PAUL SCHERRER INSTITUT

ELECTROCHEMISTRY LABORATORY

BATTERIES

We create chemistry

Cycling-Related Electrolyte (De-)Composition in an EC/EMC Based Battery System

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Motivation

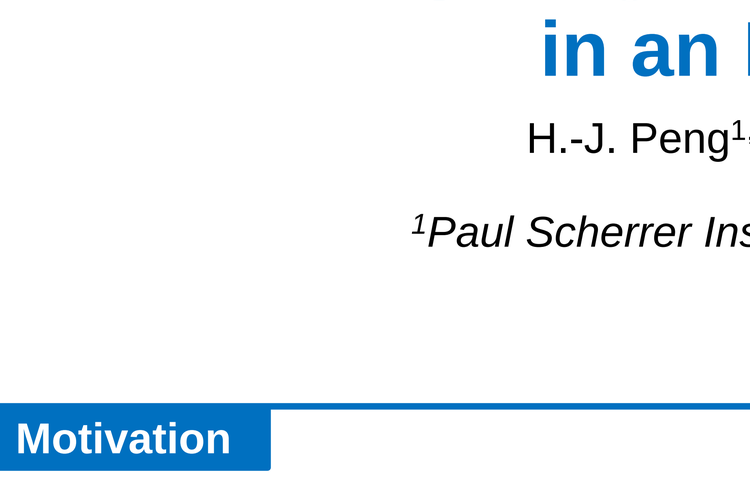
Alkoxides

- is one of the main reduction products of carbonate-based electrolytes
- trigger multi-pathway electrolyte degradation[1]
- **?** affects the electrochemical performance of the cells

Goal

- Clarify the parameters influencing the formation of alkoxide-anion
- Correlate the formation of alkoxide-anion to the cell performance

Approach



Net reaction:
2EMC ↔ DMC + DEC

➡ EMC-containing electrolyte was chosen

Mechanism of the trans-esterification reaction of EMC[1-3]

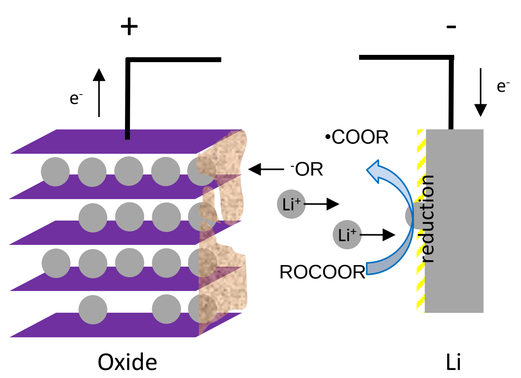
Experimental

- **WE** and cycling protocols

Active Material	Composition	Nominal specific charge [mAh/g]	Potential Window [V vs. Li^{+}/Li]	Cycling Protocol for C/2 rate	Cycling Protocol for C/10 rate
NCM111	$Li_{1.05}(Ni_{0.33}Co_{0.33}Mn_{0.33})_{0.95}O_2$	141	2.5 - 4.3	1st 2 cycles: C/10 3rd cycle onward: C/2	C/10
NCM523	$Li_{1.03}(Ni_{0.50}Co_{0.20}Mn_{0.30})_{0.97}O_2$	162	2.5 - 4.3	1st 2 cycles: C/10 3rd cycle onward: C/2	C/10
HE-NCM	$Li_{1.17}(Ni_{0.22}Co_{0.12}Mn_{0.66})_{0.83}O_2$	250	2.5 - 4.8	1st cycle: C/15 2nd cycle: C/10 3rd cycle onward: C/2	

- **Electrolyte: 1 M $LiPF_6$ in EC: EMC = 3:7** (wt%)
- **Separator**: glass fiber (+ Celgard 2400, for SEM)
- **CE**: Li (half-cell) / graphite (full-cell)
- Electrolyte analysis:
  extract electrolyte with 1 ml PC → gas chromatography

Conclusion



The formation of alkoxide-anion…

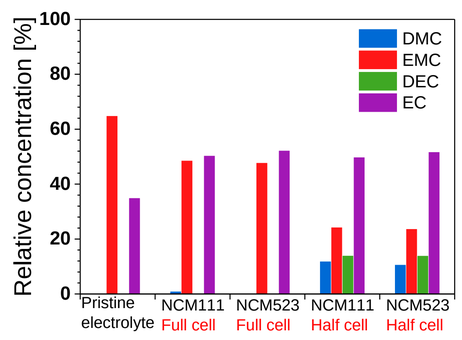
- is coming from poor anode passivation
- is temporarily decreased at higher upper cut-off potentials
- results in the instability of cathode/electrolyte interface and capacity fading

Parameters affecting alkoxide-anion formation

Anode passivation & cycling rate

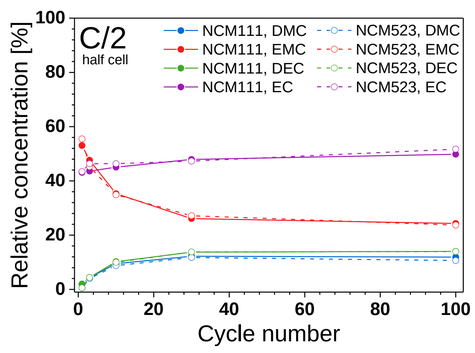
Full-cells vs. Half-cells

→ Electrolyte composition after 100 cycles



C/2 vs. C/10

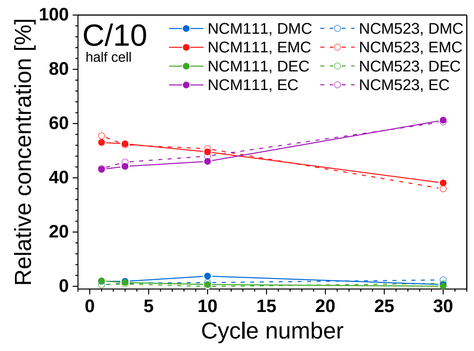
→ Change of electrolyte composition during 100 cycles



NCM111 & NCM523

The formation of alkoxide-anion ↓ when

- graphite is used as CE
- cycling rate ↓



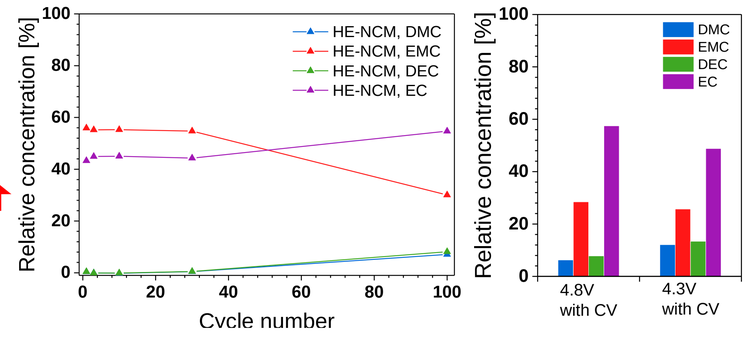
Upper cut-off potential

HE-NCM

The formation of alkoxide-anion ↓ when

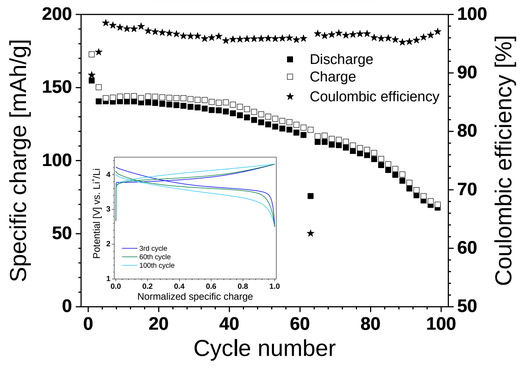
- upper cut-off potential ↑

↳ better passivated CE in HE-NCM system

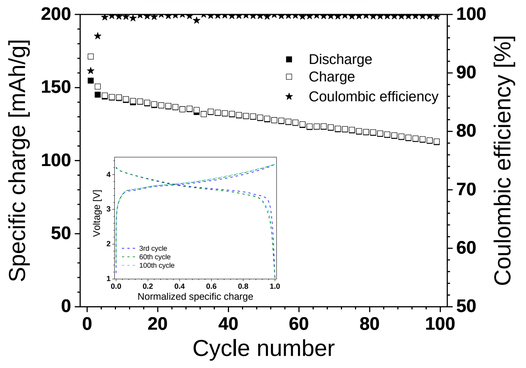


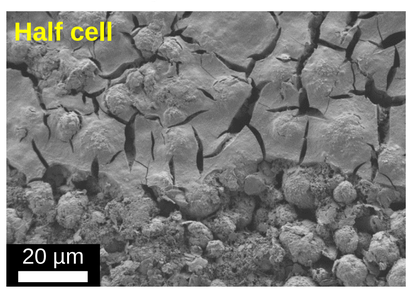
Influence on the cell performance

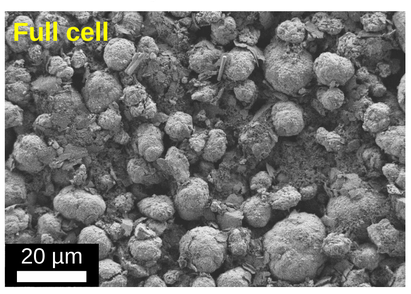
NCM111 Half-cell



NCM111 Full-cell







In half cell
- higher overpotential
- significantly more degradation products on the cathode surface
- more pronounced performance decay

[1] G. Gachot, S. Grugeon, M. Armand, S. Pilard, P. Guenot, J.-M. Tarascon, S. Laruelle, Journal of Power Sources, 178 (2008) 409-421
[2] E.S. Takeuchi, H. Gan, M. Palazzo, R.A. Leising, S.M. Davis, Journal of The Electrochemical Society, 144 (1997) 1944-1948.
[3] H. Kim, S. Grugeon, G. Gachot, M. Armand, L. Sannier, S. Laruelle, Electrochimica Acta, 136 (2014) 157-165.

Acknowledgments

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