Karlsruhe Institute of Technology

Institut für Angewandte Materialien
Werkstoffprozesstechnik

Electrolytes for Li-Ion Batteries with Highly Improved Safety Issues

Andreas Hofmann*, Michael Schulz*, Sylvio Indris**, Thomas Hanemann*,***

* Karlsruher Institut für Technologie, Institut für Angewandte Materialien - Werkstoffprozesstechnik, Karlsruhe, Germany
Andreas Hofmann, e-mail: *andreas.hofmann2@kit.edu*, Tel. +49 (0)721-608-25920
** Karlsruher Institut für Technologie (KIT), Institut für Angewandte Materialien - Energiespeichersysteme, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany
*** Universität Freiburg, Institut für Mikrosystemtechnik (IMTEK), Freiburg, Germany

Summary

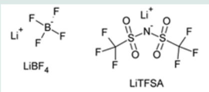
- Development of safe materials for energy storage (battery applications)
- Comprehensive study of $LiBF_4$ and LiTFSA in non-flammable ethylene carbonate – sulfone based liquid electrolytes
- Interaction of electrolytes and separator materials
- Significant improve of cell performance by use of lithium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

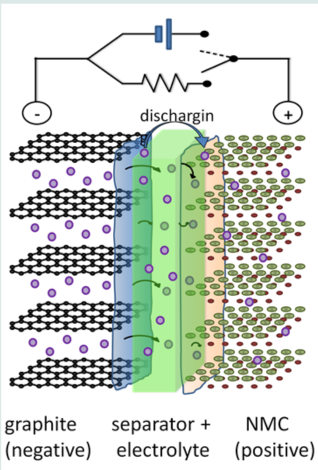
Motivation

- 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

Measurement of diffusion constants via PFG-NMR

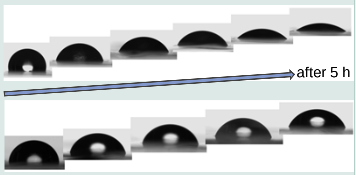
- Pulsed-field-gradient nuclear magnetic resonance (PFG-NMR)
- Lithium mobility is slightly reduced compared to EC/DMC + 1M $LiPF_6$
- Cationic and anionic species are affected in a similar manner
- Lithium transference numbers are almost identical compared to EC/DMC + 1M $LiPF_6$

Diffusion constants determined by PFG-NMR measurements.

sample	D_{Li} x 10^{-11} m^2 s^{-1}	D_F x 10^{-11} m^2 s^{-1}	t_{Li}^+
EL-0 LP30; $LiPF_6$	22.4 ± 0.3	25.5 ± 0.2	0.47 ± 0.01
EL-1 $LiBF_4$	6.55 ± 0.05	9.29 ± 0.05	0.41 ± 0.01
EL-2 $LiBF_4$/LiBOB	6.32 ± 0.05	8.76 ± 0.05	0.42 ± 0.01
EL-3 LiTFSA	4.85 ± 0.05	6.12 ± 0.05	0.44 ± 0.01
EL-4 LiTFSA/LiBOB	4.71 ± 0.05	5.92 ± 0.05	0.44 ± 0.01

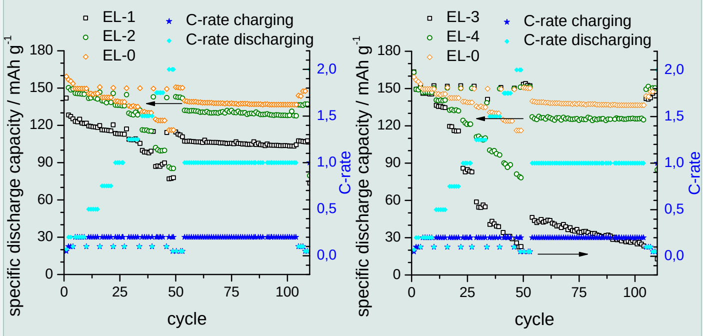
Interaction with separator materials

- 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 particle coated separators: contact angle of <10° after 15 min



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 are under study

References

A. Hofmann et al., "*Novel Ethylene Carbonate Based Electrolyte Mixtures for Li-Ion Batteries with Improved Safety Characteristics*", under revision.

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

Acknowledgements

We thank Brennstoffzellen- und Batterie-Allianz Baden-Württemberg for financial support within the project „Forschungsaversum 2013/1305".

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