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Electrolytes for Li-Ion Batteries with Improved Safety Characteristics

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Summary

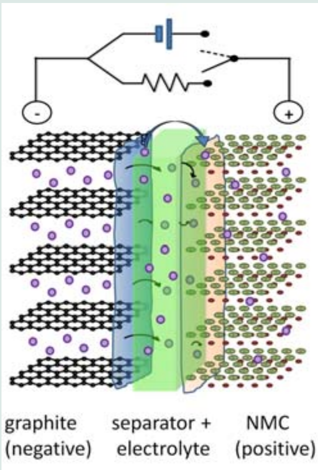
- Development of safe electrolytes for energy storage (battery applications)
- Systematic study of $LiPF_6$ as conducting salt in non-flammable ethylene carbonate – dimethyl sulfone based liquid electrolytes
- Investigation of lithium mobility via programmed current chronopotentiometry measurements
- Significant improve of cell performance by the use of selected additives

Motivation

- Enhancement of the **cell safety** of Li-Ion batteries
- Improvement of the **lithium ion mobility**
- Reduction of **fire hazard** after cell accident
- Reaching sufficient **cell performance** at moderate C-rates* up to 2C
- Use of **commercial available** electrolyte materials

Li-Ion Cells

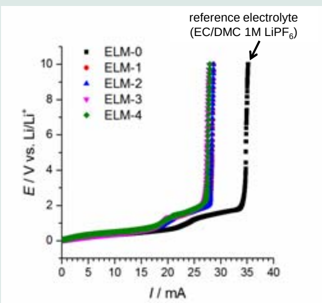
- Negative graphite electrode
- Positive $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ electrode
- Novel electrolytes based on ethylene carbonate (EC) and dimethyl sulfone (DMSN)
- Cell design: coin cells (CR 2032) and pouch bag cells (approx. 5 x 5 cm)
- Separator: Whatman glass fiber GF/B and ceramic-coated PET fibres
- Conducting salts: $LiPF_6$
- Additives: LiBOB and LiDFOB



Measurement of Lithium mobility via programmed-current chronopotentiometry

- Li||Li cell configuration
- Applying a time-dependent current $I(t) = \beta \cdot t$ ($\beta = 100$ µAs^{-1})
- Measuring the voltage response
- Determining the current limit
- Performing a pre-polarization for same ionic polarization at the electrodes
- It is shown that neither the deposition nor the dissolution of lithium is rate-dependent

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



Potential (vs. Li/Li⁺) *versus* current during programmed-current chronopotentiometry (working electrode: lithium, counter/reference electrode: lithium, four-layer glass fiber separators GF/B).

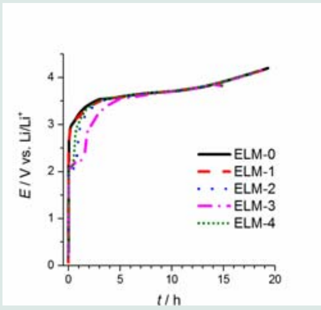
Properties of electrolyte mixtures

Tab. 2. Physicochemical properties of electrolyte mixtures. T_K crystallizing temperature; T_m melting point; fp. flash point; d density; η viscosity; κ conductivity.

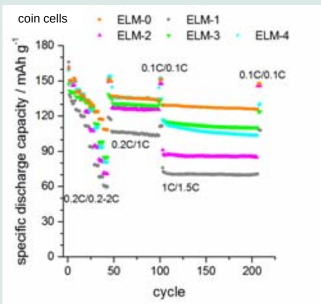
electrolyte	LM-1	LM-2	ELM-0	ELM-1	ELM-2	ELM-3	ELM-4
solvent	EC/DMC	EC/DMSN	EC/DMC	EC/DMSN	EC/DMSN	EC/DMSN	EC/DMSN
conducting salt	---	---	$LiPF_6$	$LiPF_6$	$LiPF_6$	$LiPF_6$	$LiPF_6$
additive	---	---	---	---	LiBOB	LiDFOB	LiBOB+ LiDFOB
mp. / °C (DSC, 10 K·min^{-1})	-0.6	36.1	-19.4	16.0	18.1	18.6	18.8
freezing Point /°C (DSC)	-32.7	-9.1	-56.1	-26.1	-12.3	-19.1	-17.3
fp. / °C	24	142	-	-	-	-	-
d / g cm^{-3} (25 °C) (± 0.01 g cm^{-3})	1.20	1.32	1.27	1.40	1.39	1.36	1.37
η / mPa·s (20 °C) (± 0.5 mPa·s)	1.7	4.4	4.4	11.4	11.0	11.4	11.4
κ / mS cm^{-1} (20 °C) (± 0.05 mS cm^{-1})	-	-	10.67	5.95	5.38	5.95	5.76
I_{max} / mA at b = 100 µA s^{-1} (± 0.7 mA)	-	-	34.5	28.4	28.4	27.5	27.7

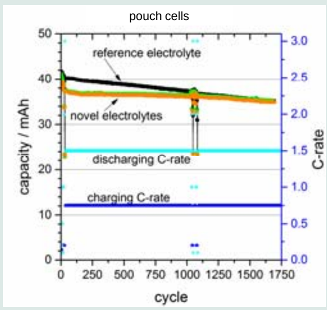
Performance in NMC|C cells

- No additional additives are needed
- High capacity retention, even under stressed conditions
- Best results for LiBOB/LiDFOB mixed additive system
- Use of >90% of specific discharge capacity at 0.5 C (discharge) at 5 °C
- Use of ~50% of specific discharge capacity at 1 C (discharge) at 5 °C
- Comparable results in pouch bag cells with ceramic coated separator



First cell charging is depicted (same behavior is observed within three cells with same electrolyte). The charging is done at 0.05 C.





NMC||C full cell tests. Left picture: Measurement of the specific discharge capacity of NMC|C coin cells. The charging/discharging characteristic is mentioned as charging/discharging C-rate. Starting from 100 cycles, CCCV-charging is used (I_e = C/15). Right picture: Power- and fading test of the capacity of pouch bag cells (nominal cell capacity: 42 mAh).

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 LiBOB and LiDFOB as additives
- Outstanding cell performance and capacity retention
- Cell performance can be predicted only in limited manner (based on lithium mobility)

References

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- Hofmann et al., "*Novel Electrolyte Mixtures Based on Dimethyl Sulfone, Ethylene Carbonate and $LiPF_6$ for Lithium-Ion Batteries*", J. Power Source 298, 322-330 (2015).
- *Hofmann et al., "Interaction of High Boiling Point Electrolytes for Li-Ion Batteries with PE and PE-Particle Coated Separators*", Int. J. Mol. Sci. 16, 20258-20276 (2015)
- 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