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

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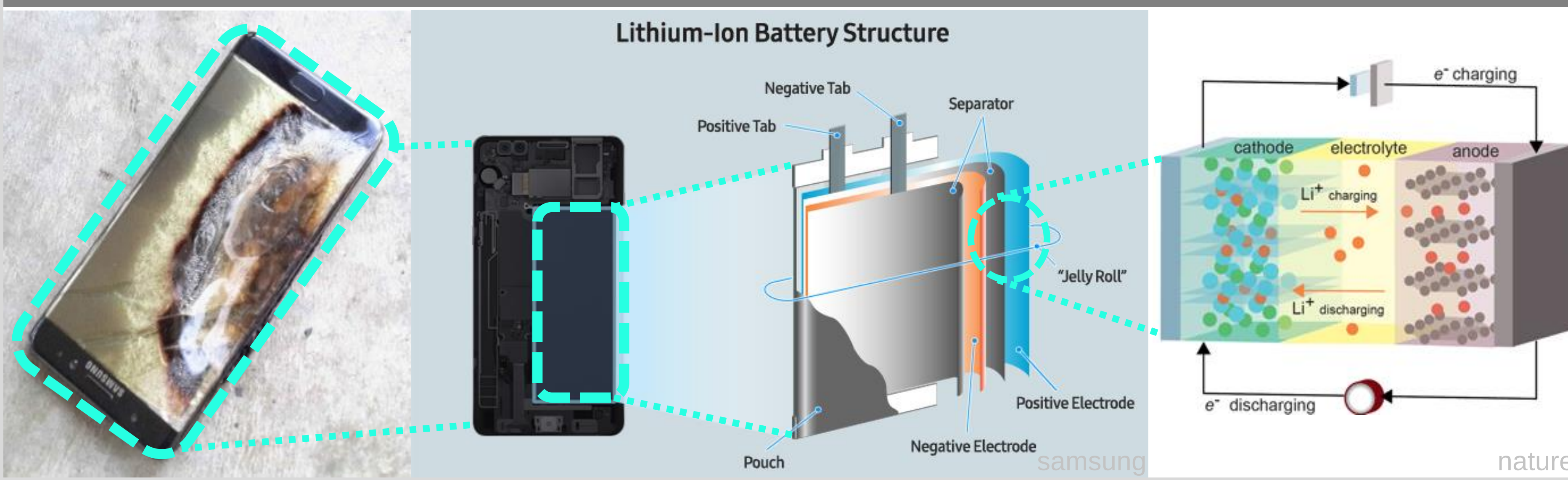

Motivation
Battery explosion

„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.

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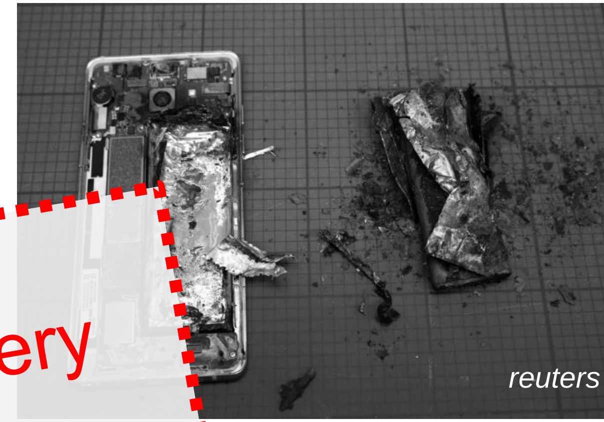


„worldwide sales stop and exchange recall for Samsung Galaxy Note 7“
2016
An ambitious design of the battery modules in the phone, led to the short circuit.

Big challenge for battery

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

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

aim at „prevention“

- Low-/non-flammable electrolytes achieved…
  - By changing chemicals:
    substitution by solvents of high boiling/flash point and thermal stabi L
    →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_2O_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
[2] X. Fan et al., Non-flammable electrolyte enables Li-metal batteries with aggressive cathode chemistries, Nat. Nanotech., 13, 2018, 715-722
[3] A. Hofmann. T. Hanemann et al., Electrolyte Mixtures Based on Ethylene Carbonate and Dimethyl Sulfone for Li-Ion Batteries with Improved Safety Characteristics, ChemSusChem, 8 (11), 2015: 1892-1900
[4] A. Hofmann, T. Hanemann et al., Novel electrolyte mixtures based on dimethyl sulfone, ethylene carbonate and LiPF6 for lithium-ion batteries, Journal of Power Sources, 298, 2015: 322-330
[5] P. Isken et al., High flash point electrolyte for use in lithium-ion batteries, Electrochimica Acta, 56 (22), 2011: 7530-7535
[6] L. Suo, K. Xu wt al., “Water-in-salt” electrolyte enables high-voltage aqueous lithium-ion chemistries, 350 (6263): 938-943
[7] J.B. Goodenough et al., Alternative strategy for a safe rechargeable battery, Energy Environ. Sci., 10, 2017: 331-336

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

aim at „rescue"

- Fire-extinguishing achieved…
  - By adding flame retardant (FR):
    thermal shieding, 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

[8] K. Amine et al., Flame-retardant additives for lithium-ion batteries, Journal of Power Sources, 119–121, 2003: 383-387
[9] J. Wang et al., Fire-extinguishing organic electrolytes for safe batteries, Nature Energy, 3, 2018: 22-29
[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
[11] K. Liu et al., Electrospun core-shell microfiber separator with thermal-triggered flame-retardants, Science Advances, 3 (1) 2017

Composition

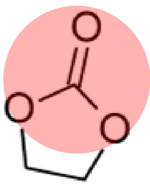
ELECTROLYTES

Lithium salt, solvent

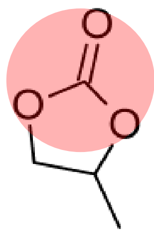
„Salt-in-solvent“ Electrolyte
Salt, solvent

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

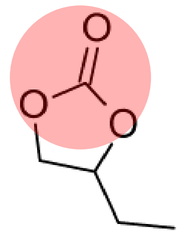
Solvent



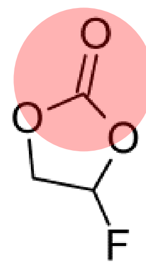
EC



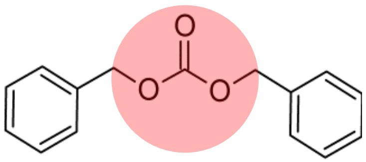
PC



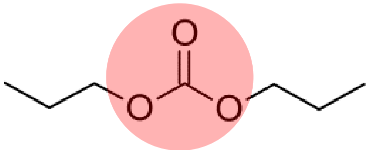
1,2-BC



FEC

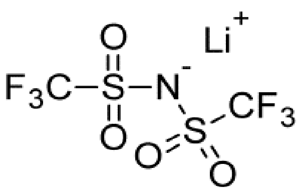


DBC



DPrC

Conducting salt



LiTFSI

Sample	EM-0	EM-1	EM-2	EM-3	EM-4	EM-5	EM-6
solvents (1:1 molar-ratio)	EC						
	DMC						
conducting salt	$LiPF_6$						
Concentration, [mol kg^{-1}]	0.771	0.75	0.75	0.75	0.75	0.75	0.75

reference
Sample: LP30

Physicochemical analysis

ELECTROLYTES

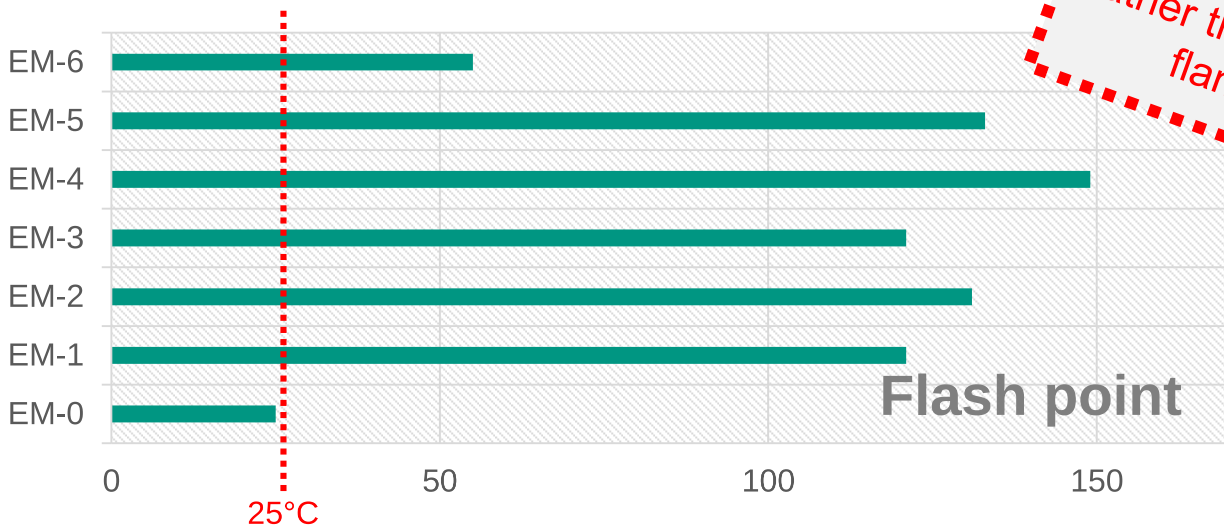
Density, phase transition, viscosity, ionic conductivity

Physicochemical Properties

thermal, density, rheological, ion-conductive

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

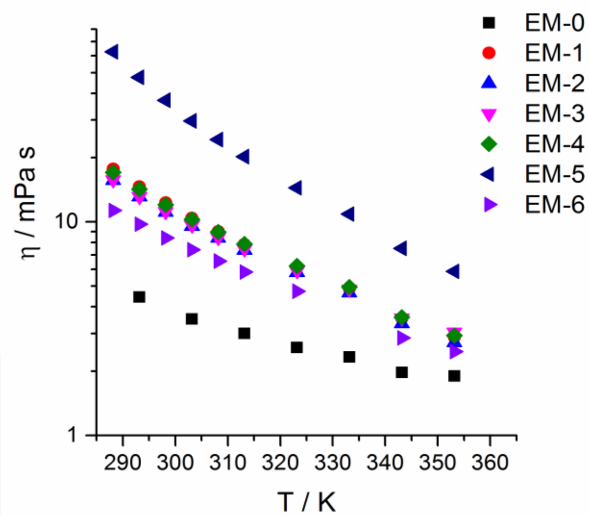
aim at „prevention“ rather than „rescue“ (e.g. by flame retardants)

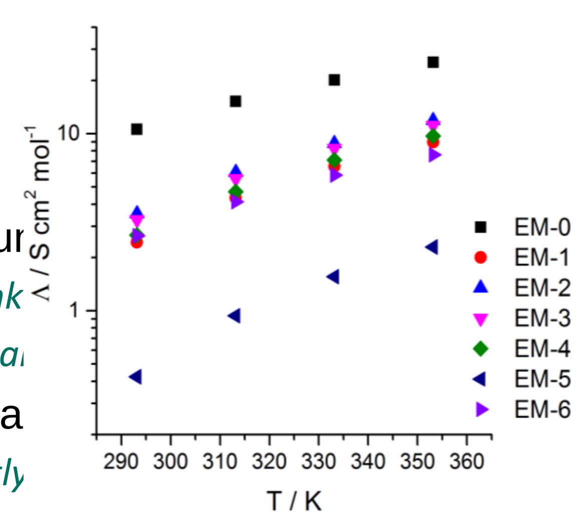


- The flash point T_f correlated with the temperature when the electrolyte burns on, after contact to a flame source (e.g. electrical spark, hot surface and external flame)
- Influenced by boiling point and flammability
- Safety improvement

Physicochemical Properties
thermal, density, rheological, ion-conductive

Balance between safety issue and the basic properties





polarity of carbonates (cyclic/linear)

Viscosity *η*

- $\eta = \eta_0 * \exp[B/(T - T_0)]$
  Fitted by VFTH equation
- $\eta = \eta_0 * \exp[E_a/RT]$
  Arrhenius-like equation
  Activation energy Ea -> potential barrier for molecule-ion movement
- „Strong“ and „fragile“ *
  Structured coordination

DSC

- Glass-forming ability and lower T_g
  large polarizable anion TFSI- and flexibel S-N-S bond
- Melting point T_m
  Application temperature-range

Ionic conductivity *Λ*

- $\Lambda = \Lambda_0 * exp[C_2/(T - T_2)]$
  Fitted by VFTH equation
- Li^+ diffusion across electrolyte
  Kinetic of Li+ cell reaction

Relationship between structure and ion transport by Walden rule

$$\Lambda * \eta^{\alpha} = C$$

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

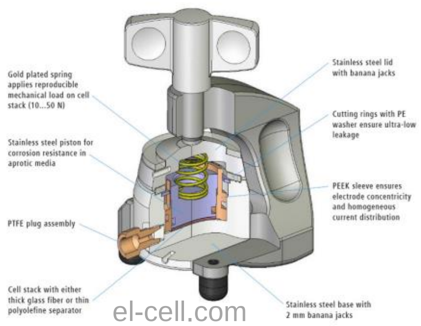
Electrochemical aspects

ELECTROLYTES

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

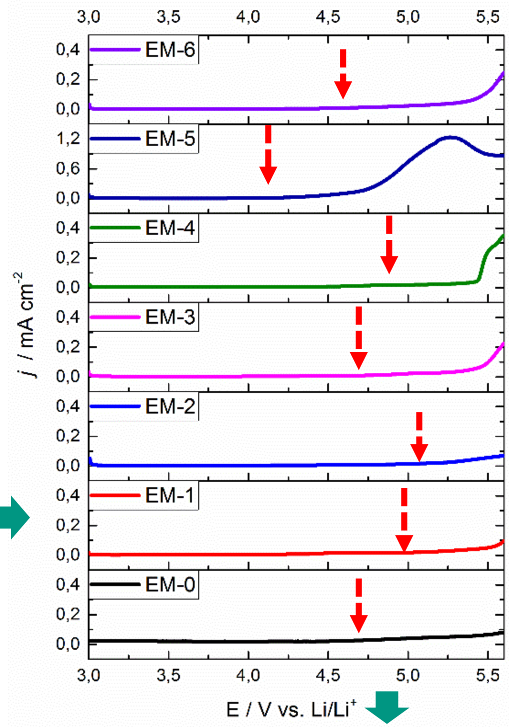
Electrochemical stability

Li vs. Pt (cyclovoltammetry)



Periodical cycling

- **3 – 6 V**
- Scan rate: **± 1 mV/s**
- @ **25°C**
- Current density j /**mA cm^{-2}** vs. E /**V**



Sample	EM-0	EM-1	EM-2	EM-3	EM-4	EM-5	EM-6
solvents	EC DMC	FEC	FEC EC	FEC PC	FEC 1,2-BC	FEC DBC	FEC DPrC
E_{ox}, Li|Pt [V] *	4.7	5.0	5.1	4.7	4.8	4.2	4.6

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

- Gentle /sharp rise of current density

  (kinetic) Electrolyte degradation;

  Different oxidative stability of components (e.g. benzyl in EM-5);

- sufficient potential Eox ≥ 4.2 V versus Li/Li+

  electrochemical windows;

- Peak-current (at **6 V**)

  lower value

  ⇒ Plating of resistive interface layer at inactive Pt surface;

  Higher value (e.g. EM-1)

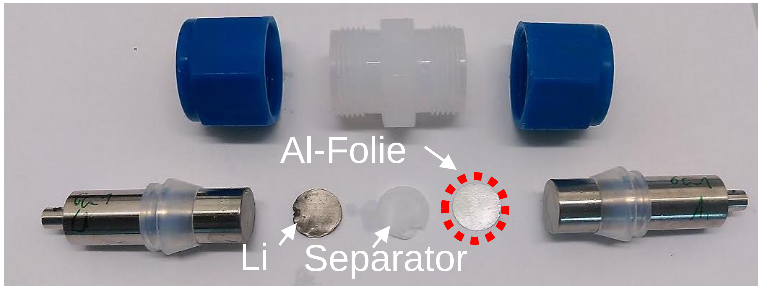
  ⇒ insufficient decomposition when only FEC included

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**

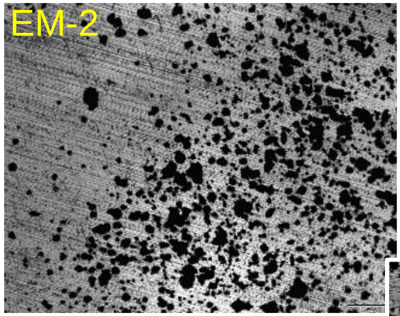
- Post-cycling examination of cycled Al foils

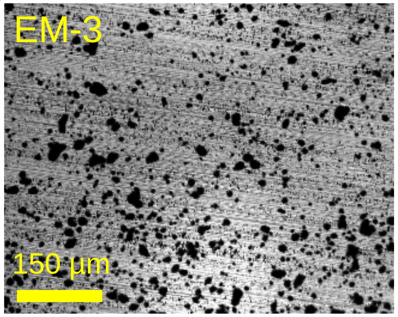


Al-corrosion process

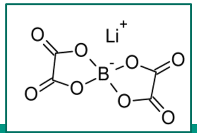
absorption of **TFSI- anions** on surface of Al foil and depletion of native passivated Al_2O_3

exposure of fresh Al sites

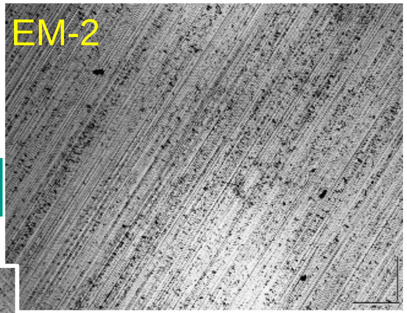


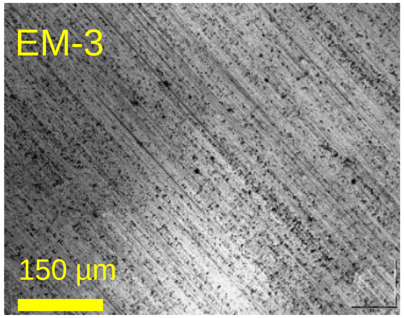


- Distributed corrosion pits of Al foils after cycling



+ **LiBOB** additives





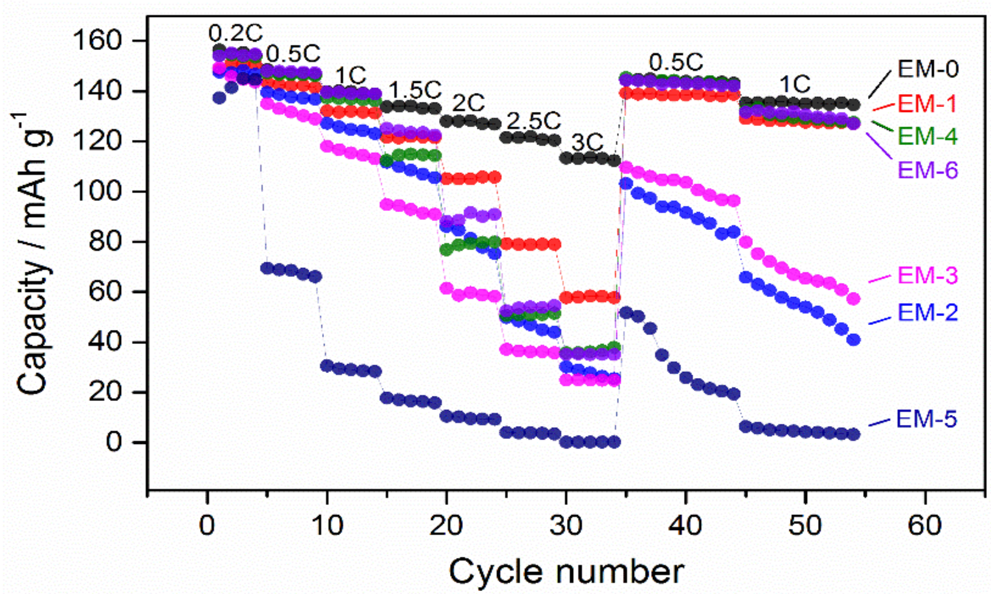
- **re-passivation** at Al surface
- suppression of corrosion

Half-cell cycling

Li vs. NMC111 ($LiN_{1/3}Mn_{1/3}Co_{1/3}O_2$)

Periodical cycling

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



Discharge capacity fading

- C-rate dependent

  >1C: capacity significantly smaller than EM-0

- Capacity retention

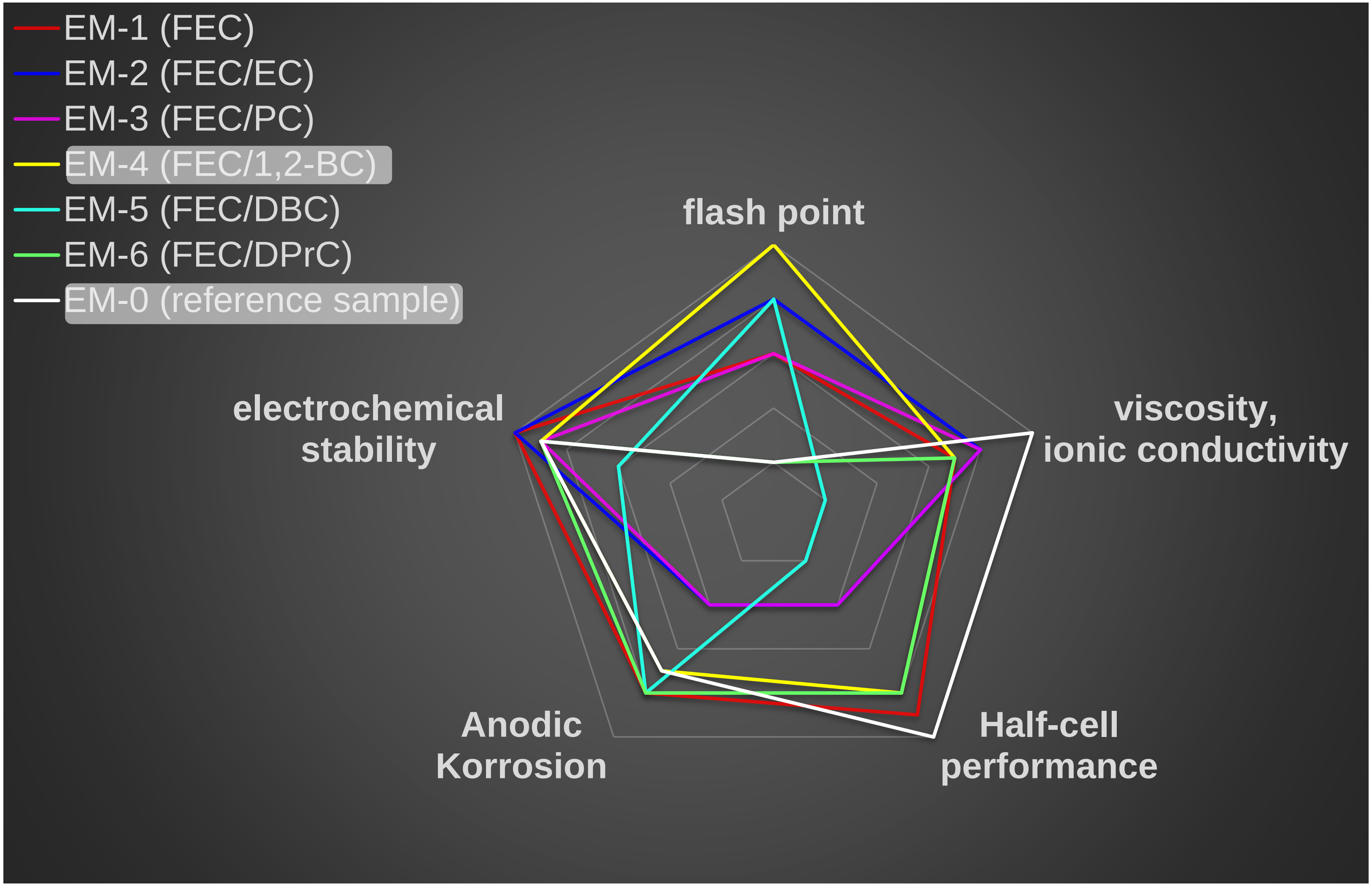
  Influence of electrolyte on the cathode

EM-1(FEC):
stable and uniform LiF-rich SEI film and less dead Li

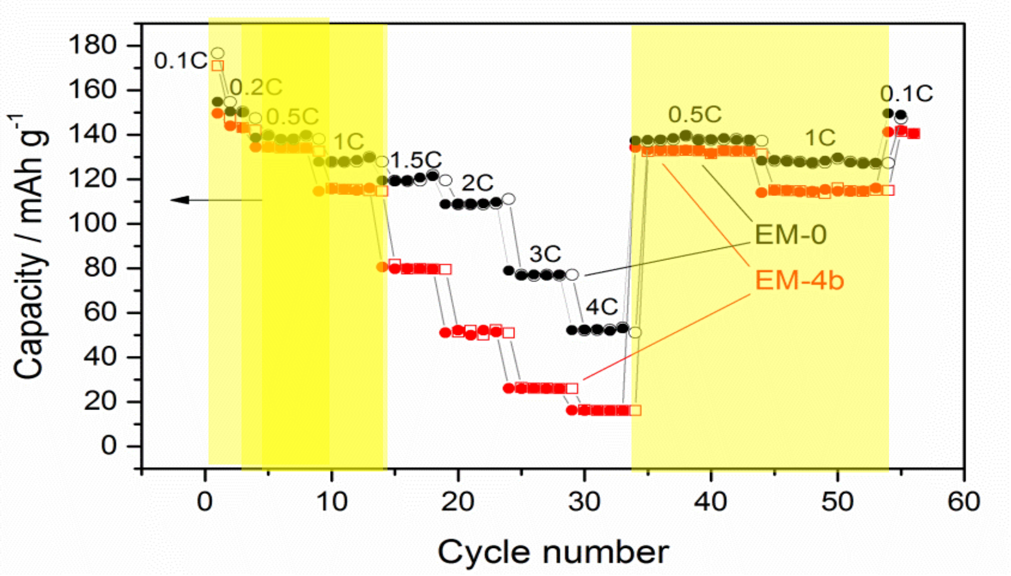
EM-2 (EC/FEC) & EM-3 (PC/FEC):
aluminum dissolution

EM-5 (DBC/FEC): higher viscosity
destruction of cathode (peeling off from collector)

Selection criteria of better electrolyte
balance between different properties



Full-cell cycling
Graphite vs. NMC (coin cell)



Additive (SEI-layer „enabler“, Al „protecter“)
- 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%)

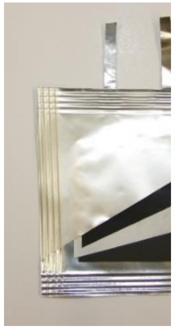
  ⇒ Growth of resistive layers, thus clogged graphite pores comsumed some Li

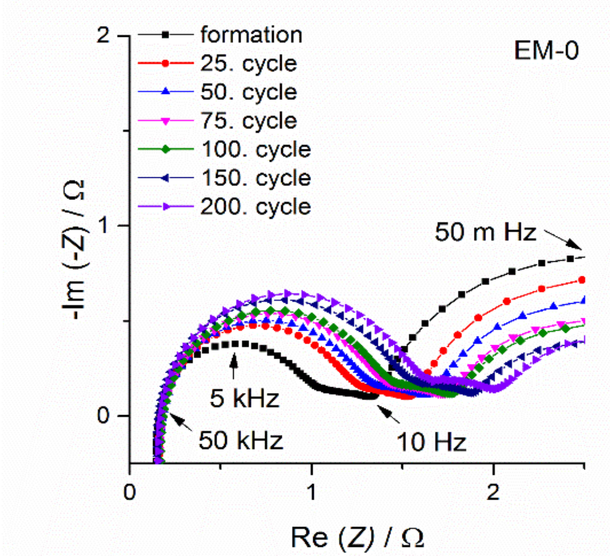
- sealing of the coin cell

  water and O_2 content

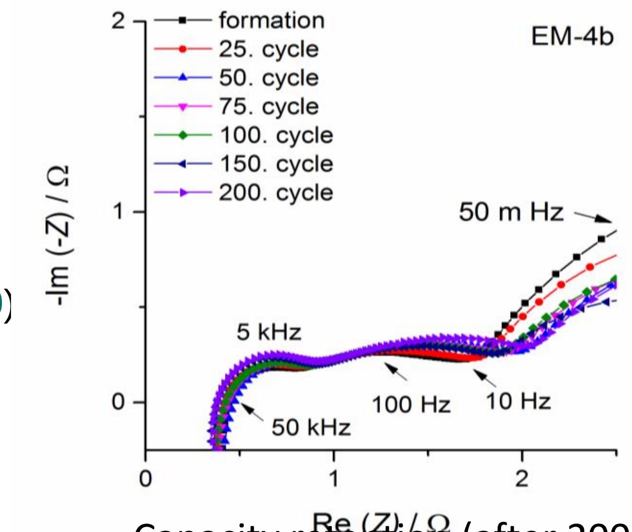
Full-cell cycling

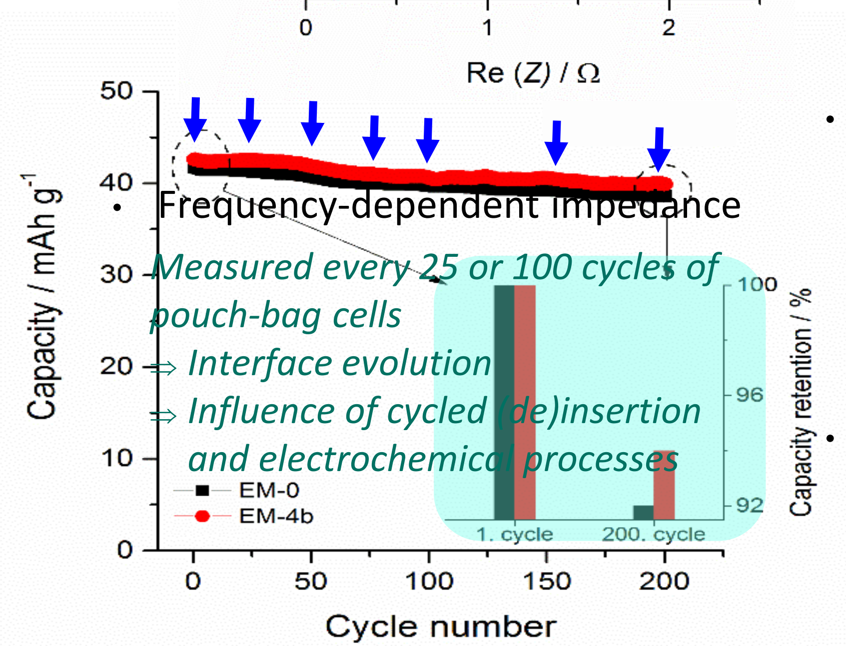
Graphite vs. NMC (pouch-bag cell)





cm-2
200)





- Frequency-dependent impedance

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

- Middle-high range (10 Hz ~ 50 kHz)

Two semicircles:
1. resistance of SEI layer
*⇒ **EM-0**: higher double layer capacitive resistance & faster increase; **EM-4**: slighter/fewer growth of interface layer*
2. electronic conductivity of electrode components

- Middle range (50 mHz ~ 10 Hz)

Li+ ions transfer resistance at the interface
*⇒ **EM-0**: lower;*
*⇒ **EM-4**: slower increasing of real part*

- Capacity retention (after 200 cycles)

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

- Capacity fading

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

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

Comparable properties

- **Outlook**
  - Other novel salts and solvents of different structures
  - Analysis of resistive interface layer

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Thank you for your attention!

Acknowledgement

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Institute for Applied Materials (**IAM-WK**)

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