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Novel Electrolytes for Li-Ion Batteries with Improved Safety Issues

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Summary

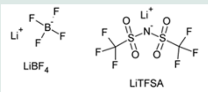
- Development of safe materials for energy storage (battery applications)
- Comprehensive study of $LiBF_4$ and LiTFSA in non-flammable ethylene carbonate – sulfone based liquid electrolytes
- Interaction of electrolytes and separator materials
- Significant improve of cell performance by use of lithium bis(oxalato) borate

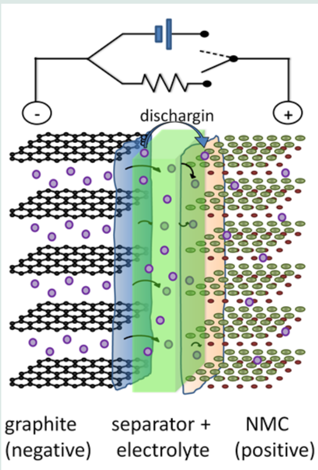
Motivation

- Enhancement of the **temperature stability** of Li-Ion battery electrolytes
- Influence of **conducting salts** on intrinsically safe electrolytes
- Improvement of the **lithium ion mobility**
- Reduction of **fire hazard** after cell accident
- Reaching sufficient **cell performance** at moderate C-rates* up to 2C

Li-Ion Cell

- Functionality of Li-ion batteries:
- Negative graphite electrode
- Positive $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ electrode
- Electrolyte based on ethylene carbonate and sulfone derivative
- Cell design: coin cells (CR 2032)
- Separator: Whatman glass fiber GF/B
- Conducting salts:
  - $LiBF_4$: lithium tetrafluoroborate
  - LiTFSA : lithium bis(trifluoromethyl-sulfonyl)azanide





Properties of electrolyte solvents

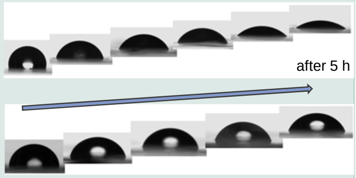
- Extraordinary high flash points of >140 °C which enhance the intrinsic electrolyte safety
- High conductivity, almost independent of the conducting salt
- Lithium bis(oxalato) borate (LiBOB) reduces conductivity and increase viscosity
- Low crystallizing temperatures of the electrolyte mixtures

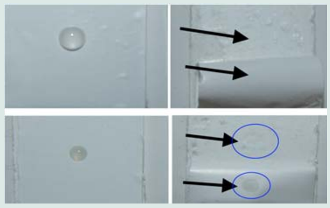
Physical properties of electrolyte mixtures. T_k crystallizing temperature; T_m melting point; fp flash point; d density; h viscosity; k conductivity.

sample	composition	T_K °C (DSC)	T_m °C (DSC)	**fp. °C**	*d* (25 °C) g cm^{-3}	η (20 °C) mPa s	κ (20 °C) mS cm^{-1}
LM1	EC/DMC (50:50)	NN	NN	**24**	1.2028	1.68	< 0.002
LM2	EC/sulfone derivative	-9.1	36.1	**142**	1.3234	4.42	< 0.006
EL-0	EC/DMC $LiPF_6$	-58.7	-20.5	**31**	1.27	4.44	10.7 ± 0.10
EL-1	EC/sulfone derivative $LiBF_4$	-47.7	23.5	**143**	1.36 ± 0.02	12.73	4.35 ± 0.05
EL-2	EC/sulfone derivative $LiBF_4$ + LiBOB	-19.3	23.0	-	1.36 ± 0.03	14.55	4.04 ± 0.05
EL-3	EC/sulfone derivative LiTFSA	-31.1	11.0	**148**	1.45 ± 0.03	20	4.37 ± 0.05
EL-4	EC/sulfone derivative LiTFSA + LiBOB	-29.1	10.4	-	1.45 ± 0.03	19.93	4.08 ± 0.05

Interaction of electrolytes with separator materials

- Drop shape analysis as method of investigation
- Different interaction of the electrolytes with separator materials according to surface polarity and surface tension
- Almost no penetration of polyolefine separators
- Best results with PET-based particle coated separators: contact angle of <10° after 15 min
- The penetration into the separator can be different from the results of drop shape analysis and better be described by wetting experiments

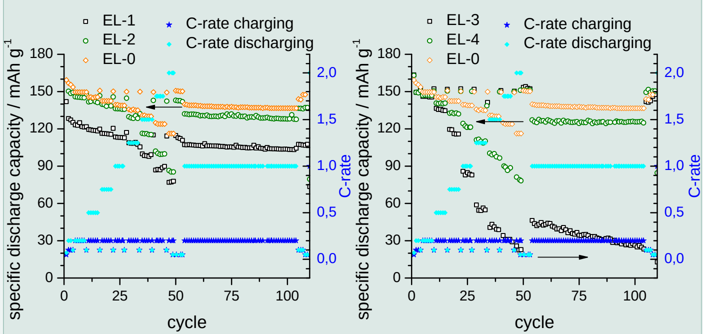




Drop shape analysis of electrolytes and penetration through the separator.

Performance in NMC|C cells

- Electrolyte formulation (conducting salts + solvent mixture) enables a cell cycling against graphite without additional additives
- Good capacity retention after 100 cycles (best: ~99,6%)
- At C-rate of 1,5C: ~78% of the initial specific capacity can be used
- By adding LiBOB, a significant improve in cell performance and cycle stability is obtained



Cycling tests (coin cells) of C|NMC cells (left) at 25°C with different current rates in a potential range of 3 – 4.2 V.

Conclusions and outlook

- Development of non-flammable electrolyte formulations (flash point > 140 °C)
- Successful realization of full cells with up to date electrodes (NMC|C)
- Significant improvement of cell performance by adding lithium bis(oxalato) borate (LiBOB) as additive
- Outstanding cell performance and capacity retention
- Calorimetric measurements reveal a significant enhancement of thermal safety

References

Hofmann et al., "*Novel Ethylene Carbonate Based Electrolyte Mixtures for Li-Ion Batteries with Improved Safety Characteristics*", ChemSusChem, **2015**, http://dx.doi.org/10.1002/cssc.201500263.

Hofmann et al., "*Novel Electrolyte Mixtures Based on Dimethyl Sulfone, Ethylene Carbonate and $LiPF_6$ for Lithium-Ion Batteries*", under review.

Hofmann et al., "Interaction of High Boiling Point Electrolytes for Li-Ion Batteries with PE and PE-Particle Coated Separators", to be submitted.

Patent pending: „Elektrolyt, Zelle und Batterie umfassend den Elektrolyten und dessen Verwendung" Patentanmeldung: 102014108254.5

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* C/*n*: current rate when the cell is charged or discharged completely in *n* h