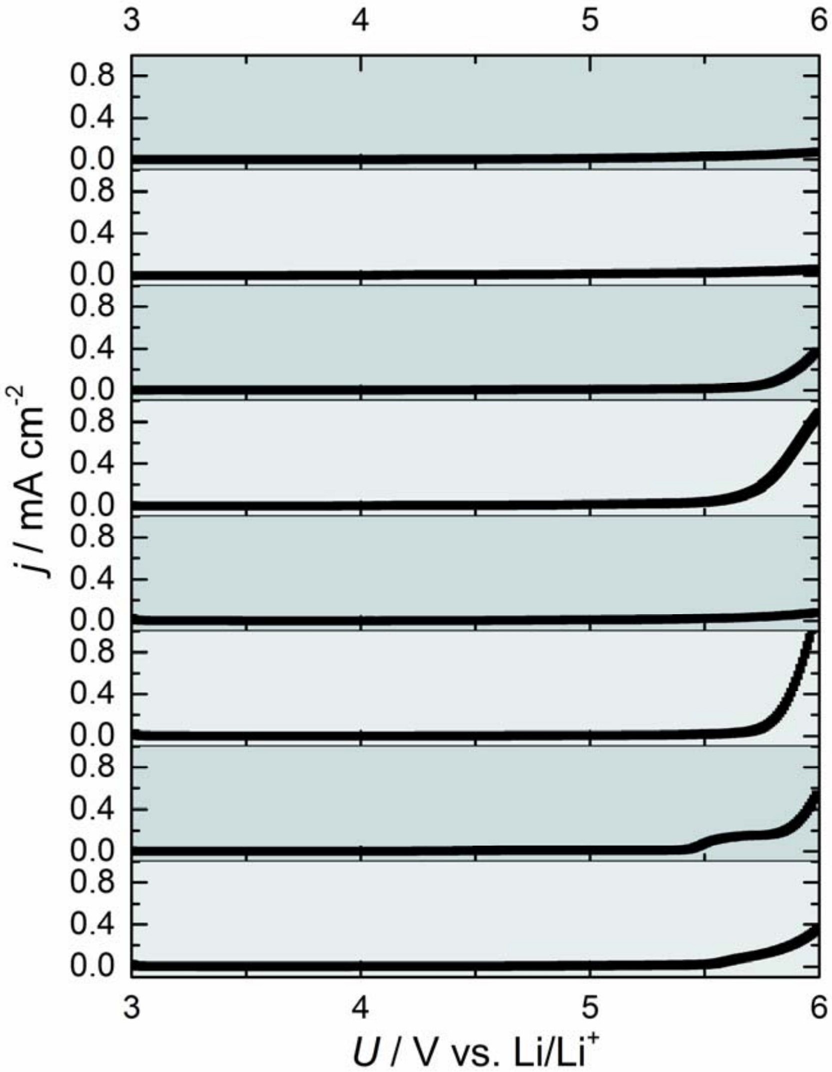
- **Liquid** at room temperature (freezing point (DSC) ~ -15 °C)
- **Liquid** in Li-ion cell down to 0 – 5 °C
- Increase of **flash points** of novel solvent mixture from

  24 °C (ethylene carbonat/dimethyl carbonate)

  to 142 °C (ethylene carbonate/dimethyl sulfone)
- **Density values** of the mixtures (25 °C): 1.3 – 1.4 g·cm^{-3}
- **Viscosity values** at 20 °C: 11 – 20 mPa·s in dependence of the conducting salt
- Fast **wettability** of ceramic coated separators (contact angle of < 20° within 5 minutes)

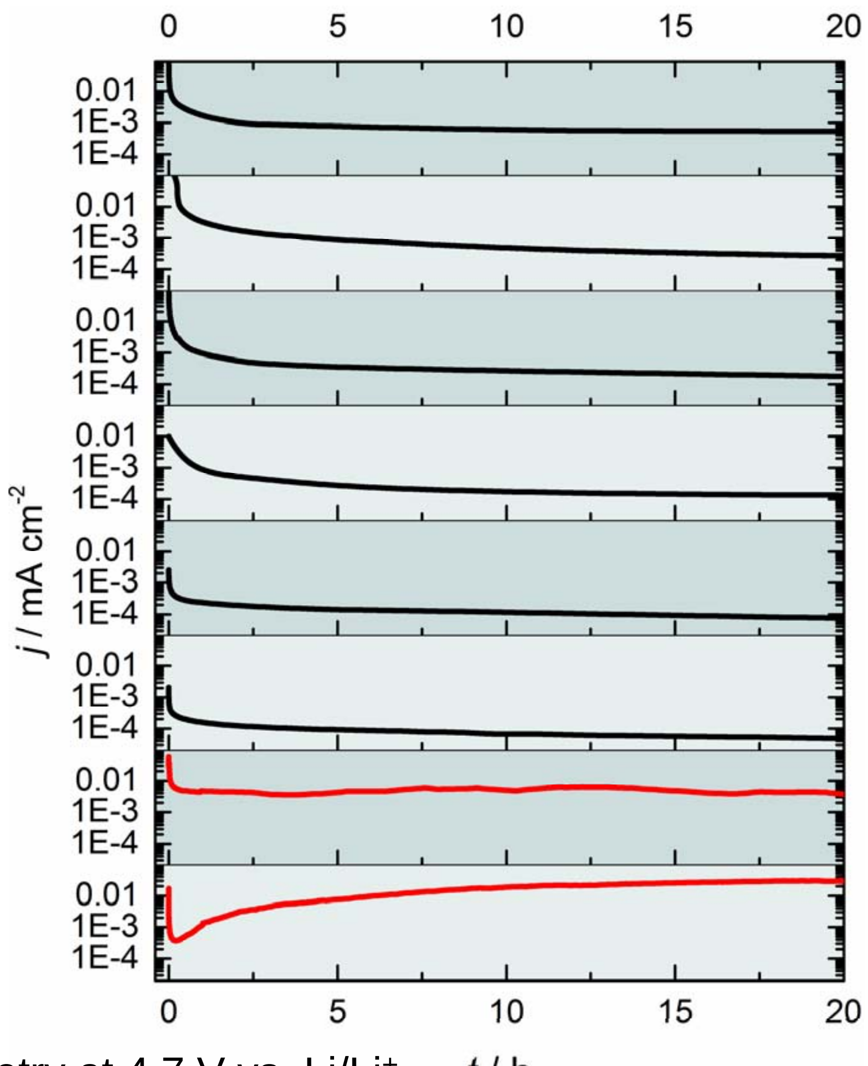
Electrochemical stability (oxidative, Pt//Li)

solvent	conducting salt	additive
EC/DMC	$LiPF_6$	
EC/DMSN	$LiPF_6$	
EC/DMSN	$LiPF_6$	LiBOB
EC/DMSN	$LiPF_6$	LiDFOB
EC/DMSN	$LiBF_4$	---
EC/DMSN	$LiBF_4$	LiBOB
EC/DMSN	LiTFSA	---
EC/DMSN	LiTFSA	LiBOB



Electrolyte stability against aluminum (Al//Li)

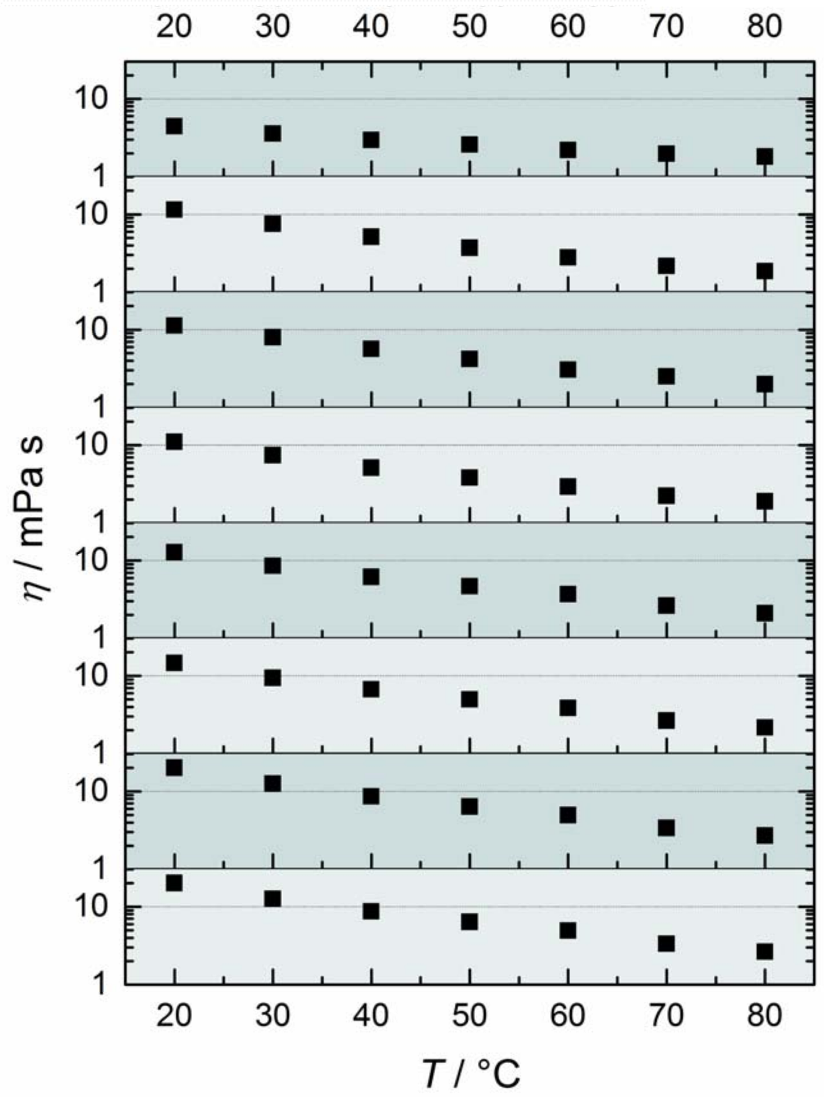
solvent	conducting salt	additive
EC/DMC	$LiPF_6$	
EC/DMSN	$LiPF_6$	
EC/DMSN	$LiPF_6$	LiBOB
EC/DMSN	$LiPF_6$	LiDFOB
EC/DMSN	$LiBF_4$	---
EC/DMSN	$LiBF_4$	LiBOB
EC/DMSN	LiTFSA	---
EC/DMSN	LiTFSA	LiBOB



Chronopotentiometry at 4.7 V vs. Li/Li^+

Conductivity and viscosity values

solvent	conducting salt (mol·kg^{-1})	additive (mol·kg^{-1})
EC/DMC	$LiPF_6$ (0.75)	
EC/DMSN	$LiPF_6$ (0.75)	
EC/DMSN	$LiPF_6$ (0.65)	LiBOB (0.1)
EC/DMSN	$LiPF_6$ (0.65)	LiDFOB (0.1)
EC/DMSN	$LiBF_4$ (1.0)	---
EC/DMSN	$LiBF_4$ (0.9)	LiBOB (0.1)
EC/DMSN	LiTFSA (1.0)	---
EC/DMSN	LiTFSA (0.9)	LiBOB (0.1)



Electrochemical properties of the electrolytes

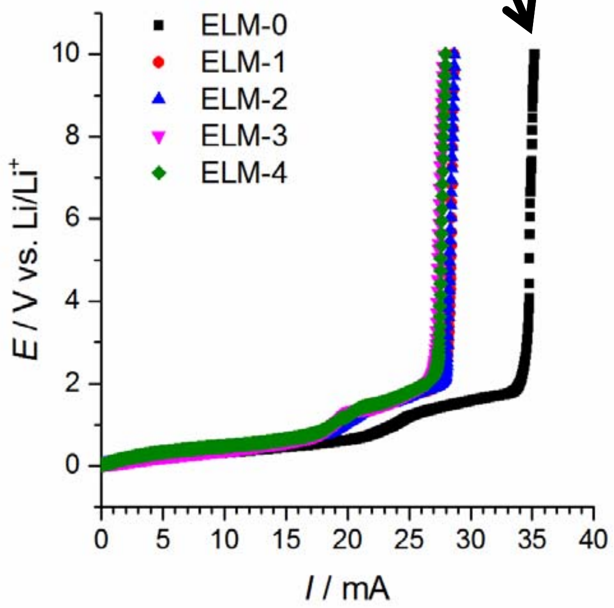
- Stable against **oxidation** (Pt as cathode material) up to 5 V vs. Li/Li^+
- High resistance against **aluminum dissolution** with exception of LiTFSA containing mixtures
- **Conductivity values** at 20 °C: 4 – 6 $mS \cdot cm^{-1}$ in dependence of the conducting salt
- Diffusion constants for $LiBF_4$ and LiTFSA containing electrolytes:
  - D(Li) = 4.7 – 6.5 $\cdot 10^{-11}$ m^2s^{-1} (standard electrolyte with $LiPF_6$: D(Li) = 22.4 $\cdot 10^{-11}$ m^2s^{-1})
  - D(F) = 5.9 – 9.3 $\cdot 10^{-11}$ m^2s^{-1} (standard electrolyte with $LiPF_6$: D(F) = 25.5 $\cdot 10^{-11}$ m^2s^{-1})

→ Medium cell performance can be expected from the electrochemical measurements

Measuring the lithium mobility with programmed current derivative chronopotentiometry

- Applying a time-dependent current
  $I(t) = \beta \cdot t \quad (\beta = 100\ \mu As^{-1})$
- cell configuration:
  - working electrode: lithium,
  - counter/reference electrode: lithium
  - four-layer glass fiber separators GF/B
- Performing a pre-polarization for same ionic polarization at the electrodes
- Determining the current limit
- It can be shown that neither the deposition nor the dissolution of lithium is rate-dependent

reference electrolyte (EC/DMC + 1M $LiPF_6$)



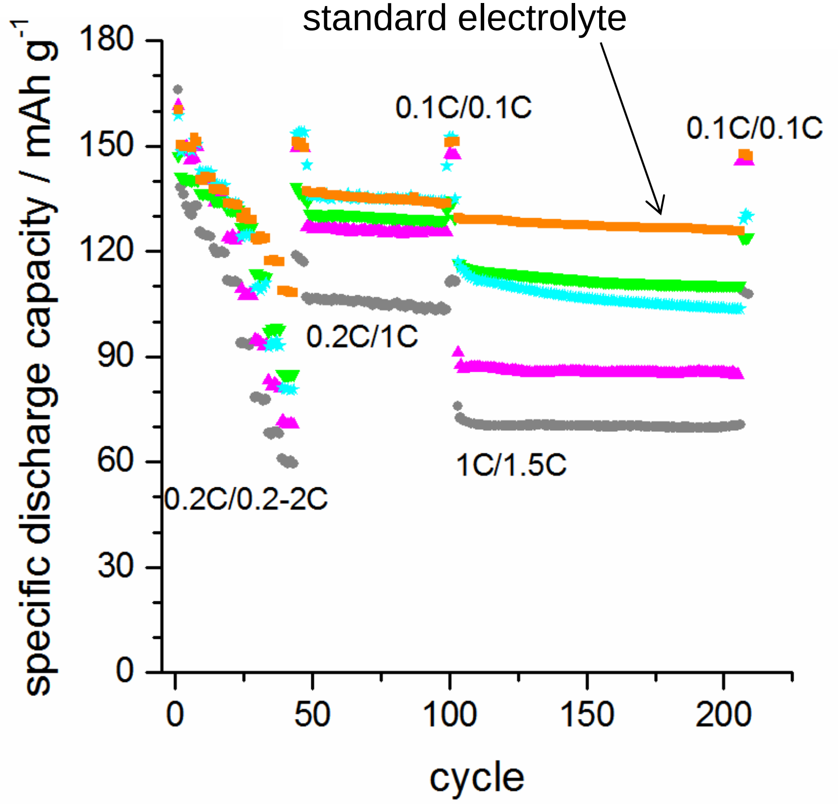
Potential (vs. Li/Li^+) *versus* current during programmed-current chronopotentiometry (ELM 1-4: $LiPF_6$ based electrolytes with ethylene carbonate and dimethyl sulfone)

→ **Similar performance of the novel electrolytes is expected based on these measurements**

Evaluation of the electrolytes via cell testings

Performance in NMC|C full cells

- Coin cells
- No additional additives are needed
- High capacity retention, even under stressed conditions
- Use of >90% of specific discharge capacity at 0.5 C (discharge) at 5 °C
- Comparable results in pouch bag cells with ceramic coated separator
- Small irreversible capacity loss
- Best results for LiBOB/LiDFOB mixed additive system



Different cell performance due to electrode interactions (SEI)

Evaluation of the electrolytes via cell testings

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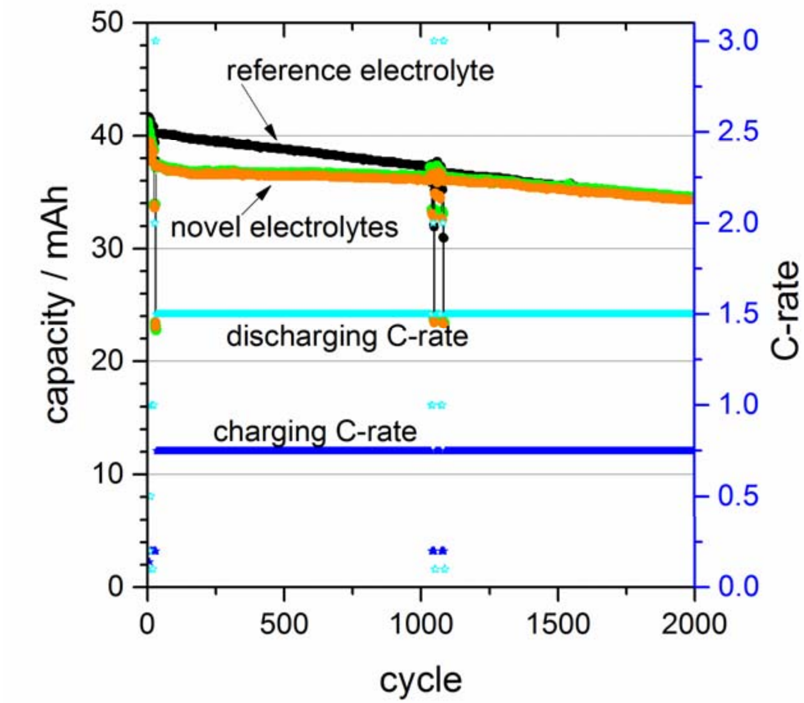
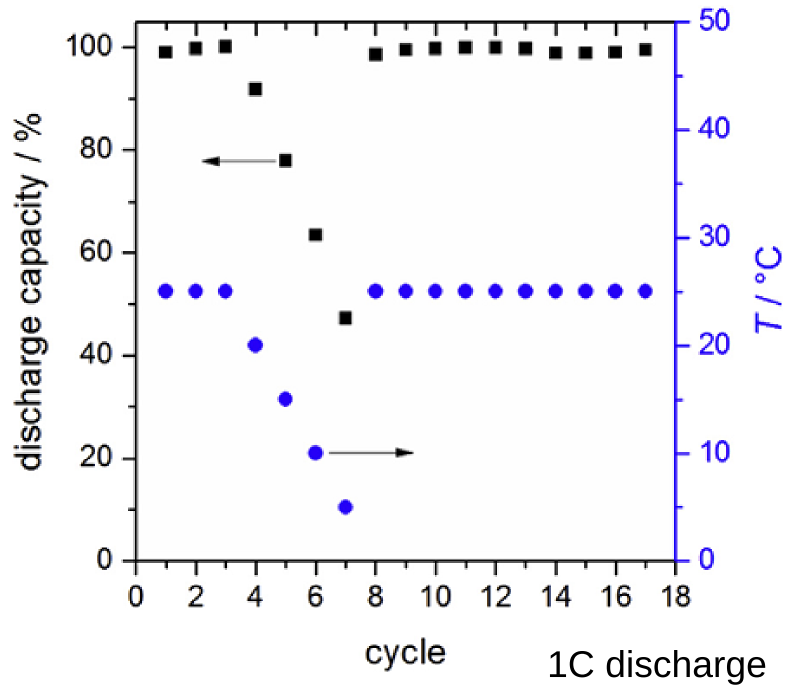
Pouch bag cells

Parameters: 50 x 50 mm; 42 mAh nominal capacity; cathode material: $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$; anode material: graphite; ceramic coated separator; T = 26 °C)



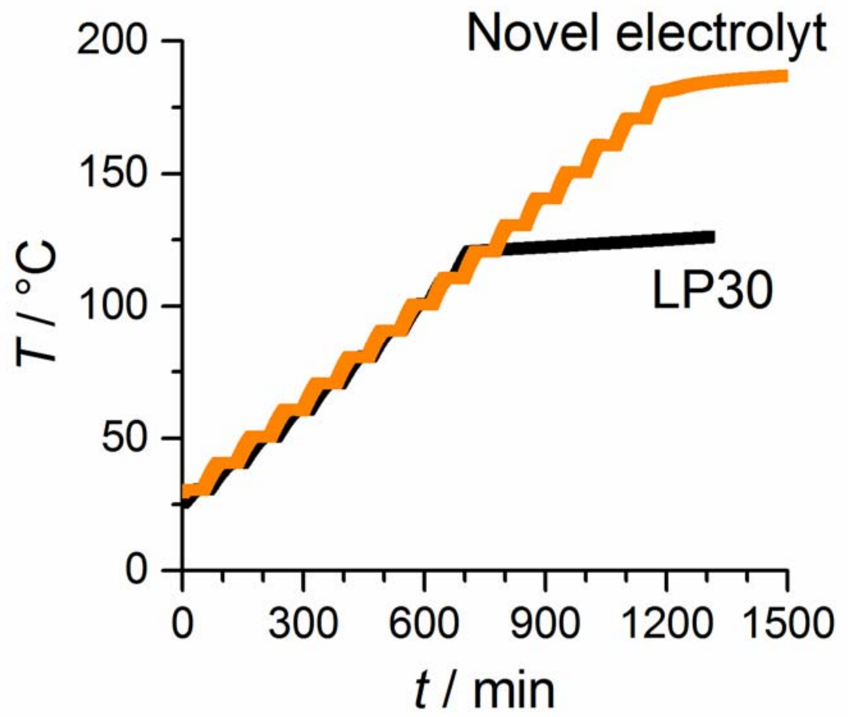


1C discharge rate at various temperatures; 0.2C charge rate at *T* = 25 °C

Medium cell performance up to 2C (T > 5 °C)
80 % capacity at ~3000 cycles

Safety aspects of the electrolytes

- Heat test measured in an accelerating rate calorimeter
- U = 4.2 V cell voltage
- Coin cells
- NMC against graphite
- Ceramic coated separator
- Temperature is detected when the cell temperature rise itself
- Temperature increase (thermal runaway) with novel electrolyte is delayed
- Large format cells are under study



Conclusions

- Development of novel electrolyte formulations based on **ethylene carbonate** and **dimethyl sulfone**
- High intrinsic safety based on high flash point of >140 °C
- Physicochemical properties support a well-working electrolyte
- High electrochemical stabilities are proved
- Novel lithium mobility test is evaluated
- In the full cell, the performance can not be predicted entirely based on lithium mobility tests
- It is supposed that the electrode materials and the SEI influence the lithium mobility significantly
- Cell tests demonstrate that the electrolyte can be used at medium C-rates and at T > 5°C
- Calorimetric tests with promising safety features

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Rockwood Lithium

HELMHOLTZ GEMEINSCHAFT

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DFG Deutsche Forschungsgemeinschaft

Thank you for your attention!

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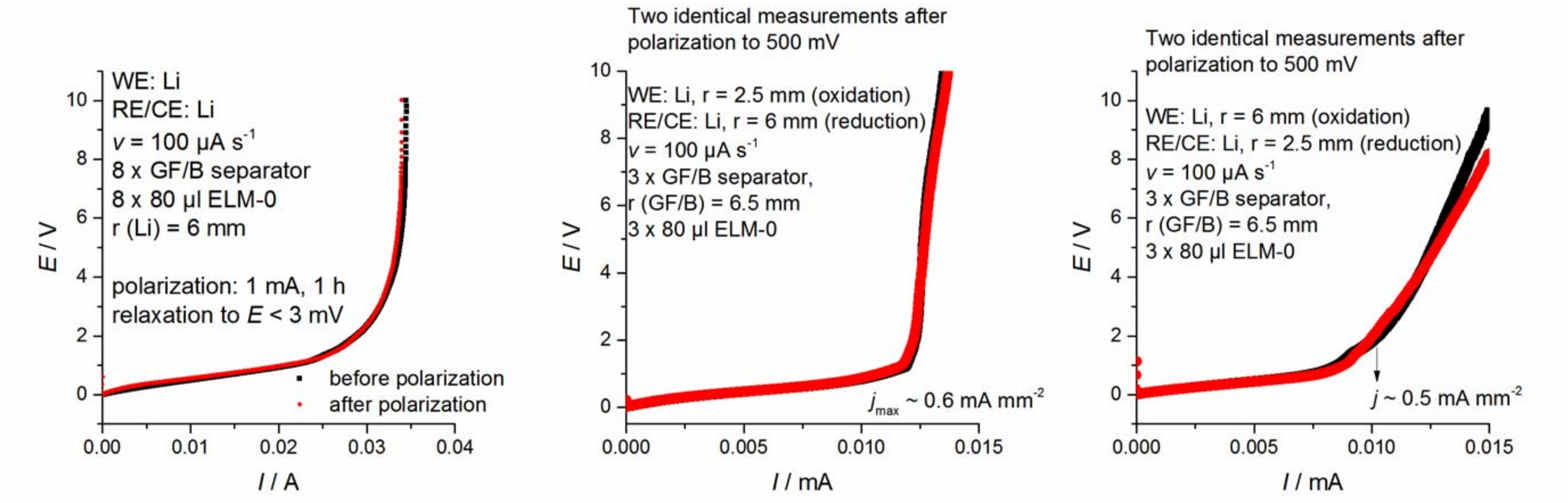
Measuring of the lithium mobility with programmed current derivative chronopotentiometry

Potential (vs. Li/Li^+) *versus* current plots:



Cell parameters:

- working electrode: lithium
- counter/reference electrode: lithium
- separator: GF/B glass fiber separator
- b = 100 µA s^{-1}.
- electrolyte: EC/DMC + 1M $LiPF_6$

- Results independent from pre-polarisation
- Current density of r = 6 mm/6 mm lithium ~ 0.3 mA mm^{-2}
- Current density of r = 2.5 mm/6 mm lithium ~ 0.4-0.6 mA mm^{-2}
- a larger current density is presumably obtained by a larger electrolyte/separator area (d = 13 mm) compared to the lithium area (d = 5 mm).
- Lithium dissolution and lithium plating not rate determining effects

Electrolyte research at IAM-WK

Issues

- High voltage electrolytes
- Improve of Safety
- Interfaces
- Structure-property relationships
- Structure-activity relationships

Focus of research

- Ionic liquids and new solvents
- Interaction of cell parts
- Additives
- Current collectors
- Conducting salts
- Electrolyte formulation

Systems

- Liquid electrolytes
- Gel polymer electrolytes
- New materials
- Li-ion cells
- solar cells