Non-Uniform Degradation of Graphite Electrodes: a Post Mortem Study Using Glow Discharge Optical Emission Spectroscopy (GD-OES)

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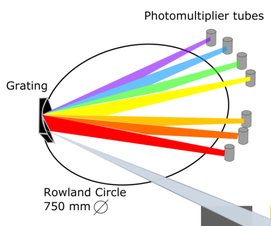
Introduction

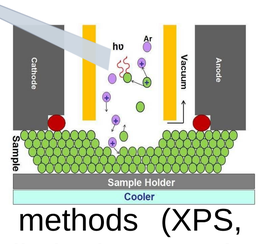
State of the art Li-ion cells employ graphite as negative electrode, whose fast charging at temperatures other than room temperature prompts non-uniformity in the utilization of the active material. Formation of metallic Li instead of Li intercalation during charging is of great concern since it dramatically impairs cell performance and imposes safety issues. This study presents a newly developed method (GD-OES) to discern between solid electrolyte interphase (SEI) growth and Li plating in aged graphite electrodes in a quantitative approach.

Methodology

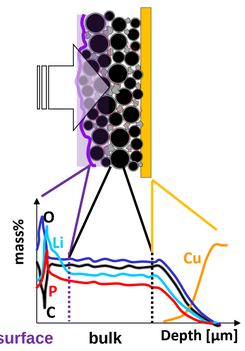
1. GD-OES principle



Layer-by-layer sample atom sputtering and simultaneous detection ⟶ depth-resolved elemental concentration



Unlike similar methods (XPS, SIMS), GD-OES is not limited to sample surface ⟶ fast direct elemental detection through the sample coating.

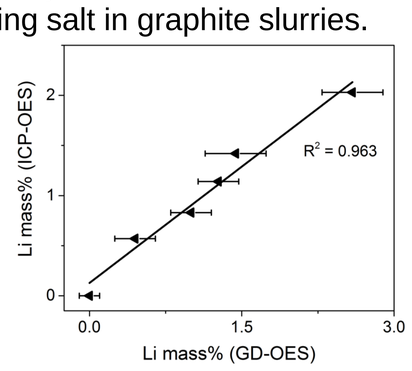


2. GD-OES method calibration

recorded elemental intensity ∝ { concentration, sputtering rate } ⟹ data quantification necessary

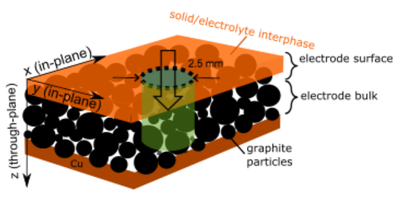
Reference coatings ⟶ systematic variation of 0-10 mass% Li-containing salt in graphite slurries.

Evaluation of the calibrated method with ICP-OES results.



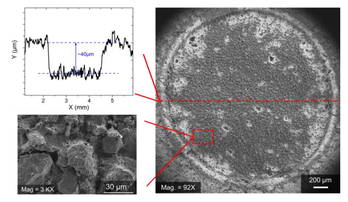
3. Resolution

The sputtering area has a diameter of 2.5mm and can go over 100µm into the coating,



Applicable to different planar positions of an electrode ⟶ detection of degradation gradient

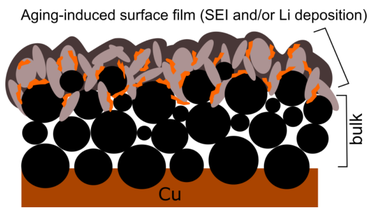
Measurement leaves a crater on the sample flat and smooth crater reflects high depth resolution.



Idea

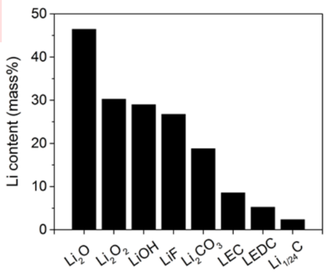
How to distinguish between SEI and Li plating?

The detected Li wt.-% using GD-OES is a superpose of SEI and Li plating contribution:



$$Li_{detected} = Li_{SEI} + Li_{metallic}$$

Li_2O contains the highest Li mass fraction among the so far reported SEI species.



Assuming SEI consists solely of Li_2O, the SEI contribution in the total detected Li is maximized. Hence, a lower limit is set for the possible amount of metallic Li in the aged graphite electrode.

Example: *GD-OES data* | *Calculated*

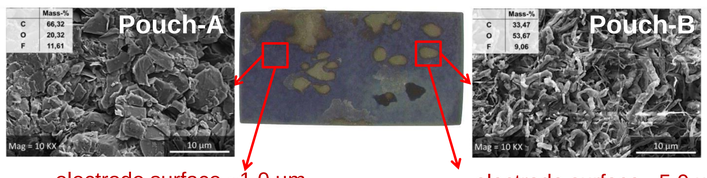
	$O_{detected}$	$Li_{detected}$	possible Li_2O	Li_{SEI} (introduced by Li_2O)	$Li_{metallic}$ ($Li_{detected} - Li_{SEI}$)
wt.-%	5.4	22.1	10.1	4.7	17.4

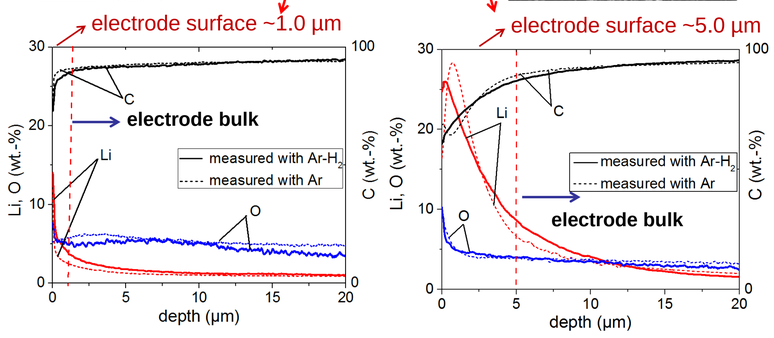
This estimation is applied on every recorded depth profiling data point to quantify the minimum amount of metallic Li present in the samples.

Application

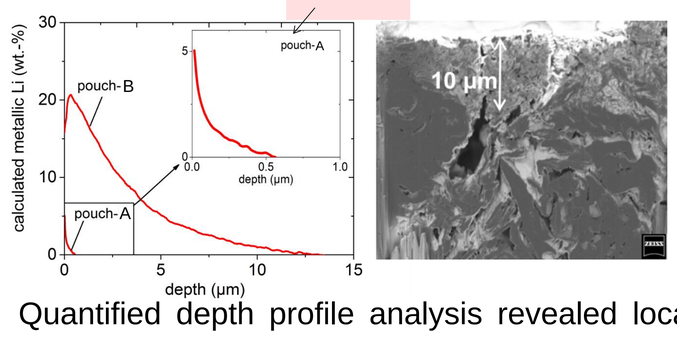
1. Quantified discrimination between SEI growth and Li plating in a large-format pouch cell

- Aged graphite electrode: 45ºC, 3C/1dC, 0-100% SOC
- Non-uniform electrode degradation/utilization disclosed in post mortem analysis.



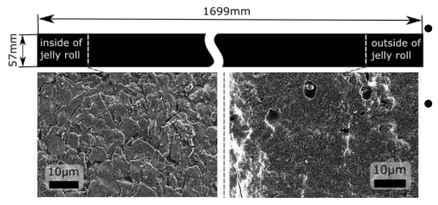


$$Li_{detected} = Li_{SEI} + Li_{metallic}$$

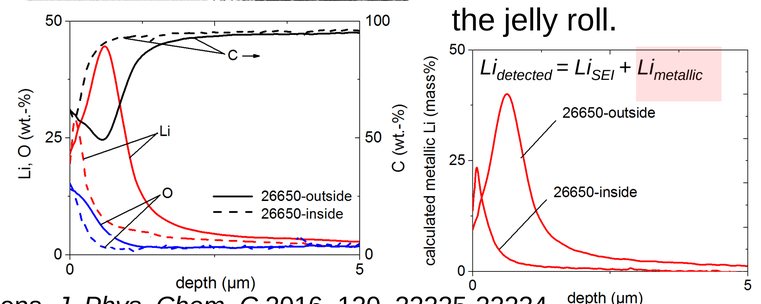


- Quantified depth profile analysis revealed local metallic Li of at least 17.4 wt.-% on the first micrometer of the electrode surface layers.
- SEM on FIB cross section of the electrode shows Li deposition spreads to a depth of ~10µm from the electrode top surface.
- Local Li deposition can hardly be diagnosed in electrochemical data.

2. Li plating gradient in a cylindrical 26650 cell



- Cell cycling: 1C at -20ºC
- Direct quantification of Li plating gradient on the two ends of the jelly roll.

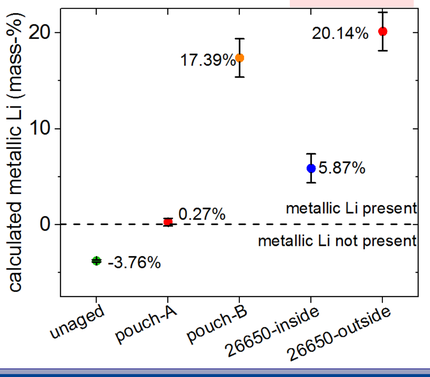


Summary

Integrated Li wt.-% in the first micrometer of the surface of the samples:

$$Li_{detected} = Li_{SEI} + Li_{metallic}$$

Positive calculated $Li_{metallic}$ values indicate the minimum amount of deposited metallic on the electrode. SEI growth gives negative $Li_{metallic}$ values.



Conclusion

- Quantified depth-resolve detection of Li deposition is carried out for the first time.
- Non-uniform degradation of large-format graphite electrodes is quantitatively detected using GD-OES depth profiling to discriminated between SEI growth and Li deposition.
- The depth of aging-induced surface film is estimated based on GD-OES Li depth profile.
- GD-OES is a powerful method to detect elemental profiles from electrode surface to current collector

N. Ghanbari*, T. Waldmann, M. Kasper, P. Axmann, M. Wohlfahrt-Mehrens, *J. Phys. Chem. C* 2016, 120, 22225-22234

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Acknowledgement

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