T02 GD-OES depth profiling - ZSW

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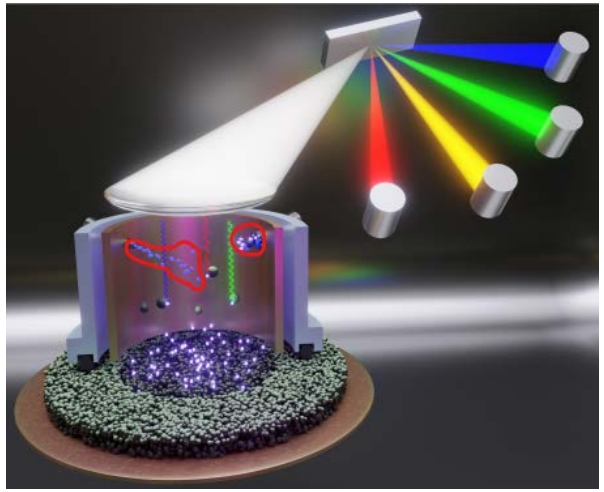
Open Innovation Test Bed for Electrochemical Energy Storage Materials

Principle

- Ar sputtering of negative electrode surface to current collector
- Detection of sputtered elements by optical emission spectroscopy (incl. Li, Si, C, O, P, Cu, …)
- Measurements at different parts of a sample due to small measuring spot (Ø 2.5mm)



Why is it useful ?

- Semi-quantitative detection of SEI growth/Li plating on graphite anodes
- Detection of Cu
- Determination of Si content in anodes

How it works

Destructive analysis of anodes taken from Post-Mortem analysis of production line

What can be seen

Depth profile of elemental distribution for anodes from electrode surface to current collector

What kind of sample ?

Anodes, ~1cm², reproduction required

Investigation time-scale : days

Maturity level : advanced

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Example 1: SEI growth on graphite anodes

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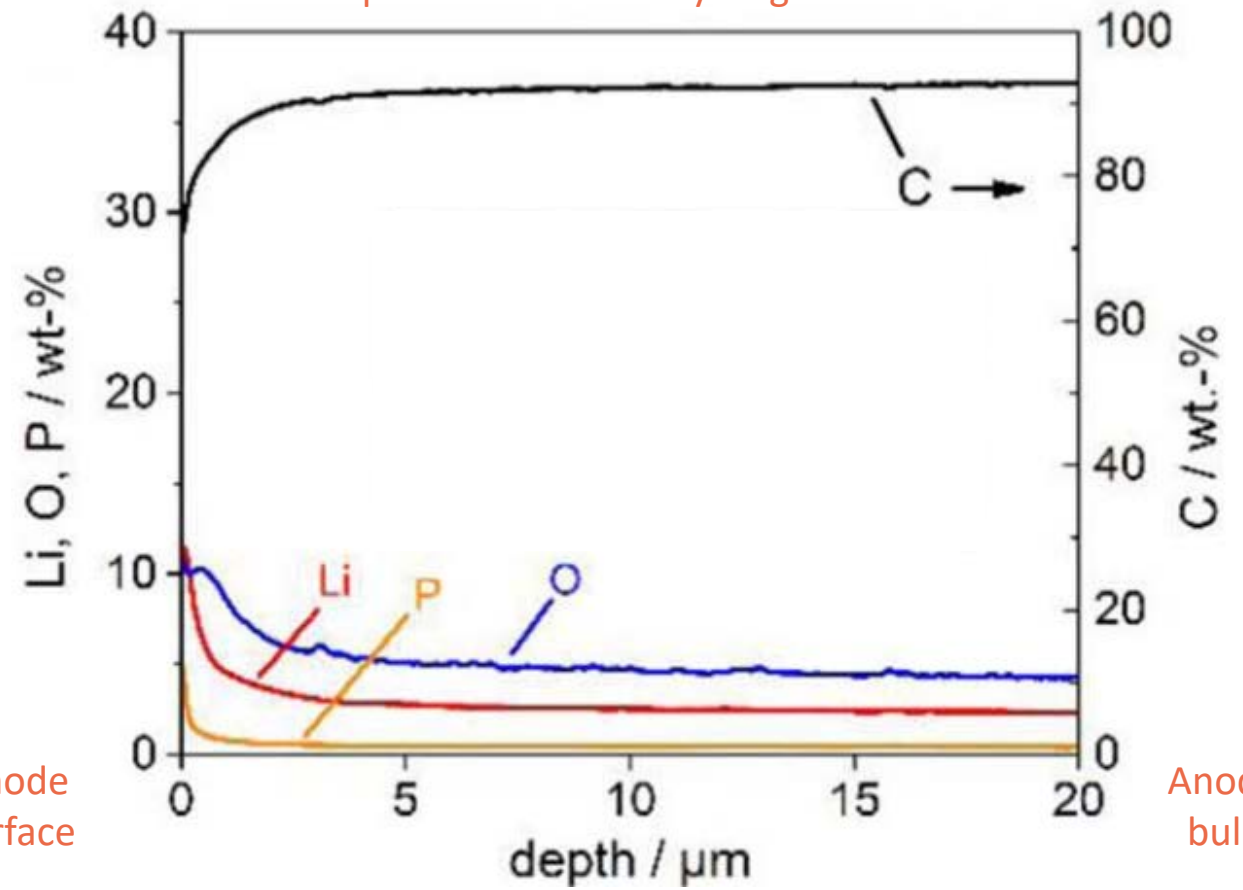
GD-OES depth profile of
Graphite anode after cycling at 45°C



Anode surface

Anode bulk

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 anode surface
- Li consumption in SEI explains most of the capacity loss during aging

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T. Waldmann, N. Ghanbari, M. Kasper, M. Wohlfahrt-Mehrens, J. Electrochem. Soc. 162 (2015) A1500, https://doi.org/10.1149/2.0411508jes
T. Waldmann, K. Richter, M. Kasper, M. Wohlfahrt-Mehrens et al., J. Electrochem. Soc. 164 (2017) A3154, https://doi.org/10.1149/2.0961713jes

Example 2: SEI growth on Si/graphite anodes

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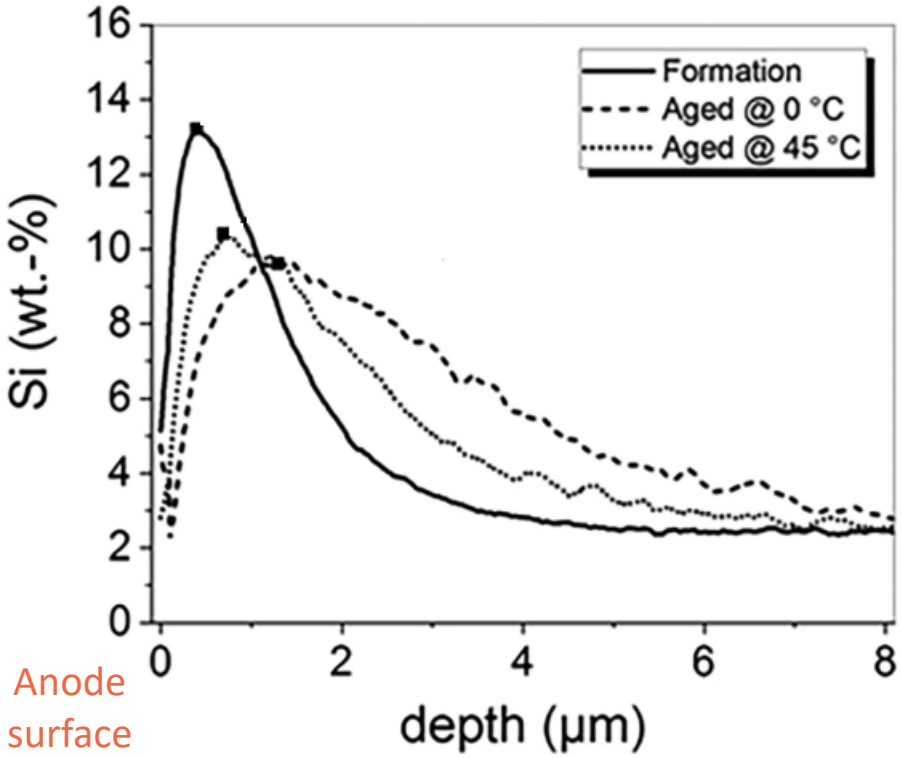
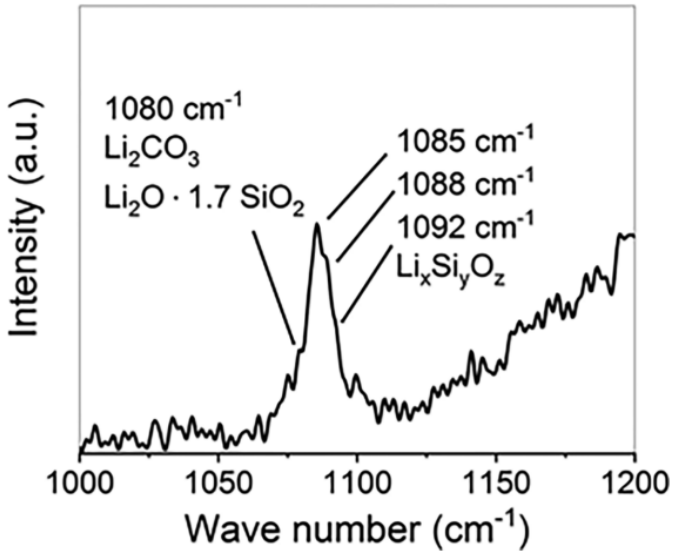
GD-OES depth profile of
Si/Graphite anode after formation/cycling



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

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K. Richter, T. Waldmann, M. Memm, M. Kasper, M. Wohlfahrt-Mehrens, J. Electrochem. Soc. 165 (2018) A3602, https://doi.org/10.1149/2.0071816jes
K. Richter, T. Waldmann, M. Kasper, C. Pfeifer, M. Memm, P. Axmann, M. Wohlfahrt-Mehrens, J. Phys. Chem. C 123 (2019) 18795, https://doi.org/10.1021/acs.jpcc.9b03873

Example 3: Li deposition on graphite anodes

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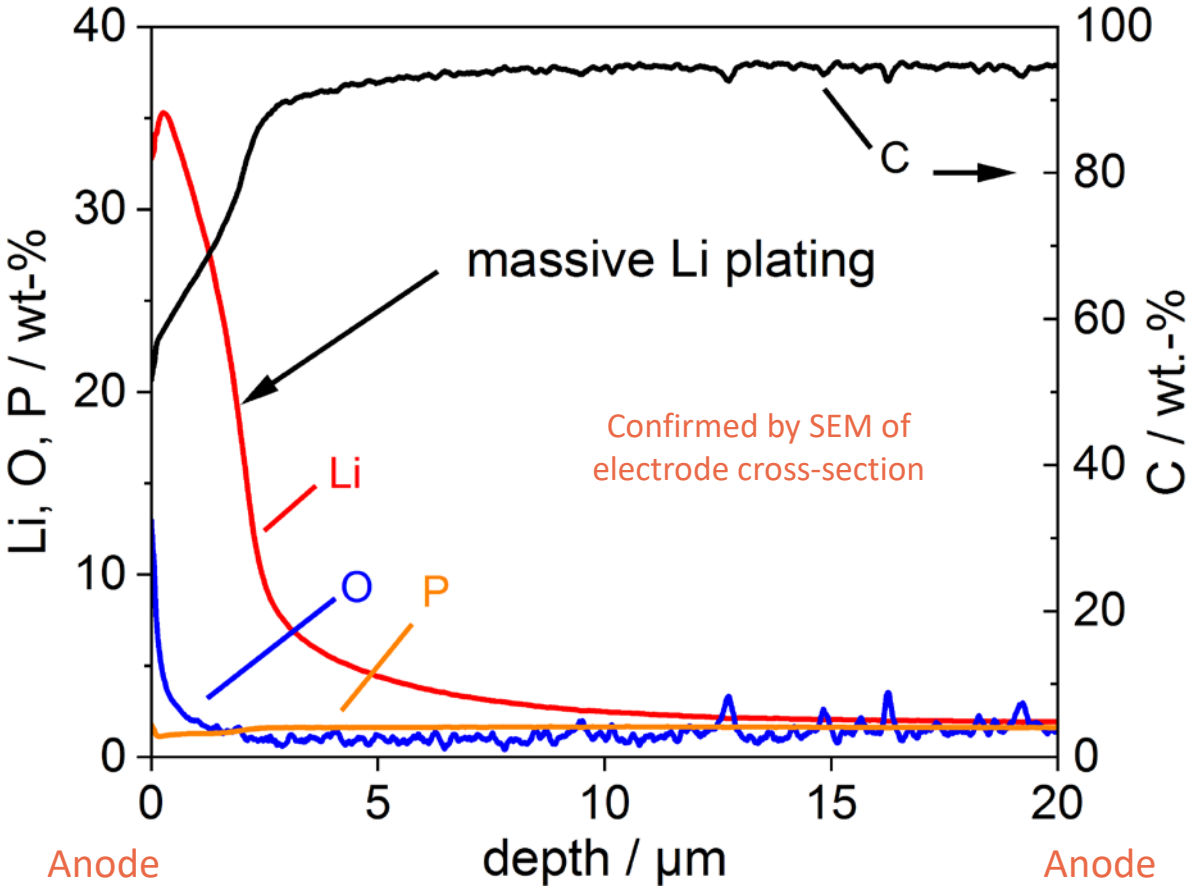
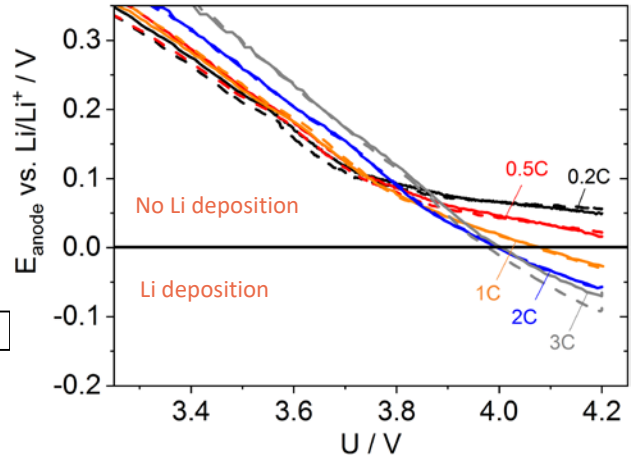
GD-OES depth profile of
Li plating on graphite anode
after 18 cycles at 0°C / 0.5C



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.

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N. Ghanbari et al., ECS Electrochem. Lett. 4 (2015) A100.; N. Ghanbari et al. J. Phys. Chem. C 120 (2016) 22225, https://doi.org/10.1021/acs.jpcc.6b07117
T. Waldmann, K. Richter, M. Kasper, M. Wohlfahrt-Mehrens et al., J. Electrochem. Soc. 164 (2017) A3154, https://doi.org/10.1149/2.0961713jes

Example 4: Cu dissolution & re-deposition

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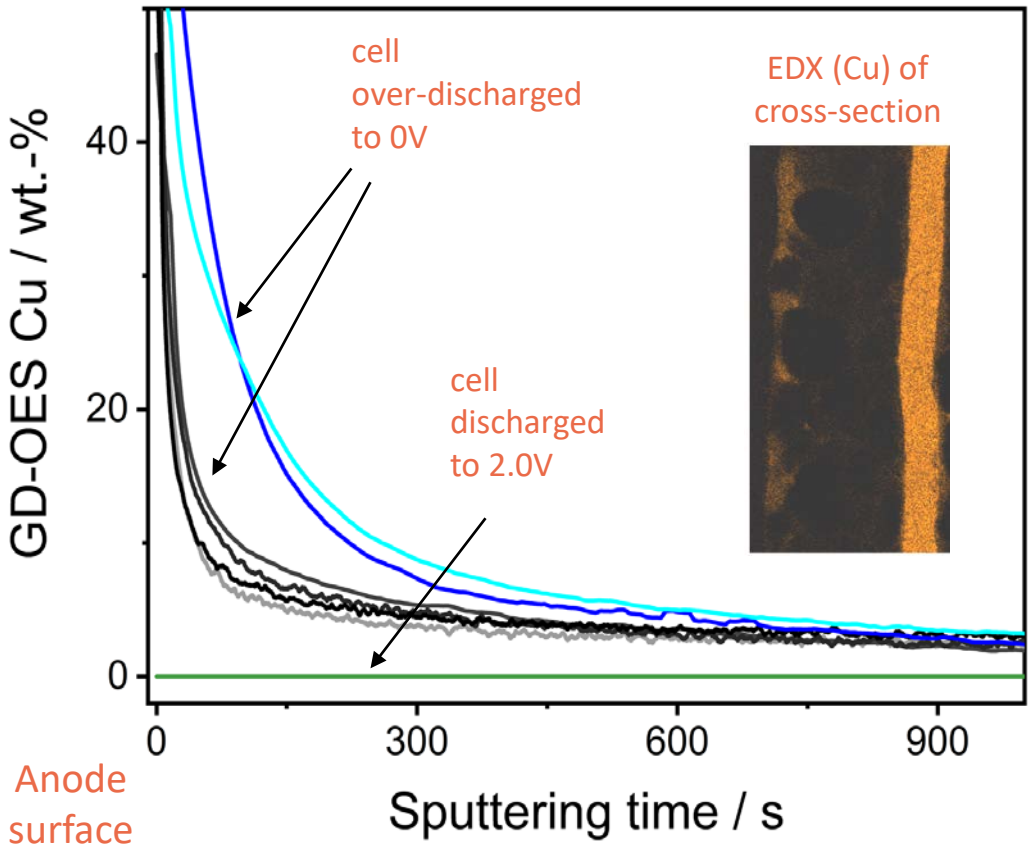
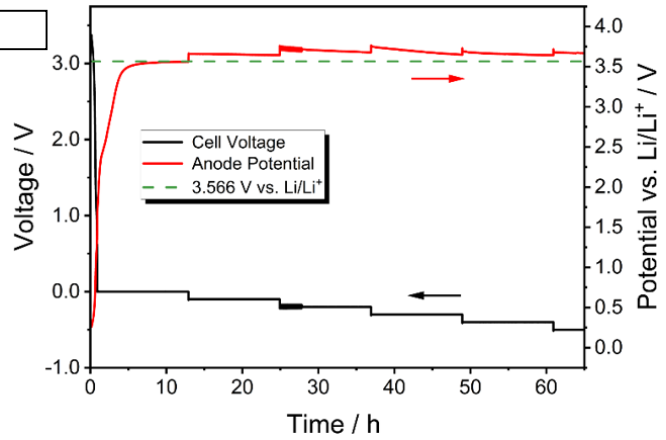
GD-OES depth profile of
Re-deposited Cu on graphite anode
after over-discharge to 0V



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⁺)

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M. Flügel, T. Waldmann, M. Kasper, M. Wohlfahrt-Mehrens, ChemPhysChem 21 (2020) 2047, https://doi.org/10.1002/cphc.202000333
M. Flügel, M. Kasper, C. Pfeifer, M. Wohlfahrt-Mehrens, T. Waldmann, J. Electrochem. Soc. 168 (2021) 020506, https://doi.org/10.1149/1945-7111/abdc5f