P-067

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GD-OES Depth Profiling – A valuable new Technique to Study various Aging Effects in Li-ion Cells

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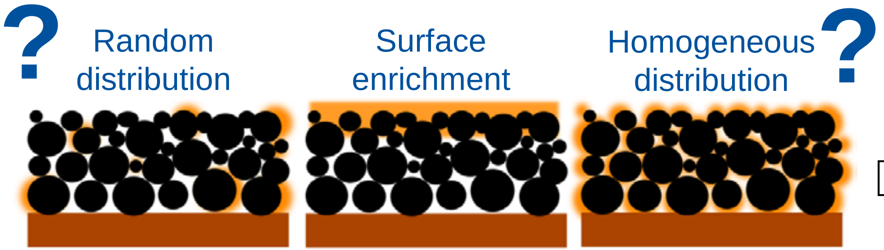
Where do side-reactions happen in anodes of Li-ion cells?



Limitations of established methods:
SEM, XPS: limited to surface
ICP, XRD: limited to bulk
EDX: Li not detectable

Here: Comparison of four examples:
- SEI on graphite anodes
- SEI on Si/graphite anodes
- Li plating on graphite anodes
- Cu re-deposition on graphite anodes

Method development: GD-OES* depth profiling

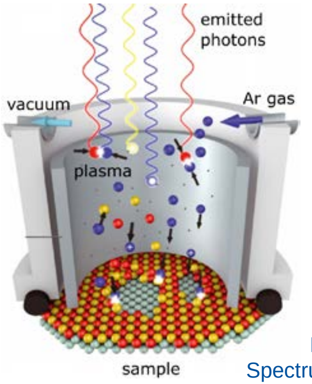


Image source: Spectruma Analytics GmbH

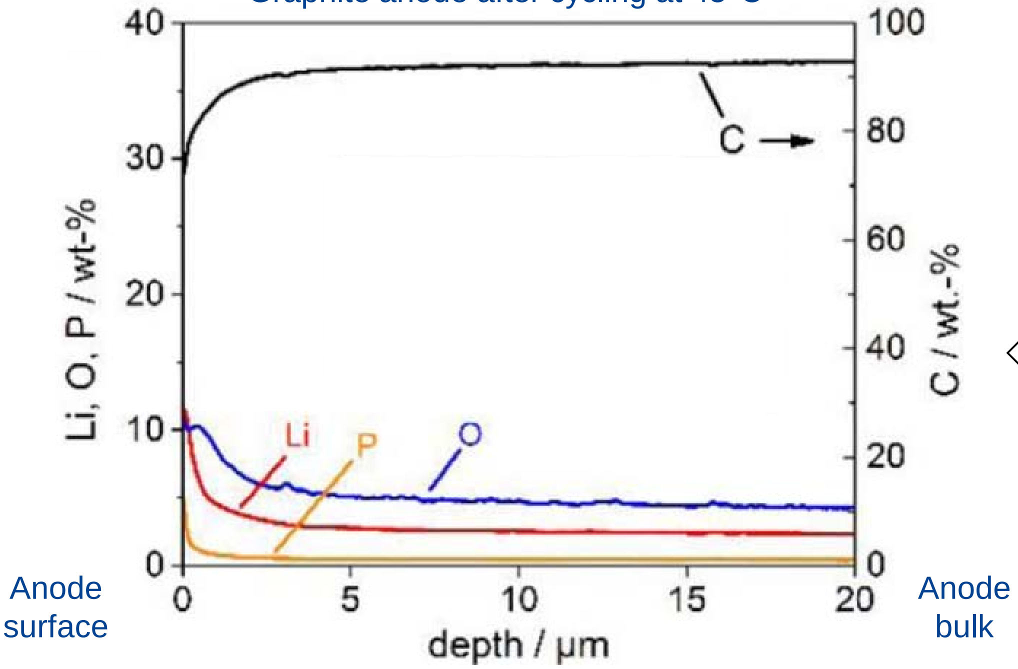
1) Sample sputtering in Ar plasma
2) Elemental detection by optical emission spectroscopy

- Calibration via samples with known elemental contents (Li, C, P, O, Si, Cu)
- Critical cross-checking by complementary methods (EDX of cross-sections, simulations, interrupted GD-OES sputtering, investigation of GD-OES craters)

*Glow discharge optical emission spectroscopy (GD-OES)

Example 1: SEI growth on graphite anodes

GD-OES depth profile of
Graphite anode after cycling at 45°C



After formation:

- Very thin initial SEI (<0.5µm) mostly on anode surface as indicated by Li peak
- Li consumption = initial capacity loss during formation

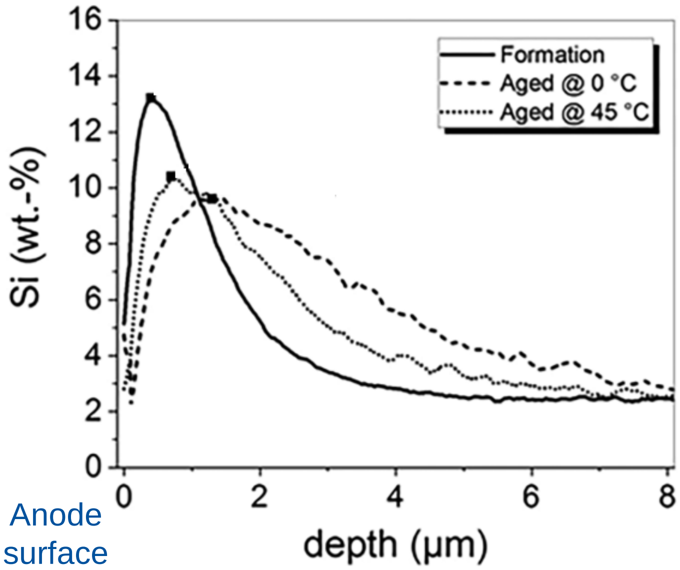
After long-term cycling (see Figure):

- SEI-thickness increased (~2µm) compared to initial SEI
- SEI growth mostly on <u>anode surface</u>
- Li consumption in SEI explains most of the capacity loss during aging

T. Waldmann, N. Ghanbari, M. Kasper, M. Wohlfahrt-Mehrens, J. Electrochem. Soc. 162 (2015) A1500.
T. Waldmann, K. Richter, M. Kasper, M. Wohlfahrt-Mehrens et al., J. Electrochem. Soc. 164 (2017) A3154.

Example 2: SEI growth on Si/graphite anodes

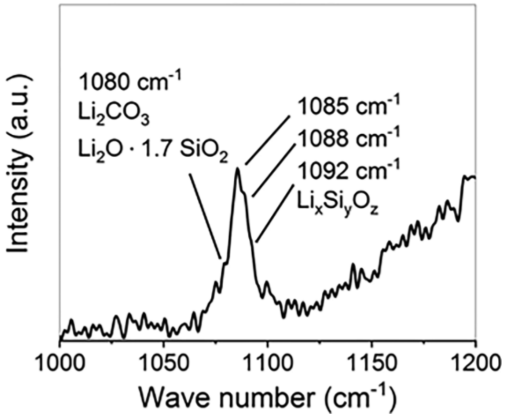
GD-OES depth profile of
Si/Graphite anode after formation/cycling



Anode surface

Anode bulk

Raman spectroscopy
of Si/Graphite anode surface

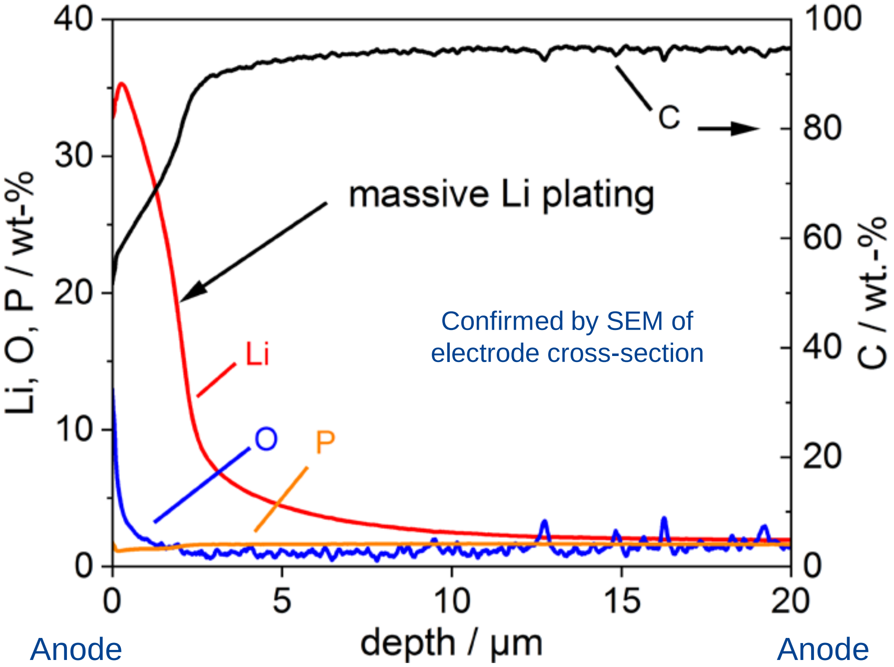


- Li peak indicates SEI formation mostly on Si/graphite anodes surface
- No Si peak before formation
- reduction of peak by washing with DMC
- Raman spectroscopy indicates Li silicate formation

K. Richter, T. Waldmann, M. Memm, M. Kasper, M. Wohlfahrt-Mehrens, J. Electrochem. Soc. 165 (2018) A3602.
K. Richter, T. Waldmann, M. Kasper, C. Pfeifer, M. Memm, P. Axmann, M. Wohlfahrt-Mehrens, J. Phys. Chem. C 123 (2019) 18795.

Example 3: Li deposition on graphite anodes

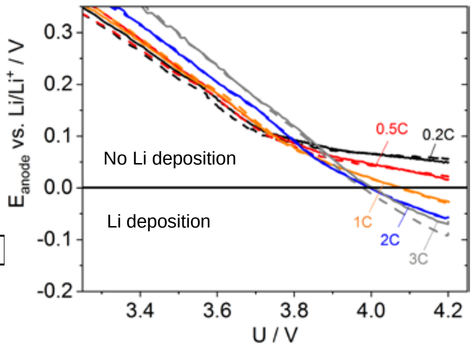
GD-OES depth profile of
Li plating on graphite anode
after 18 cycles at 0°C / 0.5C



Anode surface

Anode bulk

Anode potentials vs. Li/Li^+ measured
in pouch full cells with Li reference electrode



Thermodynamic condition for Li deposition:
Anode potential < 0V vs. Li/Li^+
($Li^+ + e^- \rightarrow Li$)

T. Waldmann et al., J. Electrochem. Soc. 163 (2016) A1232.

- Li peak shows Li deposition mostly on graphite anode surface after aging
- Consistent with simulations on electrode level

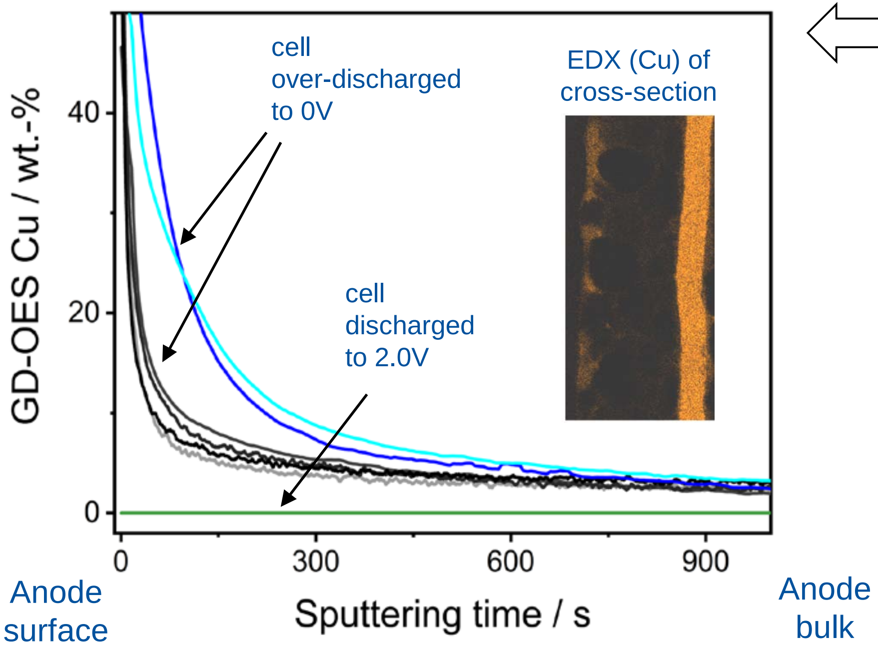
S. Hein, A. Latz, Electrochim. Acta 201 (2016) 354.

N. Ghanbari et al., ECS Electrochem. Lett. 4 (2015) A100.; N. Ghanbari et al. J. Phys. Chem. C 120 (2016) 22225.
T. Waldmann, K. Richter, M. Kasper, M. Wohlfahrt-Mehrens et al., J. Electrochem. Soc. 164 (2017) A3154.

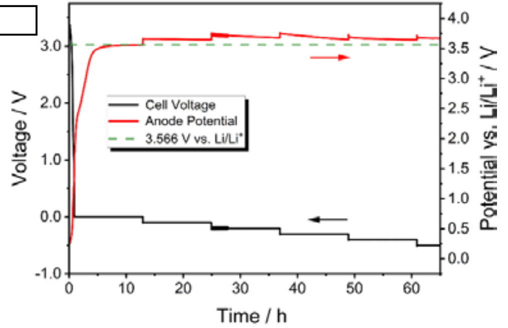
See also talk by
M. Flügel et al.

Example 4: Cu dissolution & re-deposition

GD-OES depth profile of
Re-deposited Cu on graphite anode
after over-discharge to 0V



Anode potentials vs. Li/Li$^+$ measured
in pouch full cells with Li reference electrode



Thermodynamic condition
for Cu dissolution:
Anode potential > 3.56V vs. Li/Li$^+$
(dissolution: Cu → Cu$^+$ + e-
re-deposition: Cu$^+$ + e- → Cu)

- Li peak shows Cu re-deposition on graphite anode surface after over-discharge to 0V
- No Cu dissolution for cell opened at 2V
- According to Gibbs Phase Rule:
  Constant anode potential at 3.56V vs. Li/Li$^+$
  → dissolution as Cu$^+$ (Cu^{2+}: 3.38V vs. Li/Li$^+$)

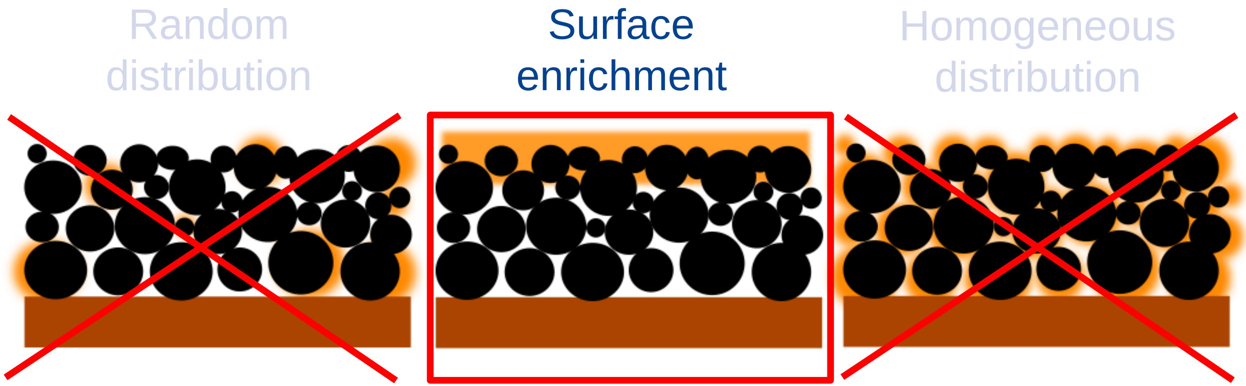
M. Flügel, T. Waldmann, M. Kasper, M. Wohlfahrt-Mehrens, ChemPhysChem 21 (2020) 2047.
M. Flügel, M. Kasper, C. Pfeifer, M. Wohlfahrt-Mehrens, T. Waldmann, J. Electrochem. Soc. 168 (2021) 020506.

Conclusions

Side-reactions mostly observed on anode surfaces for four exemplary mechanisms:

- SEI growth on graphite anodes (electrolyte decomposition)
- SEI growth on Si/graphite anodes (Li silicate formation)
- Li deposition on graphite anodes (condition for deposition fulfilled first on surface)
- Cu dissolution & re-deposition (possibly reaction of Cu compound with SEI on surface)

Consistent with critical comparison with complimentary methods & simulations.



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