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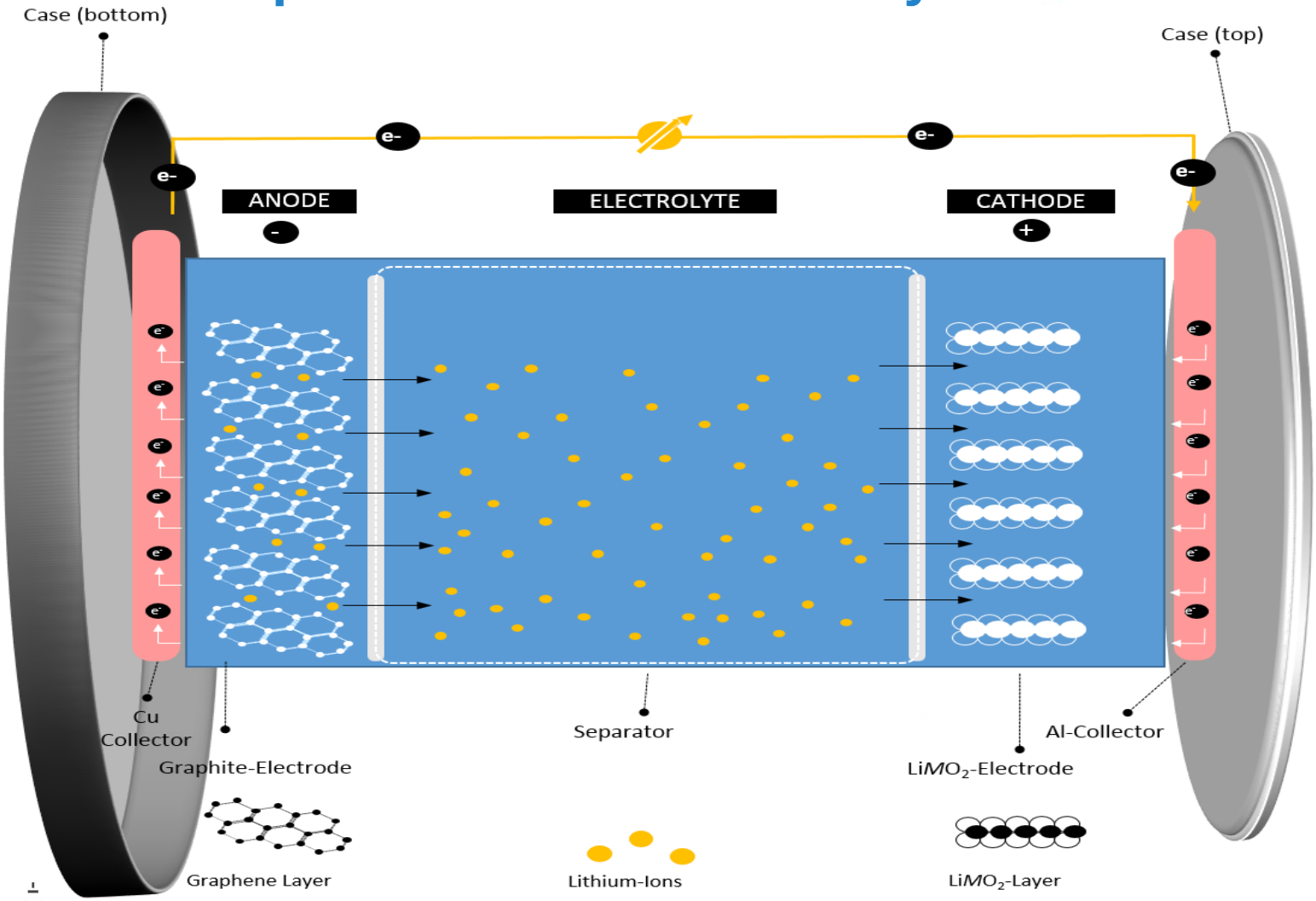
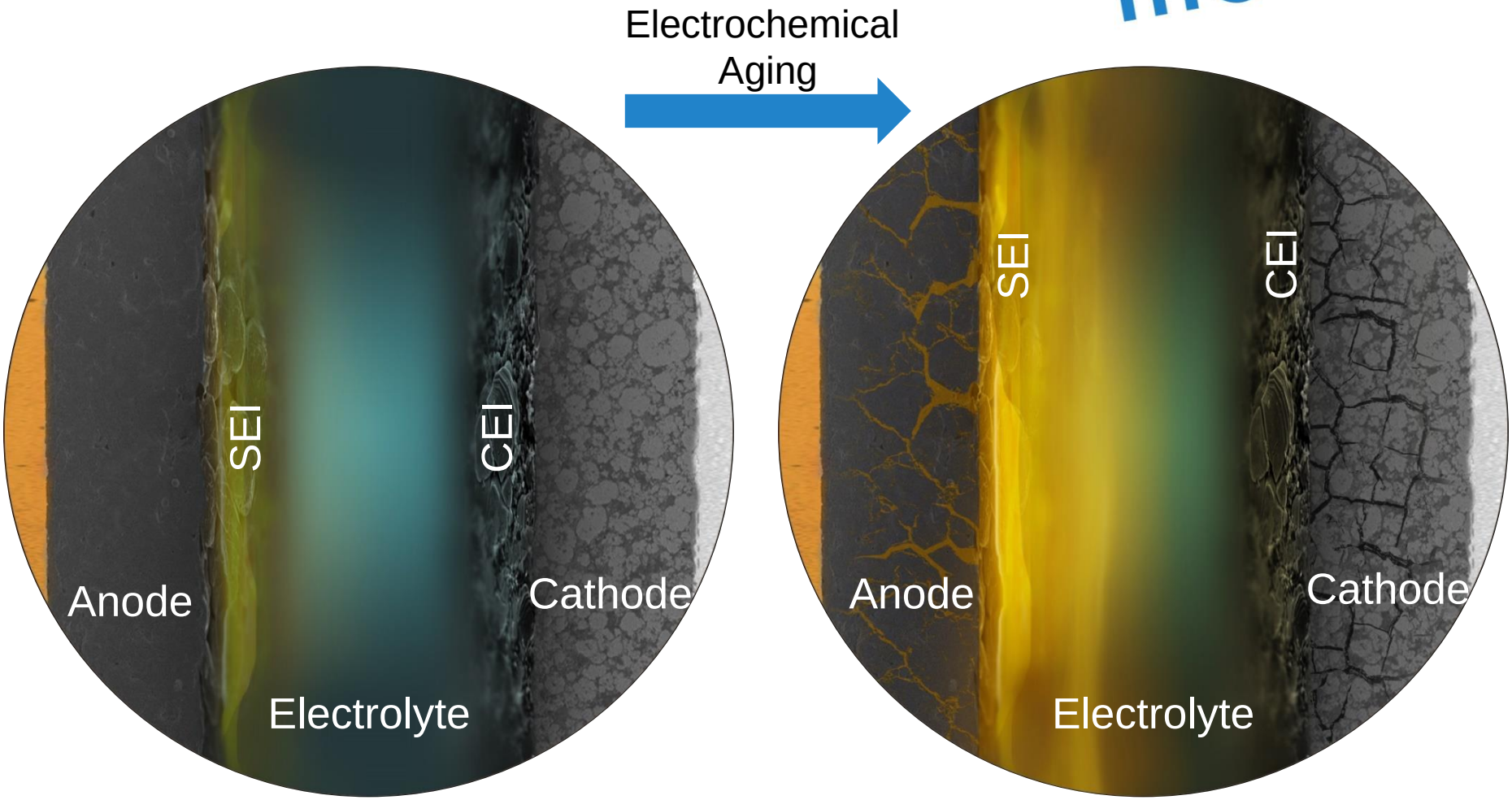
Matrix-Matched Calibration Approach for Sector-Field Glow Discharge-Mass Spectrometry in the Field of Lithium Ion Batteries

Anwendertreffen Analytische Glimmentladungsspektrometrie 2017, Bremen, 17.05.2017

Basic Principle – Lithium Ion Battery



Aging Effects in LiBs

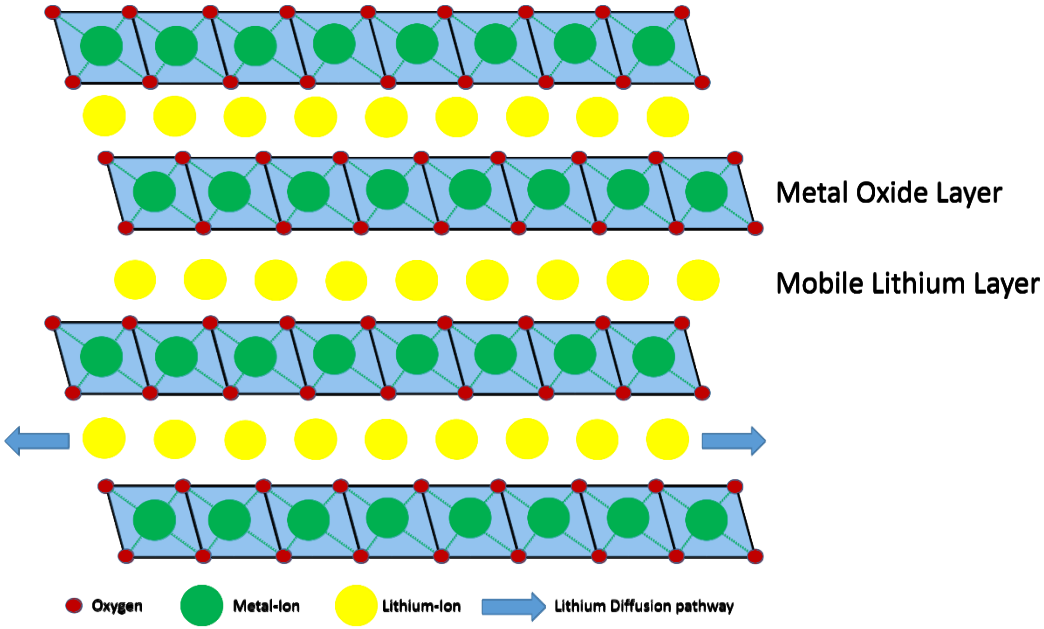


Fresh Cell

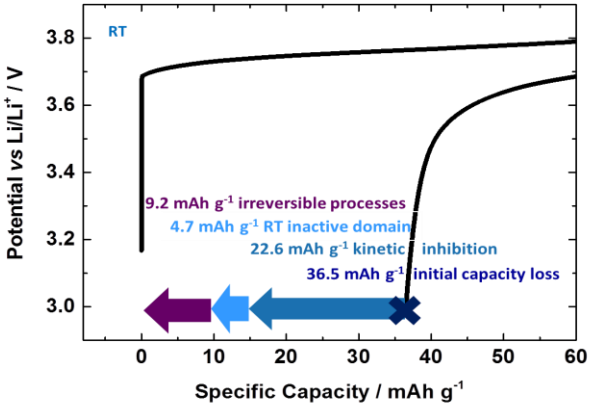
Aged Cell

Post-mortem analysis: How much Lithium is in the Cathode?

- As the capacity loss can not be attributed exclusively to TMD other effects like kinetic hindrance of lithium re-insertion affect it



Electrochemical observation



[1] J. Kasnatscheew, M. Evertz, B. Streipert, R. Wagner, R. Klopsch, B. Vortmann, H. Hahn, S. Nowak, M. Amereller, A.C. Gentschev, P. Lamp, M. Winter, *Phys. Chem. Chem. Phys.*, 18 (2016), 3956-3965.

Analytical observation

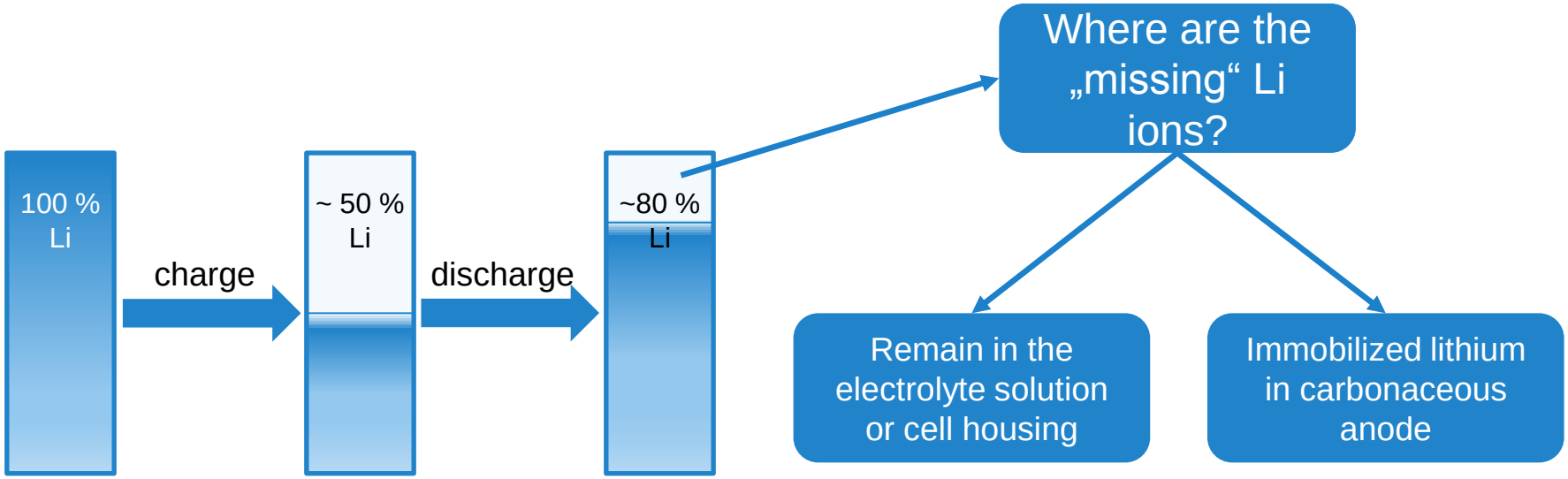
Sample liquefaction

ICP-OES measurement

Data evaluation

Lithium Loss in Cathode Materials

- After 50 cycles loss of Lithium in the range of 15 to 20 % were observed in various cathode materials



- Analytical Investigation of anodes are of special interest
- Especially depth-resolved and surface analysis

Challenges for the Glow Discharge

- Only semi-quantitative results (error up to 500 %) are accessible using the standard GD-MS calibration procedure
  - Based on Fe matrix
- Thus, self prepared standards are essential for accurate analysis
- Carbonaceous materials are the most challenging due to the low excitation yield of carbon to other elements
- Two ways accessible:
  - Sintered materials using Li, etc. sources
  - Matrix matched standards

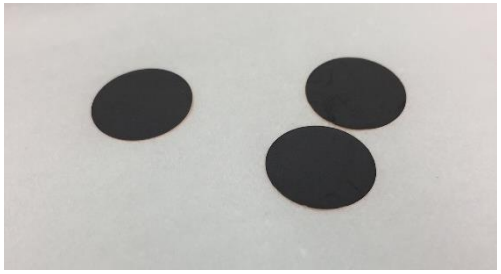
Electrode Preparation

- $Li_1Ni_{1/3}Co_{1/3}Mn_{1/3}O_2$ acts as source for the corresponding element
- Composite graphite (MesoCarbon Microbeads / Hard Carbon) acts as carbonaceous source

Homogenization in ball-mill using NMP as solvent

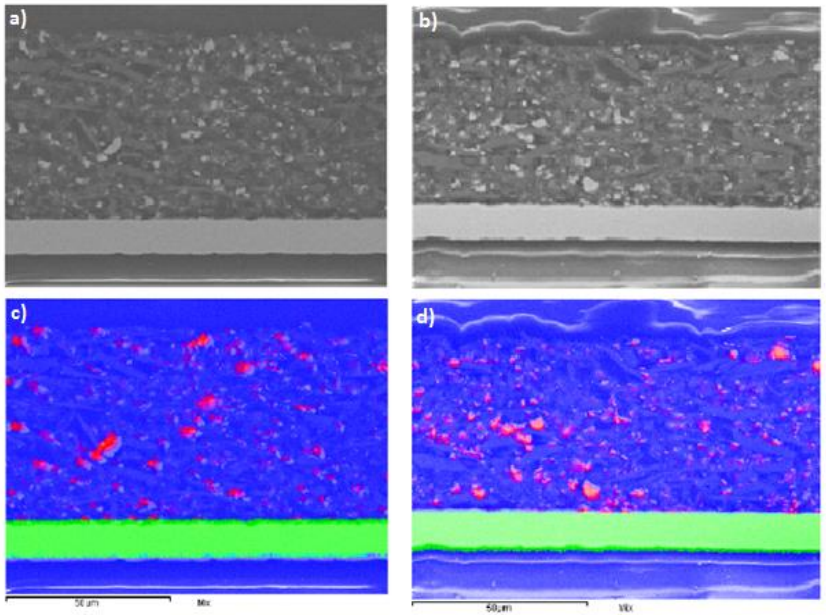
Drying @ 80 °C

Punch out electrodes with 12 mm in diameter

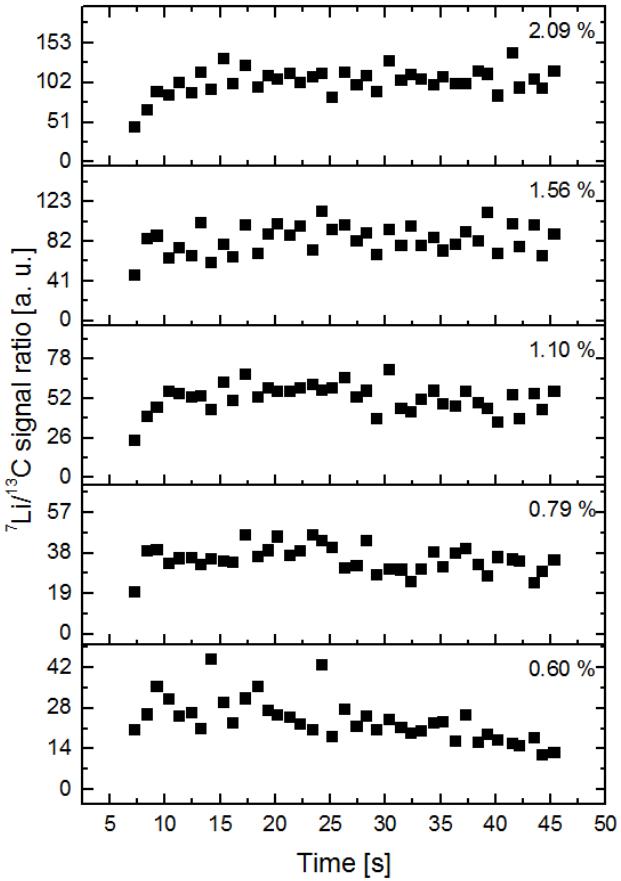


Characterization of Standards

SEM/EDX images



LA-ICP-MS

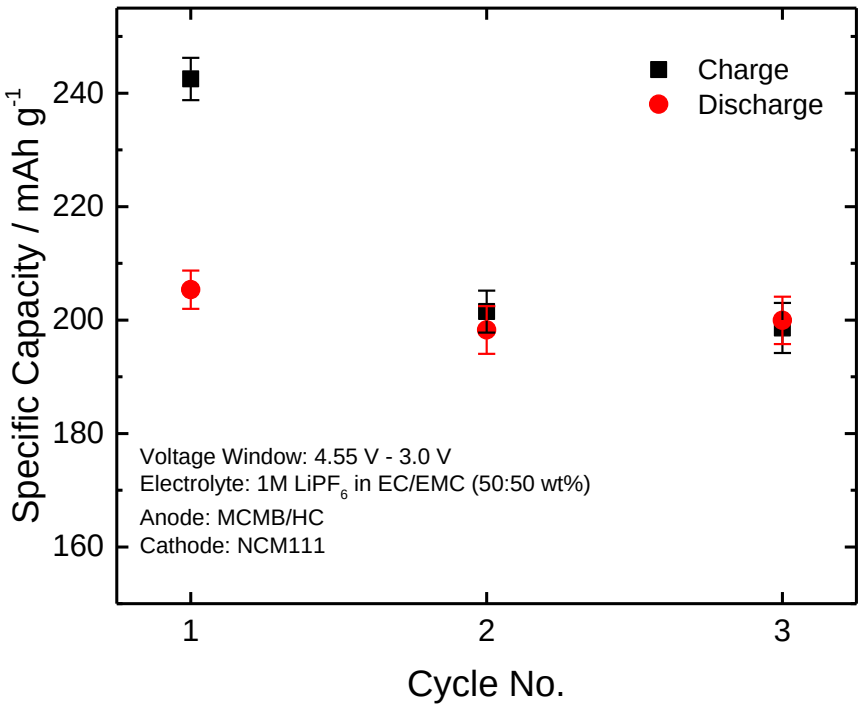


Good homogeneity observed via SEM/EDX and LA-ICP-MS

[2] T. Schwieters, M. Evertz, M. Mense, M. Winter, S. Nowak, J. Power Sources (356), 2017, Pages 47–55.

GD-SF-MS: Charge/Discharge Aging and Set-up

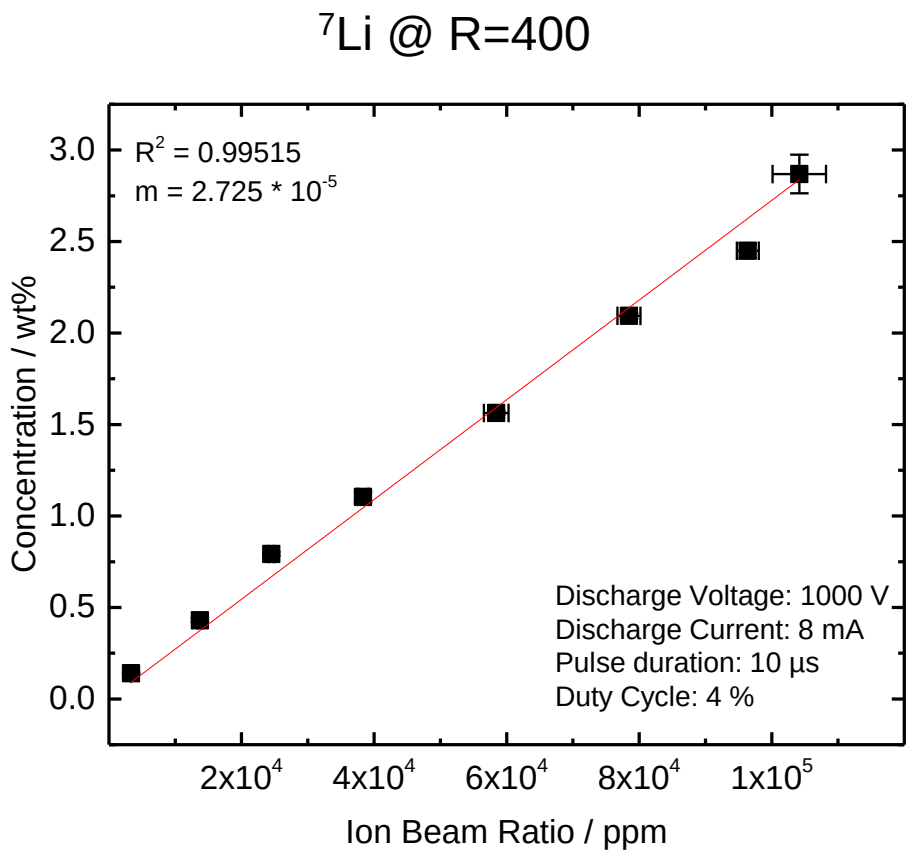
- Thermo Fisher Element GD was used with an equipped pulsed source
- Every calibration sample was pre-sputtered 10 minutes and then measured in low and medium resolution
- Discharge Voltage: 1000 V
- Discharge Current: 8 mA
- Pulse duration: 10 µs
- Duty Cycle: 4 %



Calibration Curves

- Good linearity over the calibration ranging from 0.1 wt% to 3 wt% of ^{7}Li at low resolution
- At medium resolution also linearity greater 0.985 could be observed for elements of interest

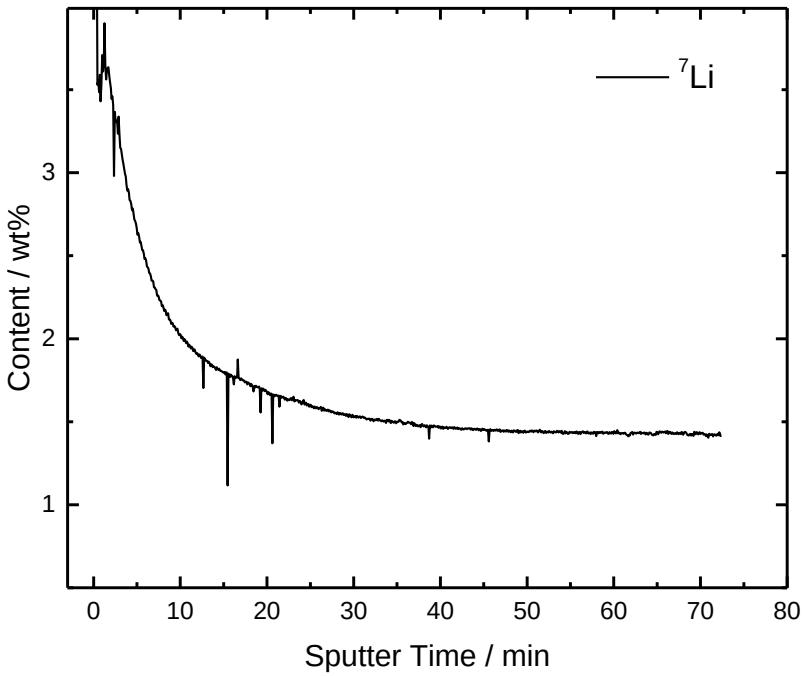
	LOD / ppm	LOQ / ppm
^{7}Li @ R=400	80	240
^{7}Li @ R>4000	162	486
^{55}Mn @ R>4000	265	797
^{59}Co @ R>4000	393	1180
^{58}Ni @ R>4000	333	1001



[3] M. Evertz, T. Schwieters, M. Börner, M. Winter, S. Nowak, submitted to *J. Anal. At. Spectrom.*, 2017.

Post-mortem analysis: Lithium Deposition on Carbonaceous Electrodes

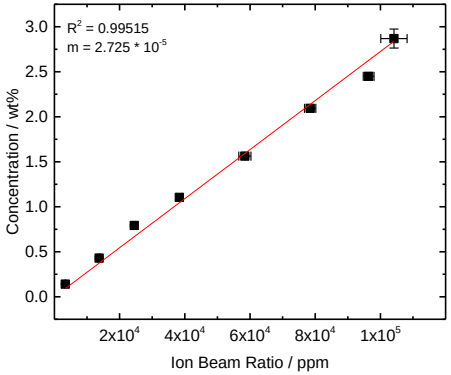
- Samples dried prior to analysis in vacuum
- Accumulation of lithium on the surface of the electrode
  - Origin is the insulation and protective solid electrolyte interphase film
- In deeper layers of the electrode a stable signal of ^{7}Li is observed
- Content of lithium intercalated and irreversible lost
- Validation *via* ICP-OES shows lithium contents of 1.2 wt% in the bulk electrode
- Reason is high irreversible capacity loss of the negative electrode material



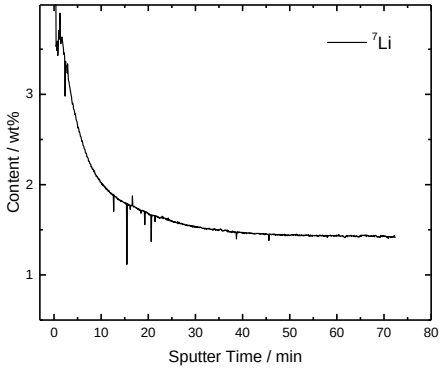
Conclusion

- Matrix-matched self prepared calibration materials were prepared with rising content of lithium up to 2.8 wt%

- Calibration curves in low and medium resolution were monitored with $R^2 > 0.985$



- Sputtering shows an accumulation of lithium in the first minutes of sputtering and a stable signal at 1.5 wt% lithium



Outlook

- Lithium deposition investigation using different carbonaceous materials in a half-cell set-up
  - Investigation of standard electrolyte
  - Investigation of ^{6}Li-enriched electrolyte

- Lithium deposition of cathodes in a half-cell set-up

- Transition Metal Dissolution of LNMO full-cells and detection of lithium losses

Acknowledgment

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Prof. Dr. Martin Winter

Dr. Sascha Nowak

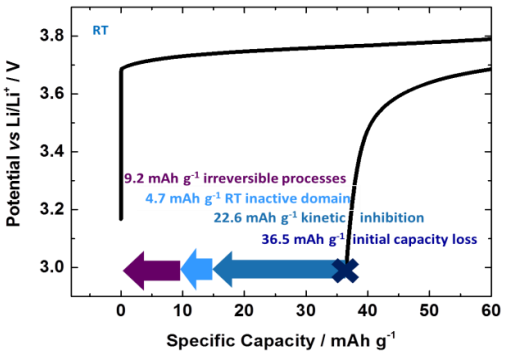
Marcel Diehl

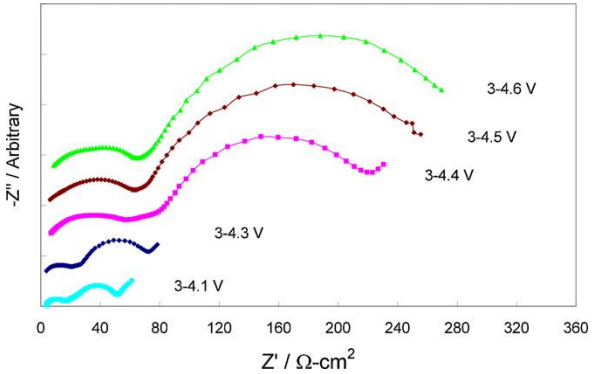
Analytics & Aging

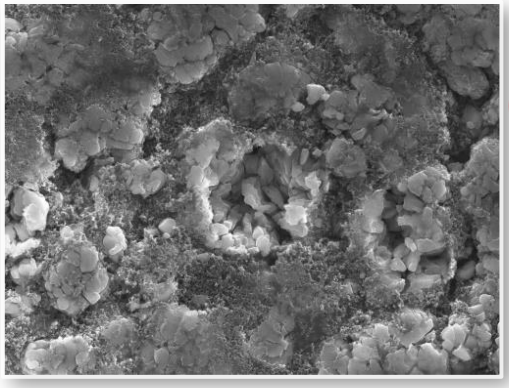
Westfälische Wilhelms-Universität Münster

Back Up

Aging Effects of Active Materials







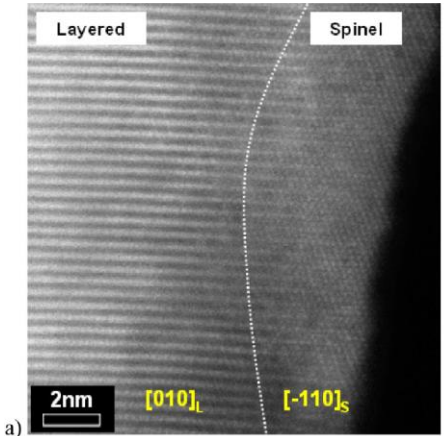
Loss of Lithium

Overall cell impedance rise

Li ion degradation at high voltages

Transition metal dissolution

Irreversible phase changes



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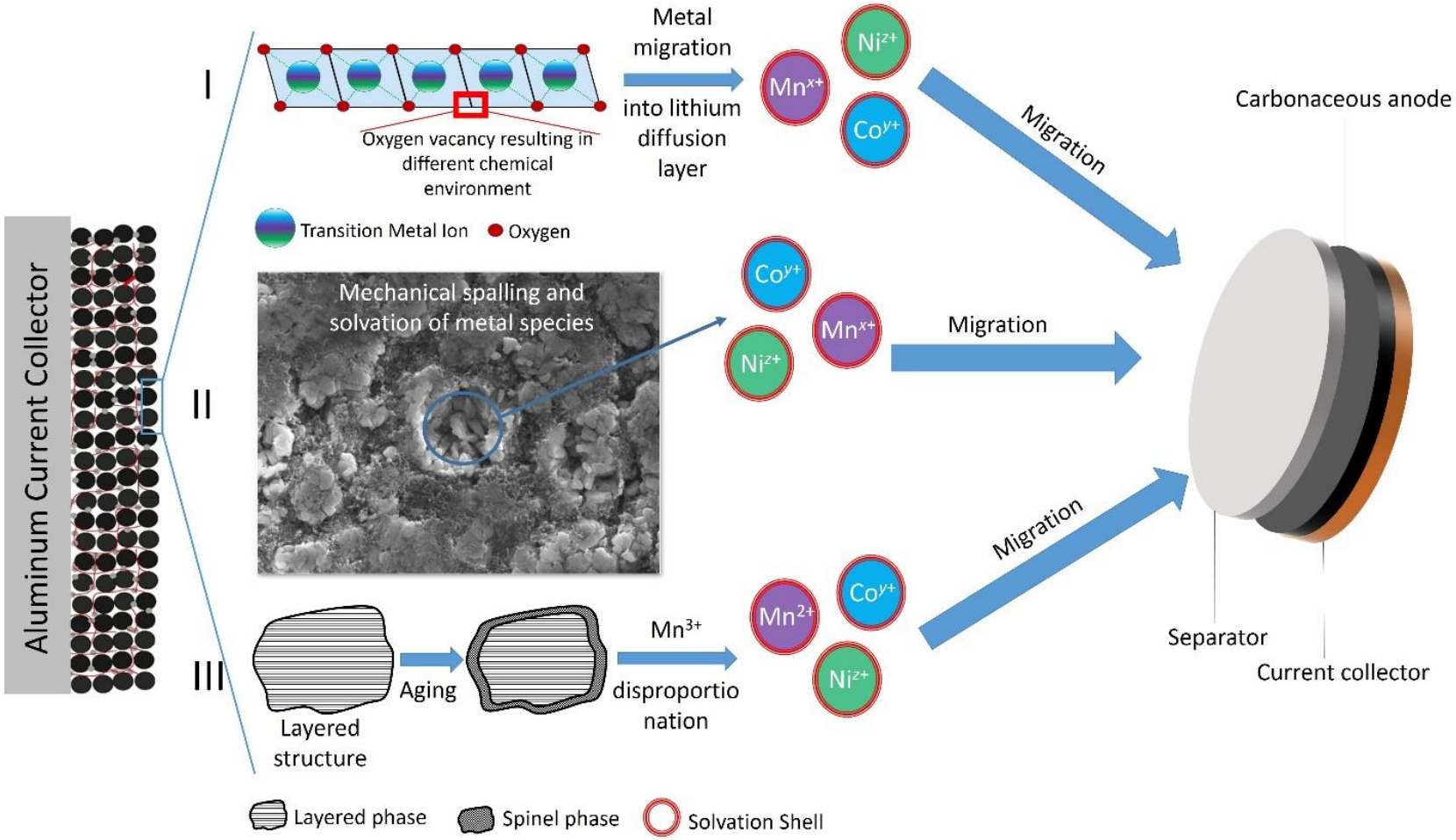
[2] M. Evertz, F. Horsthemke, J. Kasnatscheew, M. Börner, M. Winter, S. Nowak, *J Power Sources*, 329 (2016), 364-371.
[3] A. Boulineau, L. Simonin, J.-F. Colin, E. Canévet, L. Daniel, S. Patoux, *Chem. Mater.* 24 (2012), 3558−3566
[4] H. Zheng, Q. Sun, G. Liu, X. Song, V.S. Battaglia, *J Power Sources*, 207 (2012) 134-140.

Conclusion:
Transition Metal Dissolution



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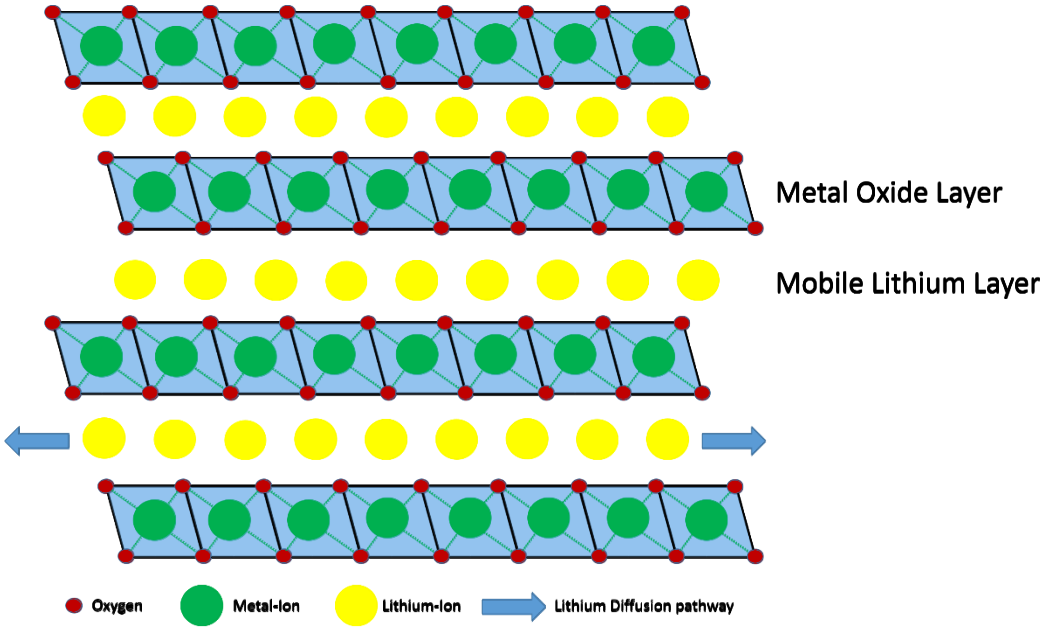

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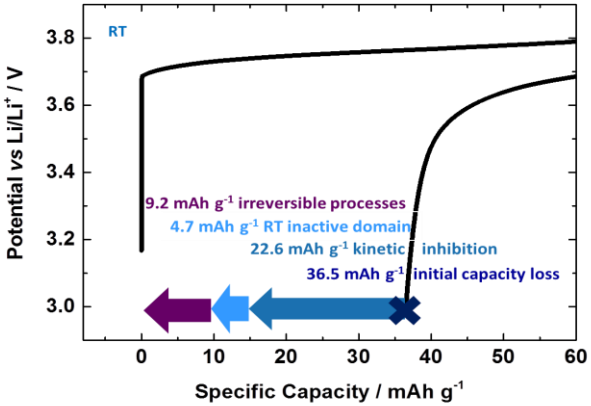

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