

# Effect of Conducting Salts in Ionic Liquid based Electrolytes for Li-Ion-Batteries

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## Summary

- Study of conducting salts in ionic liquid – propylene carbonate liquid electrolytes
- Interaction of ionic liquid based electrolytes with graphite and NMC electrodes
- Li<sup>+</sup> conductivity, safety, cycle stability

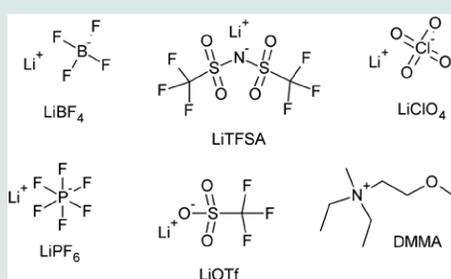
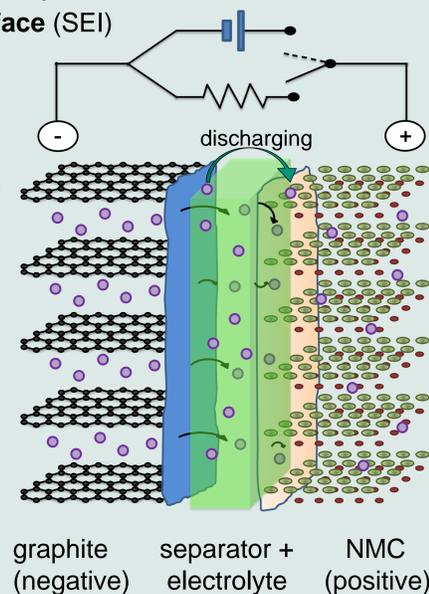


## Motivation

- Enhancement of the **temperature stability** of Li-Ion battery electrolytes
- Influence of **conducting salts** on ionic liquid based electrolytes
- Improvement of the **lithium ion mobility**
- Study of the **solid electrolyte interface (SEI)**

## Li-Ion Cell

- Functionality of Li-ion batteries
- Negative graphite electrode
- Positive NMC electrode  
(NMC =  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ )
- Electrolyte based on DMMA-TFSA and propylene carbonate
- Cell design:  
Swagelok type cells and coin cells (CR 2032)
- Separator: Whatman glass fiber, thickness: 450  $\mu\text{m}$
- Conducting salts:
  - $\text{LiBF}_4$ : lithium tetrafluoroborate
  - $\text{LiPF}_6$ : lithium hexafluorophosphate
  - $\text{LiClO}_4$ : lithium perchlorate
  - $\text{LiOTf}$ : lithium triflate
  - $\text{LiTFSA}$ : lithium bis(trifluoromethylsulfonyl)azanide (= lithium bis(trifluoromethylsulfonyl)imide)
  - DMMA (as cation): N,N-diethyl-N-methyl-N-(2-methoxyethyl)ammonium

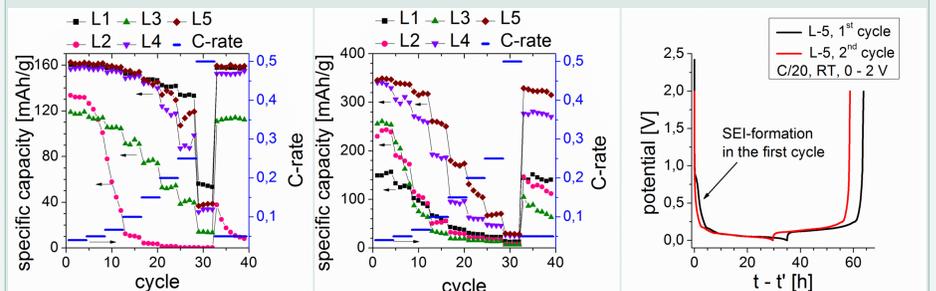


## Composition, conductivity and viscosity of selected salt mixtures

sample	conducting salt (1 mol/kg)	solvent (1:1 wt%)	conductivity [mS/cm] (20 °C)	viscosity [mPa·s] (20 °C)	density [g/cm <sup>3</sup> ]
L-0	-	PC – DMMA-TFSA	9.8 ± 0.9	7.9 ± 0.2	1.29 ± 0.20
L-1	$\text{LiBF}_4$	PC – DMMA-TFSA	3.1 ± 0.2	39.6 ± 0.6	1.35 ± 0.02
L-2	$\text{LiOTf}$	PC – DMMA-TFSA	2.3 ± 0.2	55.1 ± 0.5	1.39 ± 0.03
L-3	$\text{LiClO}_4$	PC – DMMA-TFSA	2.2 ± 0.1	69.7 ± 1.8	1.37 ± 0.02
L-4	$\text{LiPF}_6$	PC – DMMA-TFSA	1.9 ± 0.1	78.9 ± 4.1	1.38 ± 0.03
L-5	$\text{LiTFSA}$	PC – DMMA-TFSA	1.6 ± 0.1	70.7 ± 2.2	1.44 ± 0.04

- High conductivity, independent of the conducting salt
- Measurements reveal a **suitability for Li-Ion-Cells**

## Mixtures in Li|NMC and Li|C cells

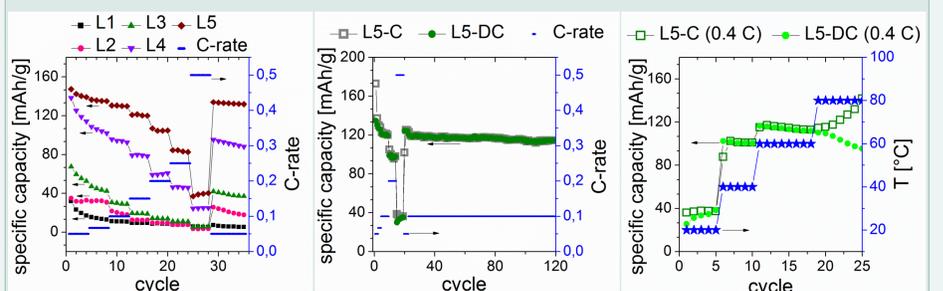


L-1 =  $\text{LiBF}_4$   
L-2 =  $\text{LiOTf}$   
L-3 =  $\text{LiClO}_4$   
L-4 =  $\text{LiPF}_6$   
L-5 =  $\text{LiTFSA}$

Cell cycling tests of Li|NMC (left) and Li|C cells (middle) at room temperature with different current rates in a potential range of 3 – 4.2 V vs.  $\text{Li/Li}^+$  (left) and 0 – 2.0 V vs.  $\text{Li/Li}^+$  (middle). On the right side there are depicted the first two cycles of C|Li cell with electrolyte L-5. ( $t'$ : the time scale is normalized at the beginning of the cycle)

- Different performing of the electrolytes in Li|NMC and Li|C cells (especially for  $\text{LiBF}_4$ )
- $\text{LiTFSA}$  and  $\text{LiPF}_6$  exhibit the best results in Li|NMC as well as Li|C cells
- SEI formation is already finished after the first cycle (Li|C cells)
- Lithium intercalation in graphite is observed for every electrolyte mixture
- Current rates up to C/4 (Li|NMC) as well as C/6 (Li|C) are realizable at room temperature\*

## NMC|C - cell performance



L-1 =  $\text{LiBF}_4$   
L-2 =  $\text{LiOTf}$   
L-3 =  $\text{LiClO}_4$   
L-4 =  $\text{LiPF}_6$   
L-5 =  $\text{LiTFSA}$

Cycling tests of C|NMC cells (left) at room temperature with different current rates in a potential range of 3 – 4.2 V vs.  $\text{Li/Li}^+$  (left). In the middle a coin cell is shown which is running for 120 cycles with mixture L5 (3 – 4.2 V, C-rate up to 0.5 C). On the right side the temperature dependence of the C|NMC cell with mixture L-5 at 0.4 C is depicted.

- $\text{LiBF}_4$ ,  $\text{LiOTf}$ , and  $\text{LiClO}_4$  exhibit a poor cell performance in NMC|C cells
- $\text{LiTFSA}$  exhibits the best results in C|NMC cells in performance testing as well as in cells at constant current rates of C/20\*
- Specific capacities of >150 mAh/g are received in a potential range of 3 – 4.2 V for the  $\text{LiTFSA}$  electrolyte reversibly
- Current rates up to C/2.5 are realizable at 40 °C
- Discharge Capacity of 80% after 400 cycles

## Conclusions

- Strong dependence of the cell performance of the applied conducting salts in the following order:  $\text{LiTFSA} > \text{LiPF}_6 > \text{LiClO}_4 > \text{LiOTf} > \text{LiBF}_4$
- Best performance in case of lithium bis(trifluoromethylsulfonyl)azanide as conducting salt
- Successful cycling of the NMC|C cells up to current rates of C/5 (specific capacity > 100 mAh/g) is possible

## Acknowledgements

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