

CHARACTERIZATION OF AGED ELECTRODES OF LITHIUM-ION-BATTERY



Slaheddine Jabri

Fraunhofer Institute for Solar Energy Systems ISE

BatteryWorld/ Battery Production and
characterization

München, 17.02.2022

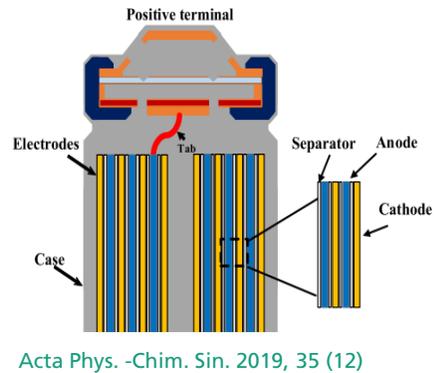
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AGENDA

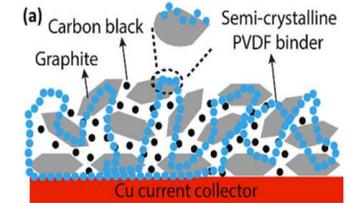
- Introduction
- Motivation
- Problematic
- Sample preparation
- Results
- Conclusion

Introduction – Lithium-ion-battery

- High theoretical capacity (170 mAh/g)
- Long lifetime
- Good thermal stability
- Inexpensive
- Non-toxic



Anode:
Graphite



Electrolyte:

Acta Phys. -Chim. Sin. 2019, 35 (12), 1382–1390

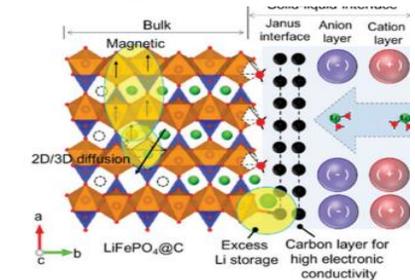
- Ethylene carbonate (EC)
- ethyl methyl carbonate (EMC)
- Vinylene Carbonate (VC)
- Lithium hexafluorophosphate (LiPF₆)



Separator:
Polypropylene



Cathode:
LiMeO



Nanoscale, 2020, 12, 15036

Motivation

- Development of an analytical method to investigate the aging of Lithium-ion-battery electrodes
 - Information about the distribution of chemical elements
 - Low costs
 - Low time consuming
 - Low use of consumables
- Optimization of the sample preparation
- Comparison of the results between different analytical methods

Problematic

- Lithium reacts very quickly with humidity
- Lithium is very small and light chemical element to be detectable by usual analytical methods, for example EDX



Investigation in dry environment!

Experimental Plan

■ Aging modus of battery cell

Cycle numbers	Charge rate	Discharge rate
100	4C	4C
250	4C	4C
500	4C	4C
850	4C	4C

Jabri and Ruf



Battery Testing System



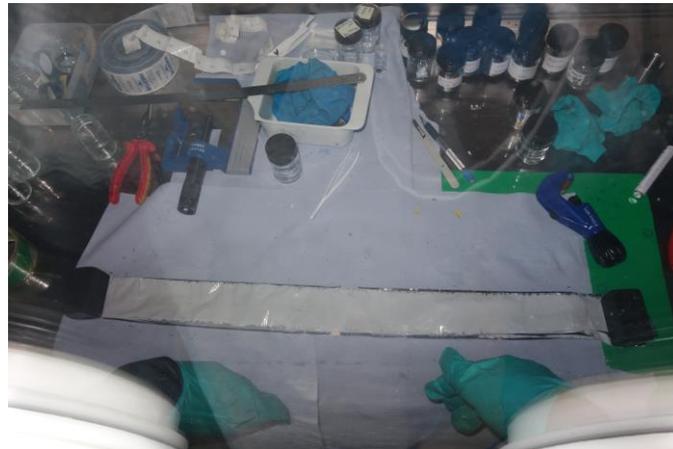
Temperature chamber



18650 LiFePO₄

Battery cell disassembly

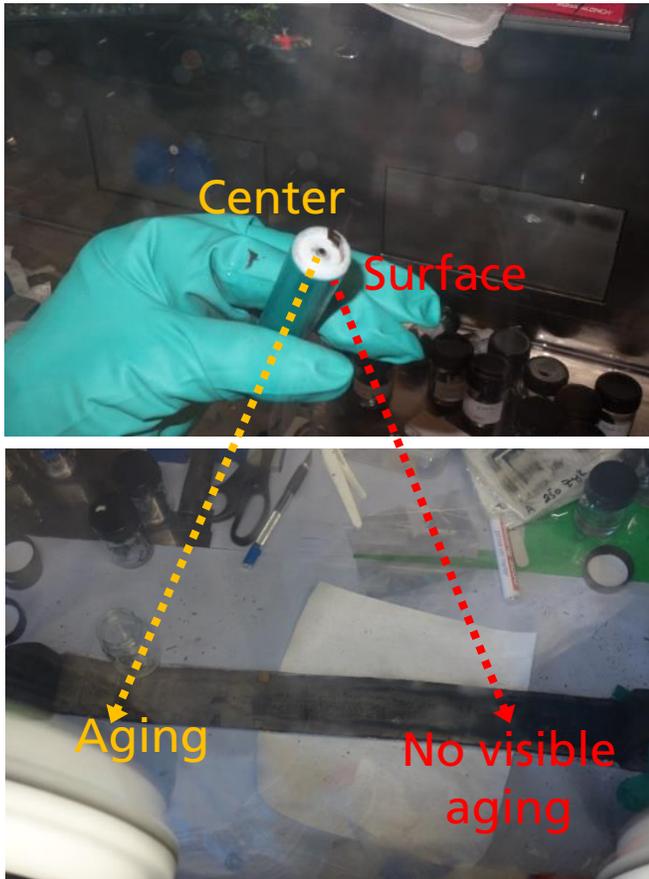
- Disassembly of battery cell inside the glove box



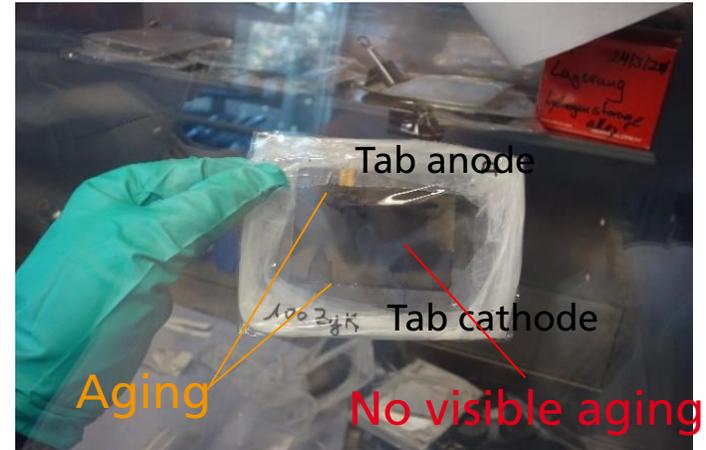
- $O_2 < 1,5 \text{ ppm}$
- $H_2O \approx 0$
- $Ar + N_2$

Sample protection against environment

■ Graphite Anode



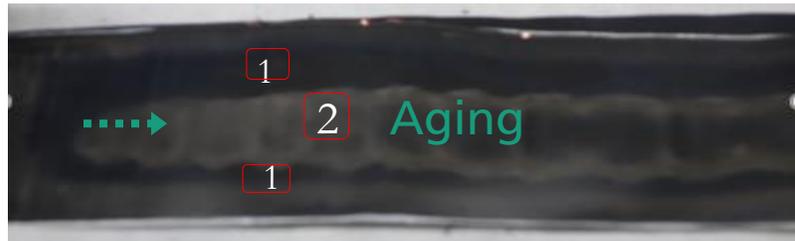
■ Covered Anode



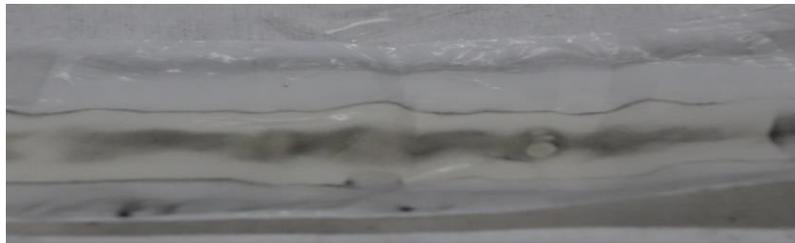
Cover glasses (100 μ m thick) and parafilm

Fotos of aged electrodes

■ 100 cycles



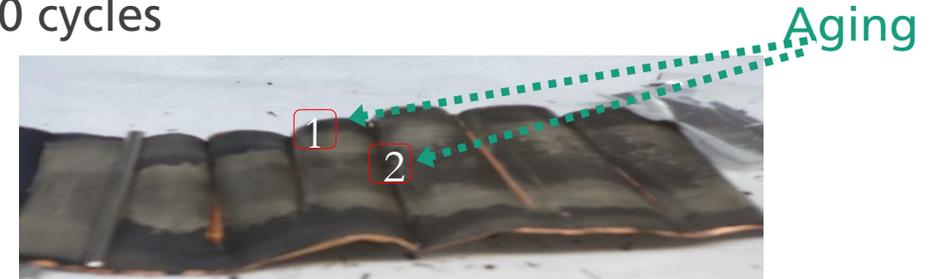
Graphite Anode – Center of battery cell



Separator - Anode interface – Center of battery cell

- Visible aging at the middle of the electrode
- Graphite delamination

■ 250 cycles



Graphite Anode - Center of battery cell



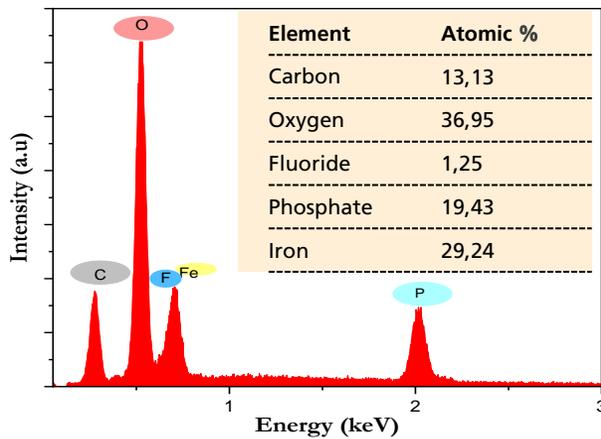
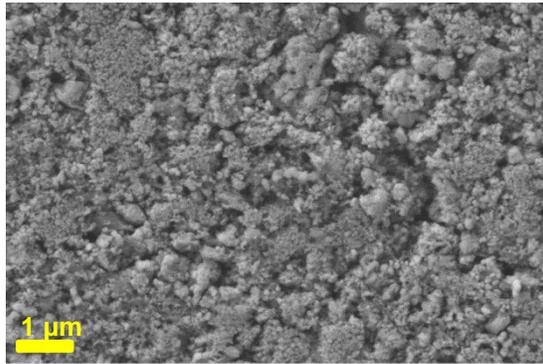
Separator - Anode face - Center of battery cell



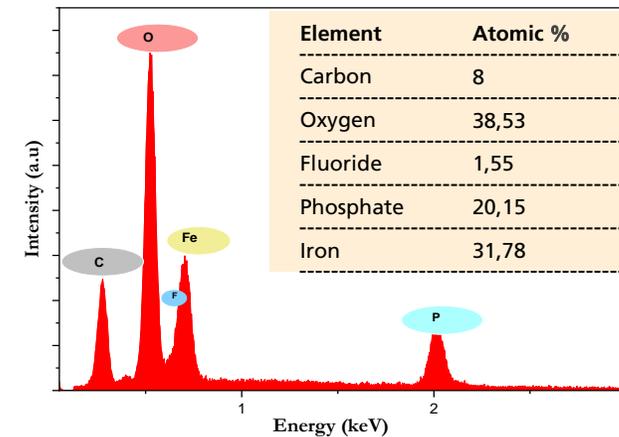
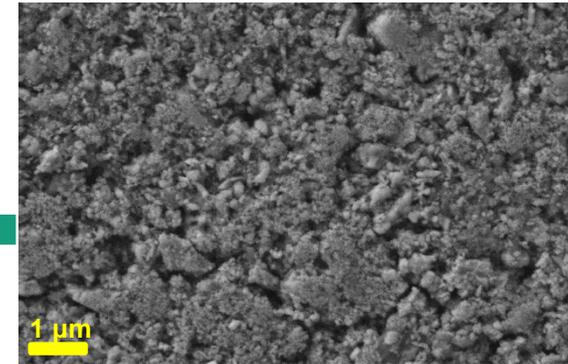
LiFePO₄ /C cathode - Center of battery cell

SEM and EDX images of LiFePO_4/C cathode

■ uncycled cathode



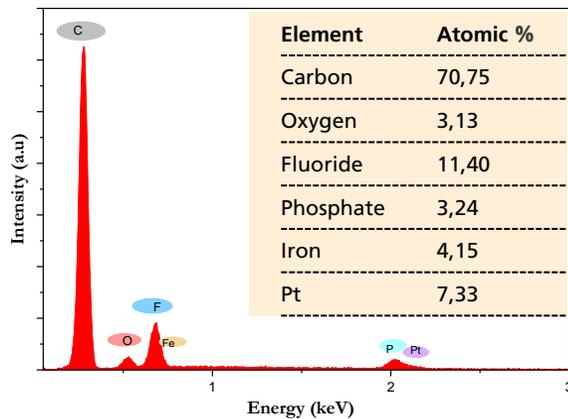
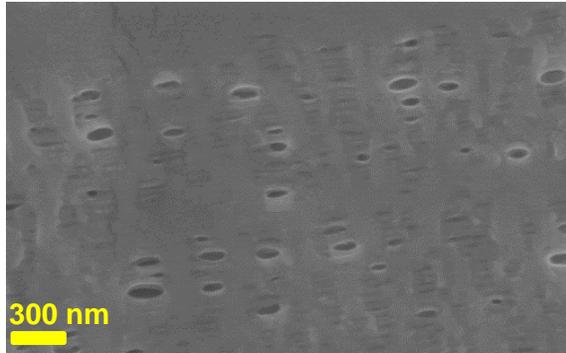
■ 100 cycles



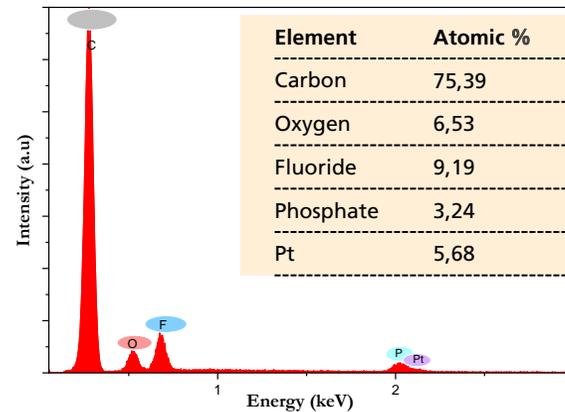
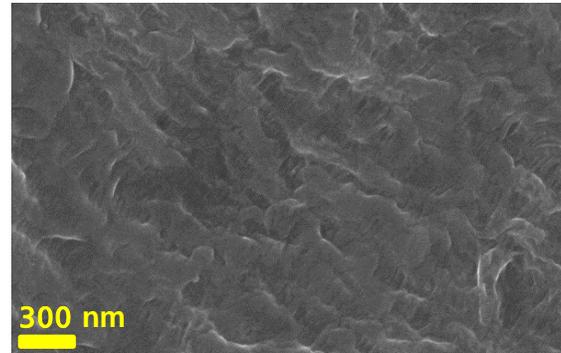
Neither chemical modification nor aging is observed in LiFePO_4 cathode

SEM and EDX images of separator - anode interface

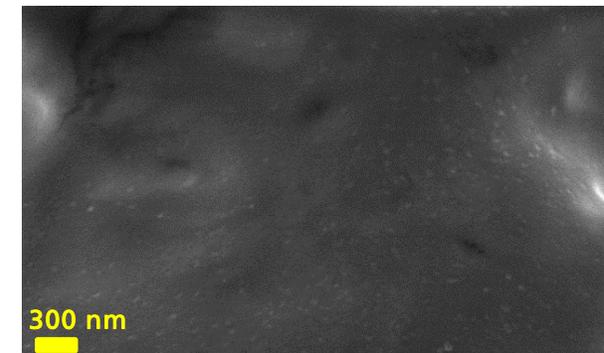
■ 'Uncycled' separator



■ 100 cycles



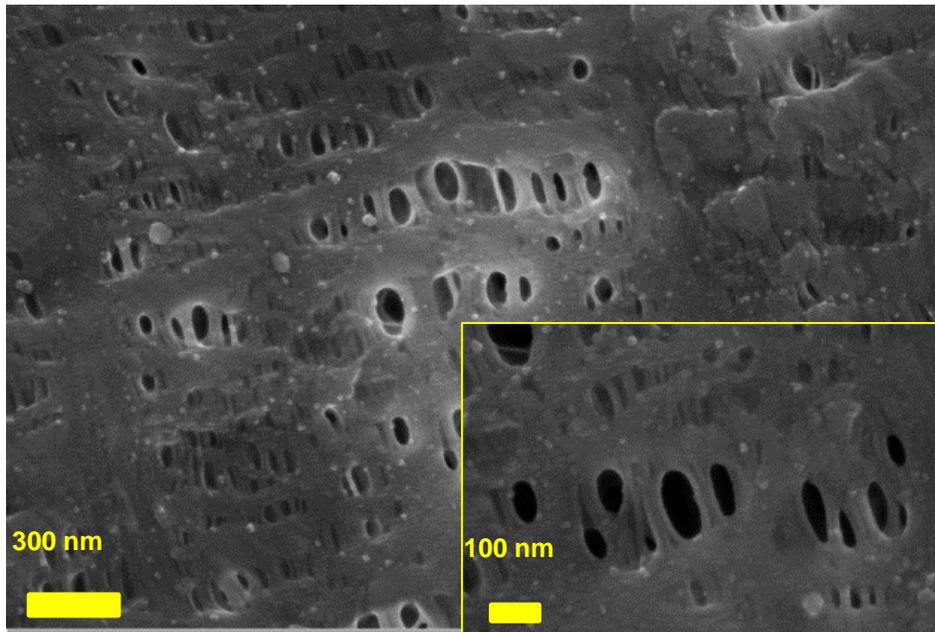
■ 250 cycles



➔ Graphite deposition on the separator – anode interface

SEM and EDX images of separator - cathode interface

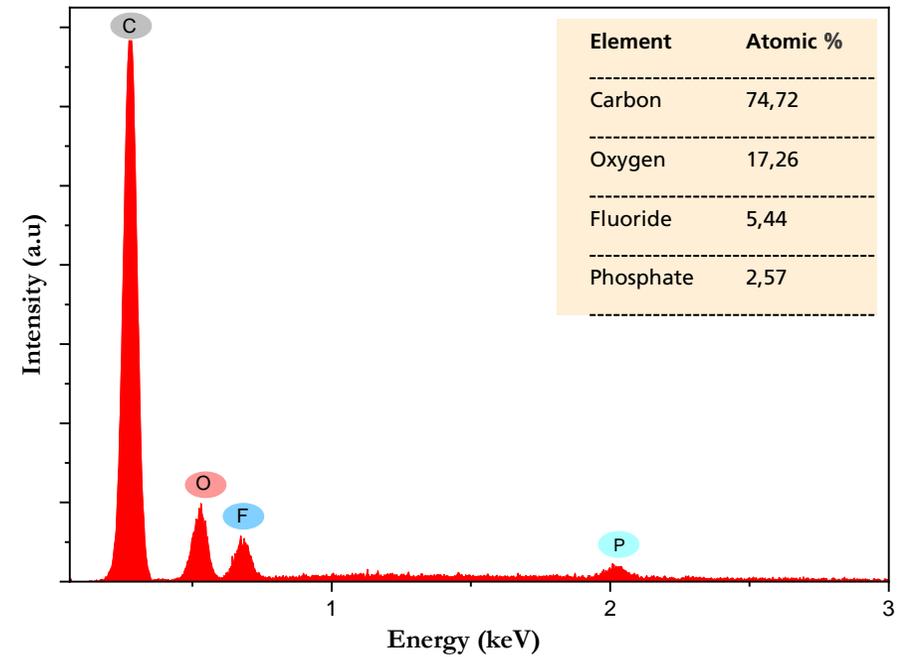
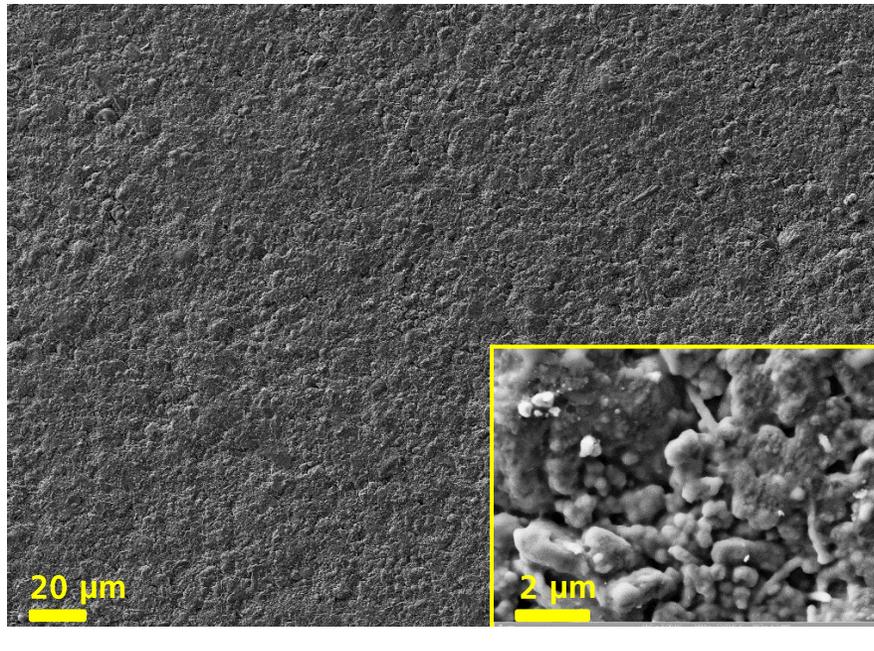
- 250 cycles



➔ Clean surface of the separator

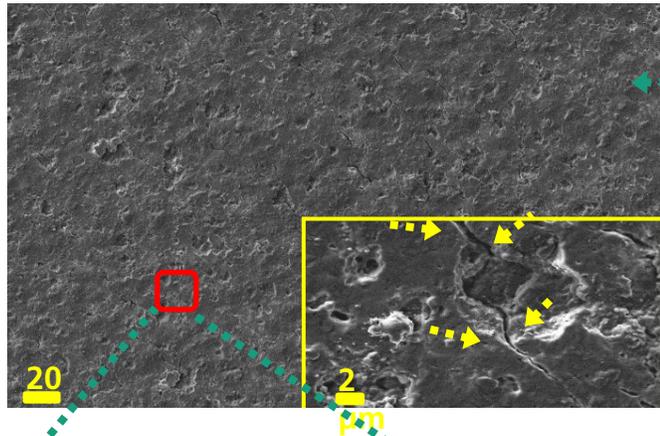
SEM and EDX images of graphite anode

■ 100 Cycles

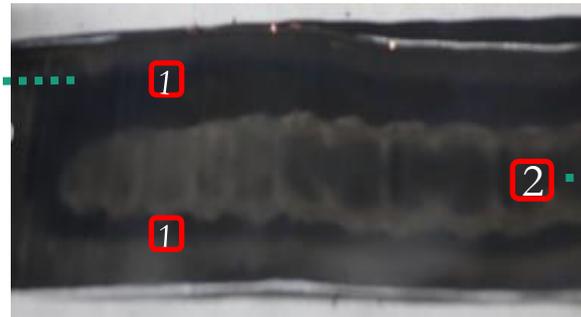


SEM and EDX images of aged graphite anode

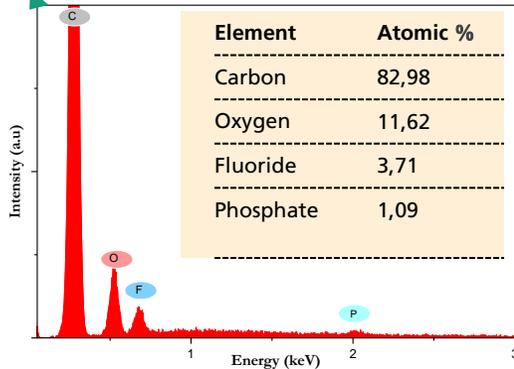
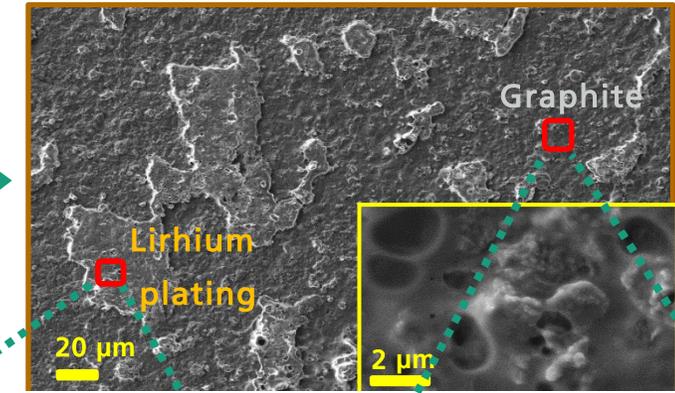
■ 100 Cycles - position 1



■ 100 Cycles

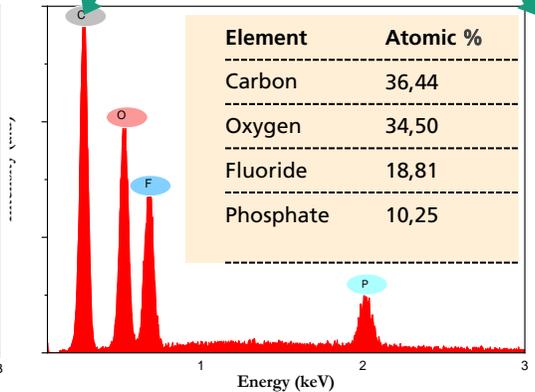
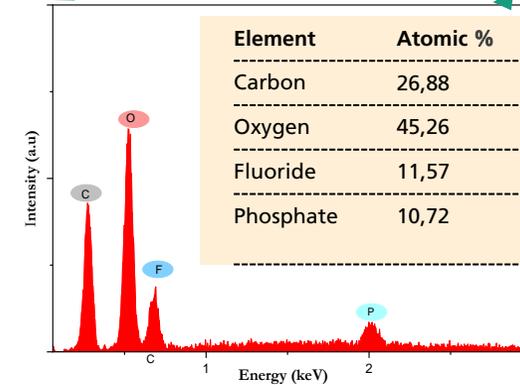


■ 100 Cycles - position 2



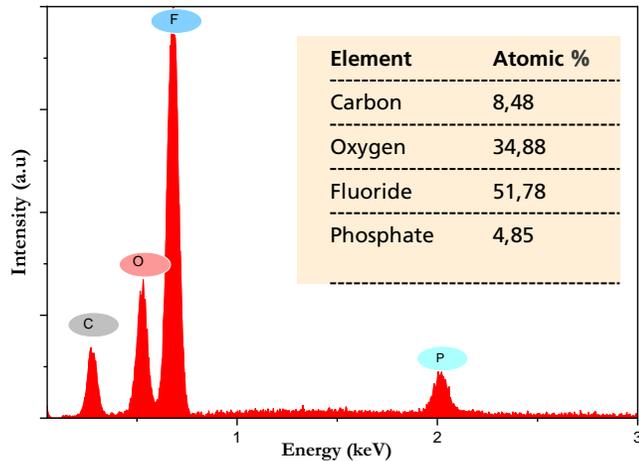
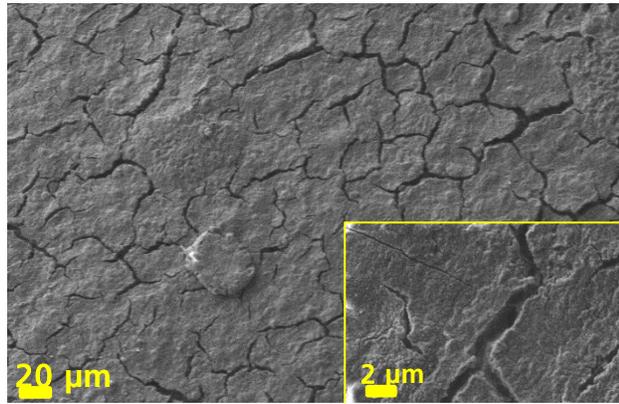
- Cracks
- Lithium plating

Lithium reacts with air and causes a higher concentration of O₂ compared to C.

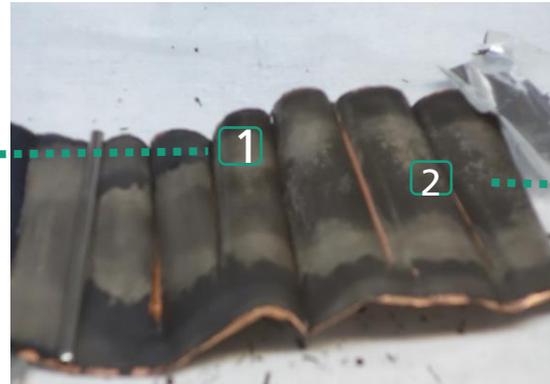


SEM and EDX images of aged graphite anode

■ 250 Cycles position 1

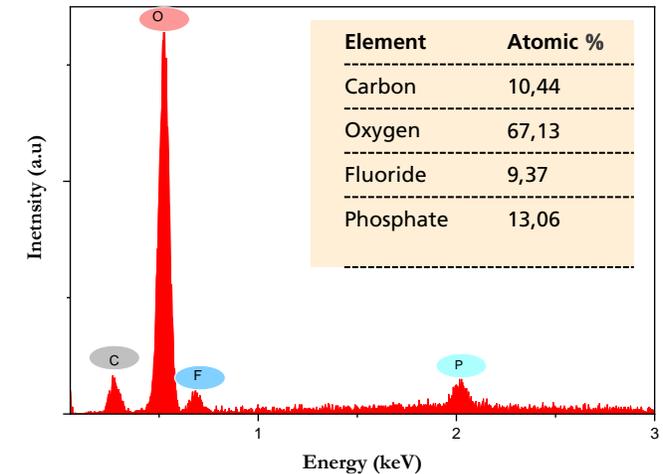
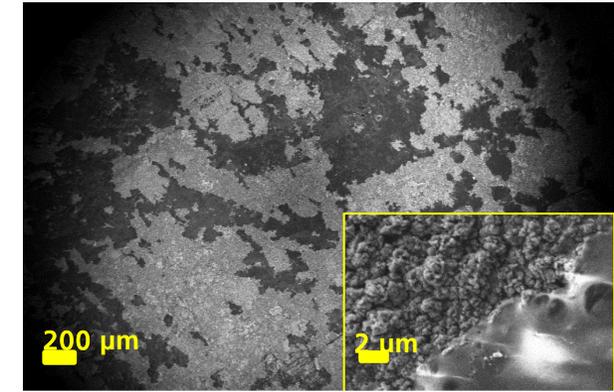


■ 250 Cycles



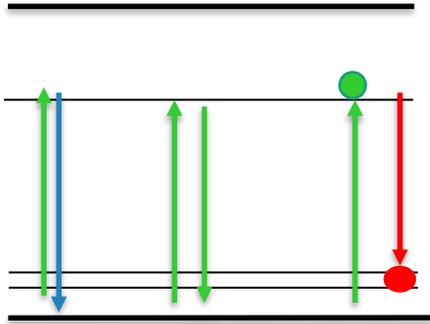
- More cracks
- Lithium Plating

■ 250 Cycles position 2



Raman spectrometry

✓ Raman spectroscopy (WiTec Spectrometer)

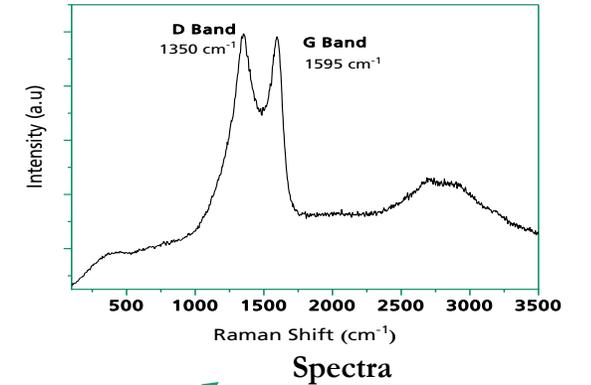


Raman- scattering Antistocks
Rayleigh Scattering
Raman-scattering Stocks



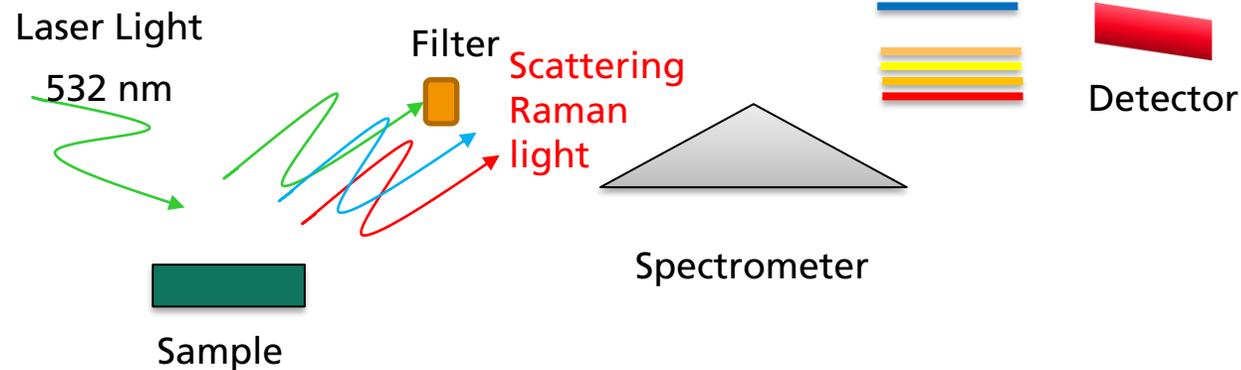
Identification of

- Material properties
- Chemical composition
- Doping



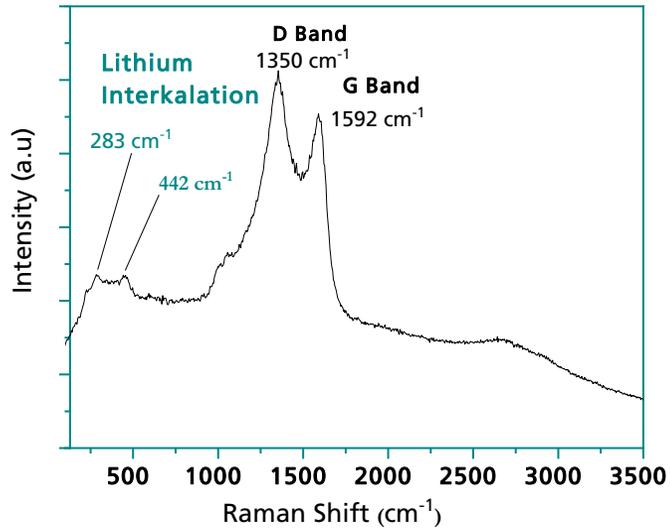
Raman mapping

- Laser wavelength: 532 nm
- Time: 1 s
- Geometry: 40 μm x 40 μm
- Number of points: 40 x 40
- Laser power: 1,4 mW

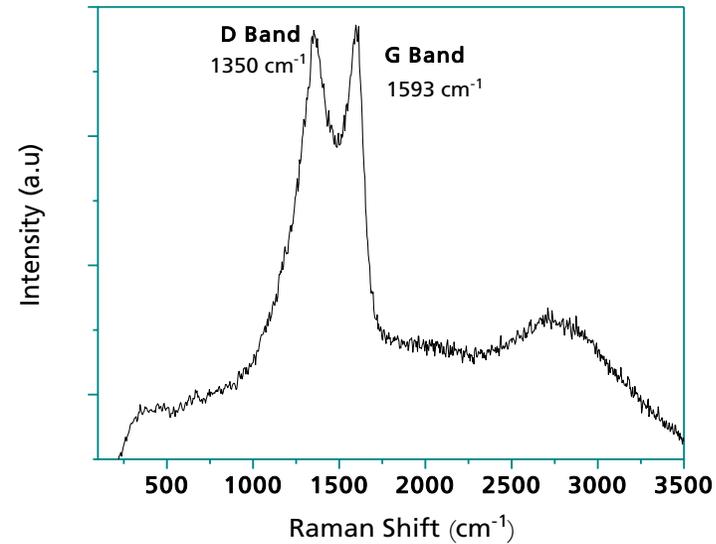


Raman results of LiFePO_4/C cathode

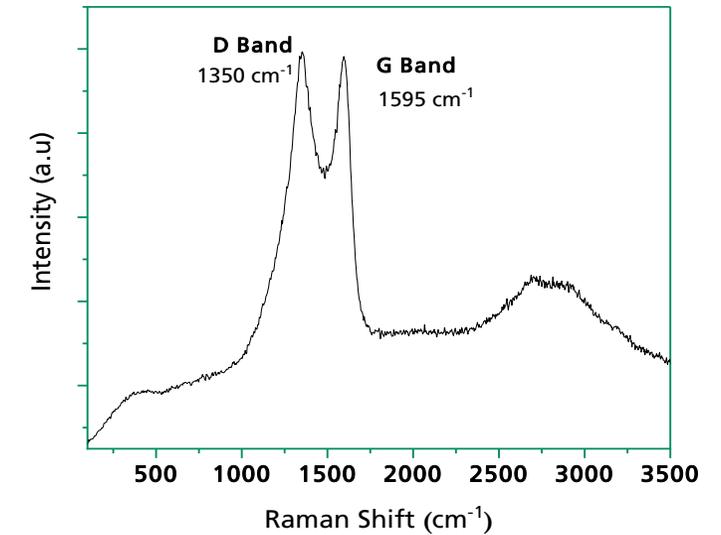
■ Uncycled cathode



■ 100 cycles



■ 250 cycles

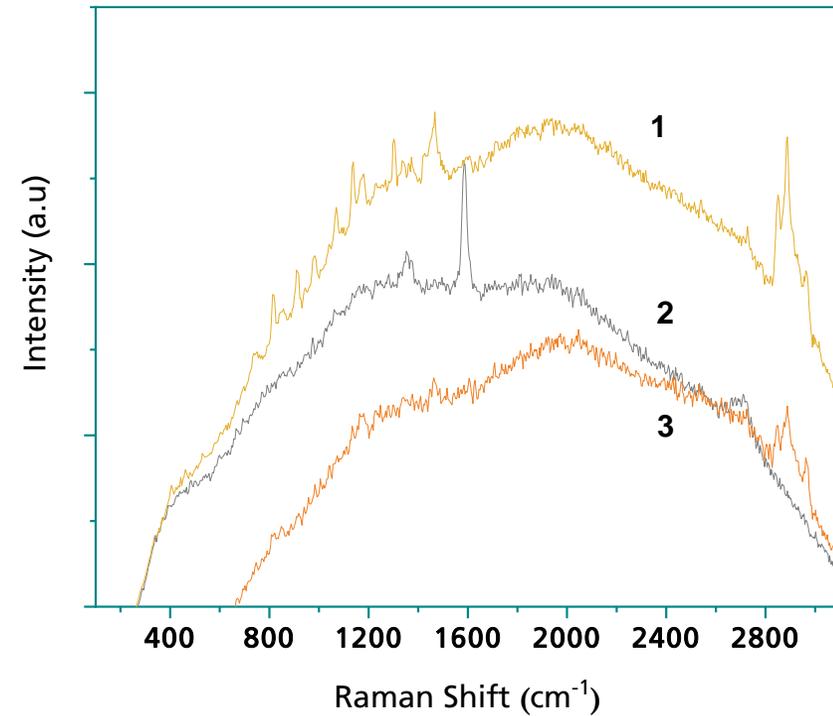
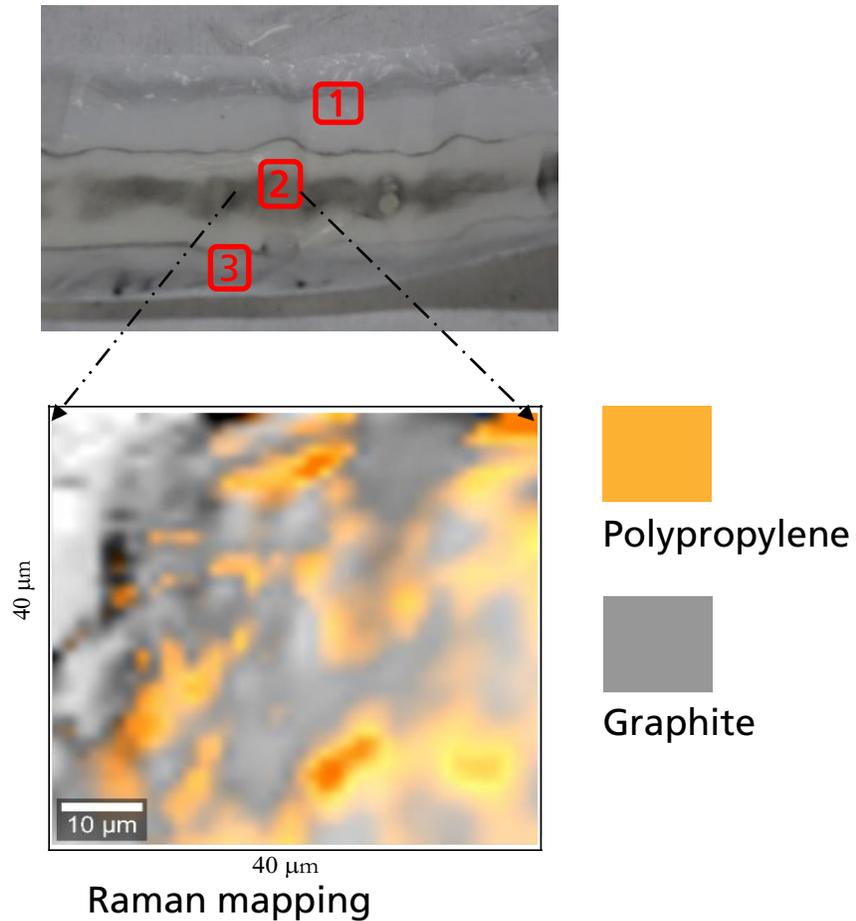


Difficulty to detect LiFePO_4

Carbon layer on the surface of the cathode

Raman results of PP separator - anode interface

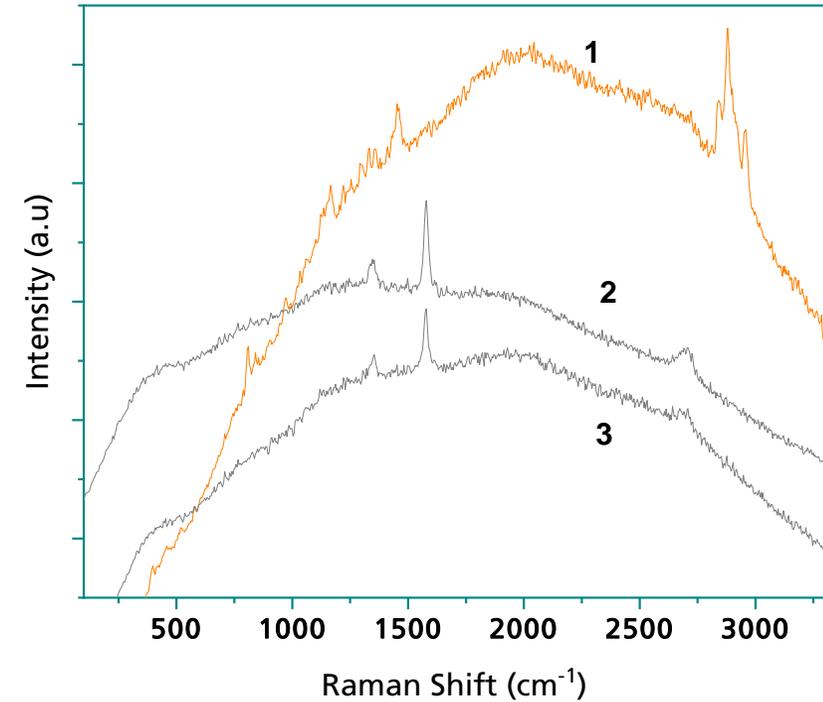
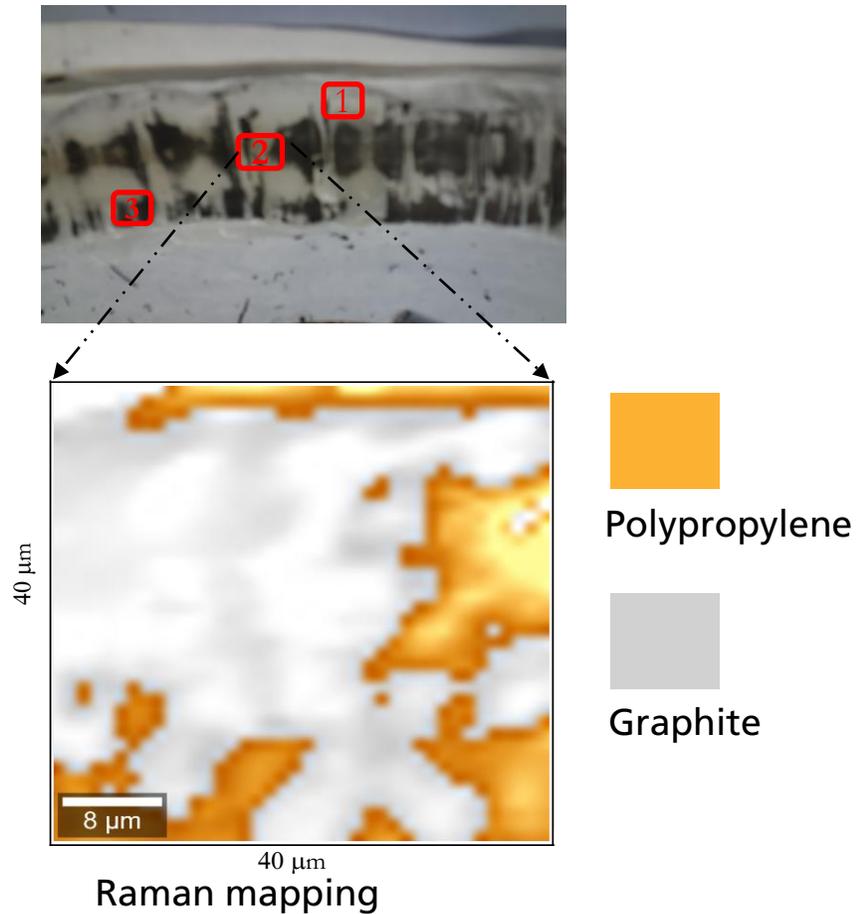
■ 100 cycles



➔ Graphite layer covers the surface of the separator

Raman results of aged PP separator - anode interface

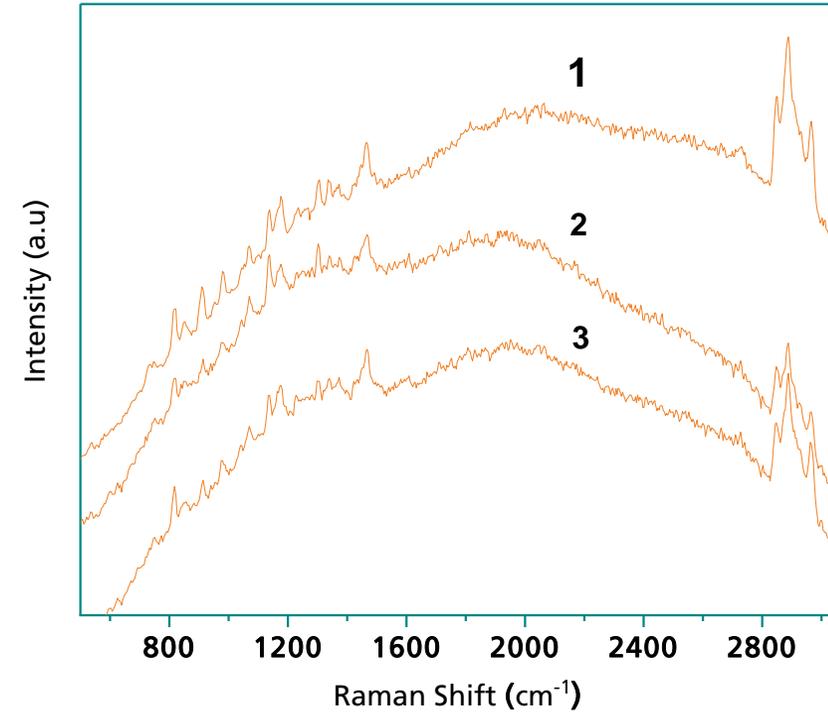
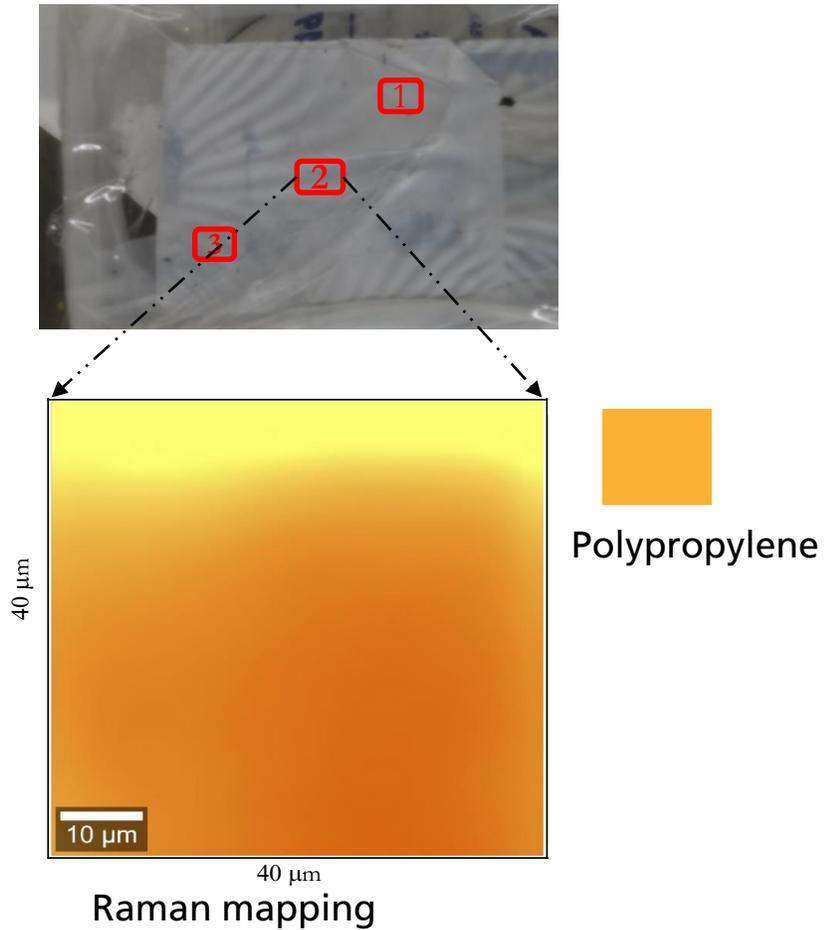
- 250 cycles



➔ Graphite layer covers a larger area of the separator

Raman results of PP separator - cathode interface

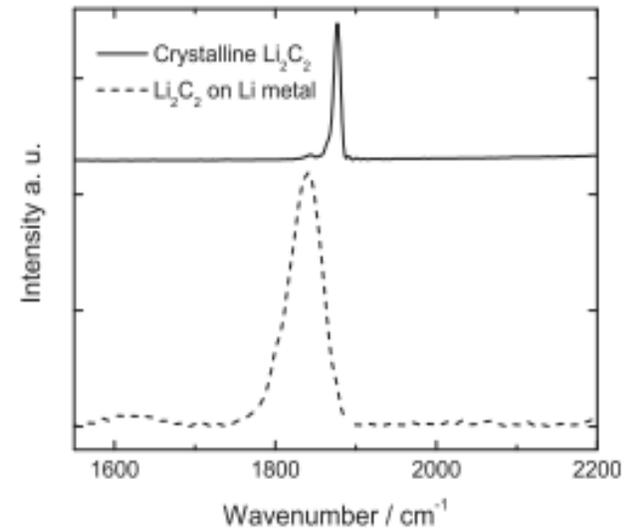
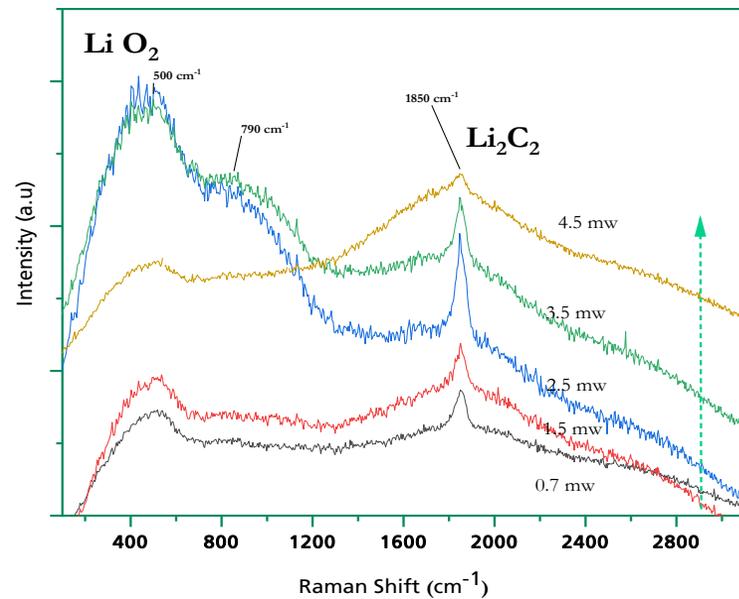
- 250 cycles



➔ Clean separator

Raman results of Lithium metal

■ Covered Lithium metal



Covered
Lithium
metal

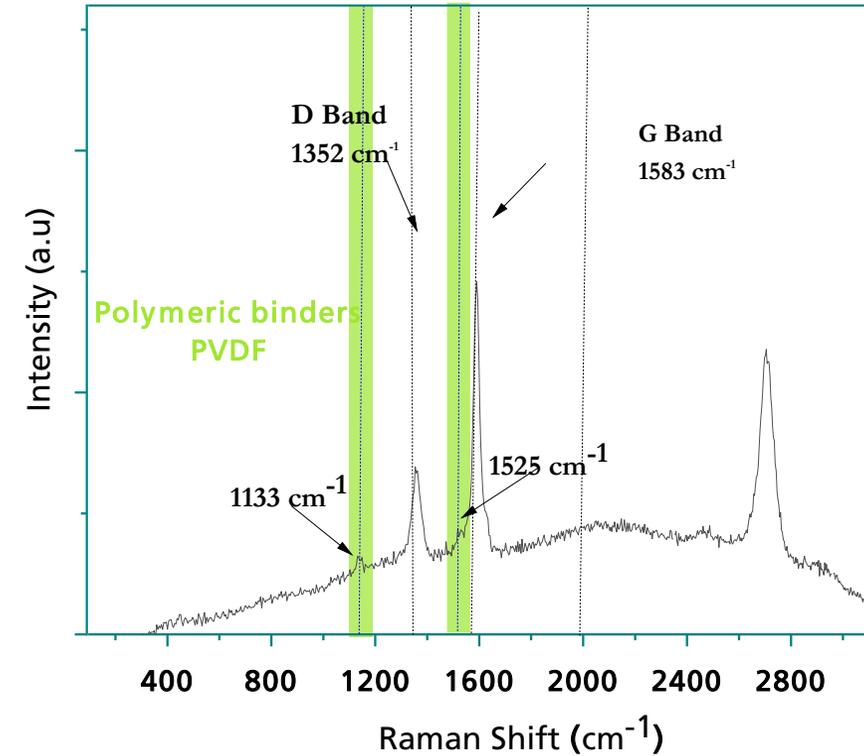
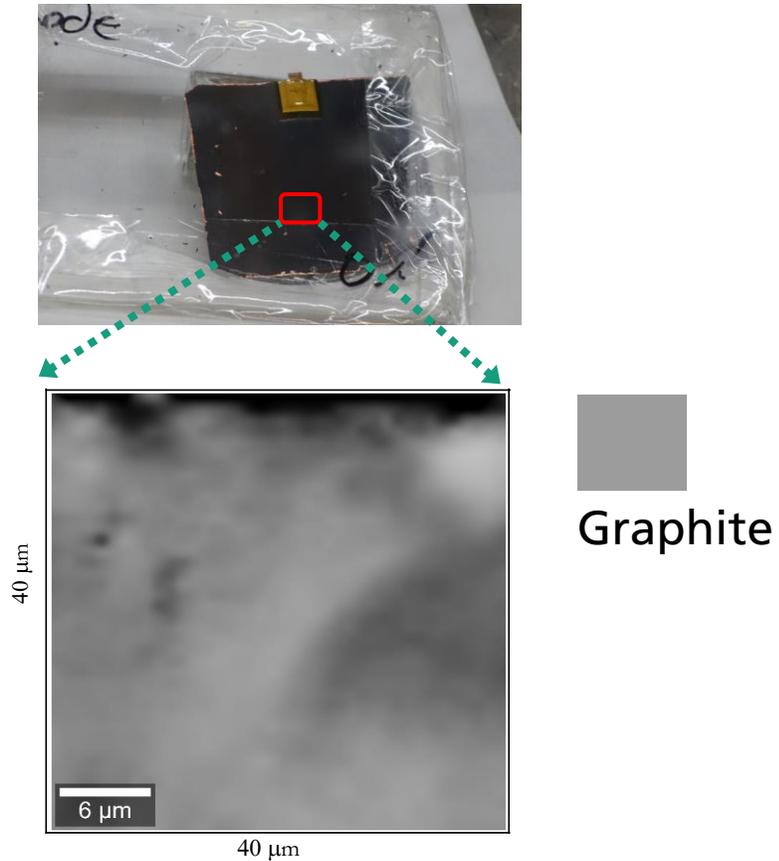
Fig. 1. Raman spectrum of synthesized Li_2C_2 (top) and purchased lithium metal (bottom) in the region of the symmetric stretching vibration of the C_2^{2-} anion.

[Inorganic Chemistry 52\(11\) 2013, 6402-6406](#)

➔ Lithium carbide Li_2C_2 band at 1845 cm^{-1}

Raman results of fresh graphite anode

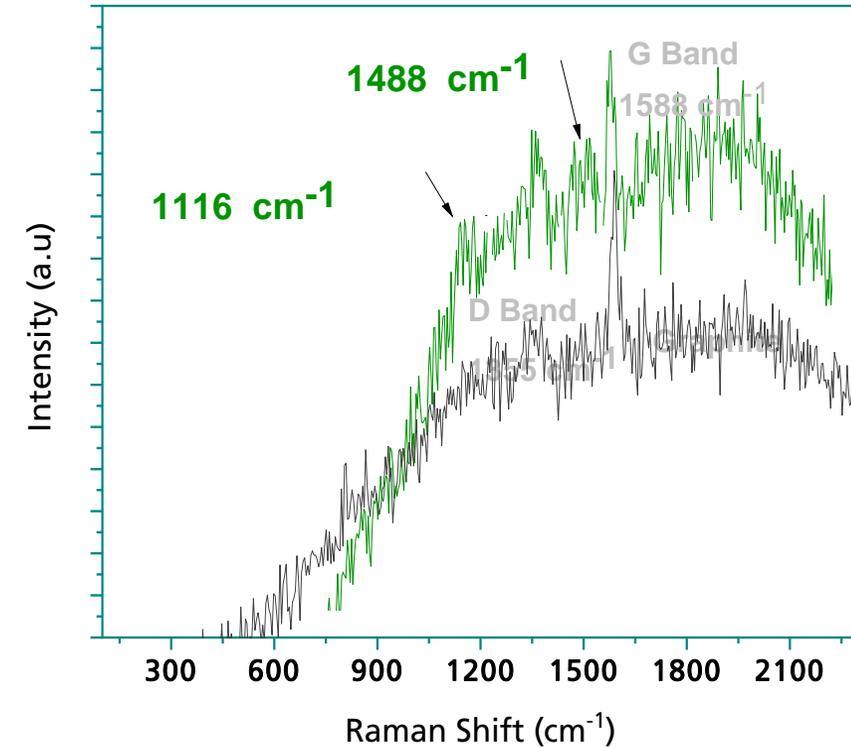
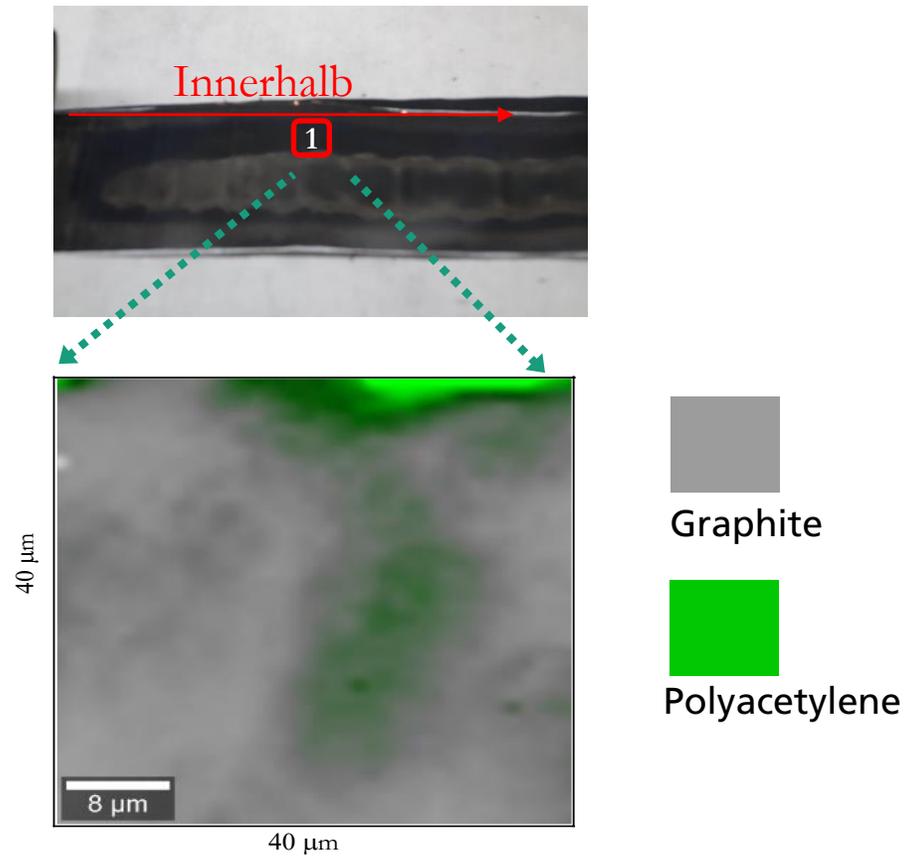
■ Raman mapping of uncycled graphite



➔ No lithium plating

Raman results of aged graphite anode - 100 cycles

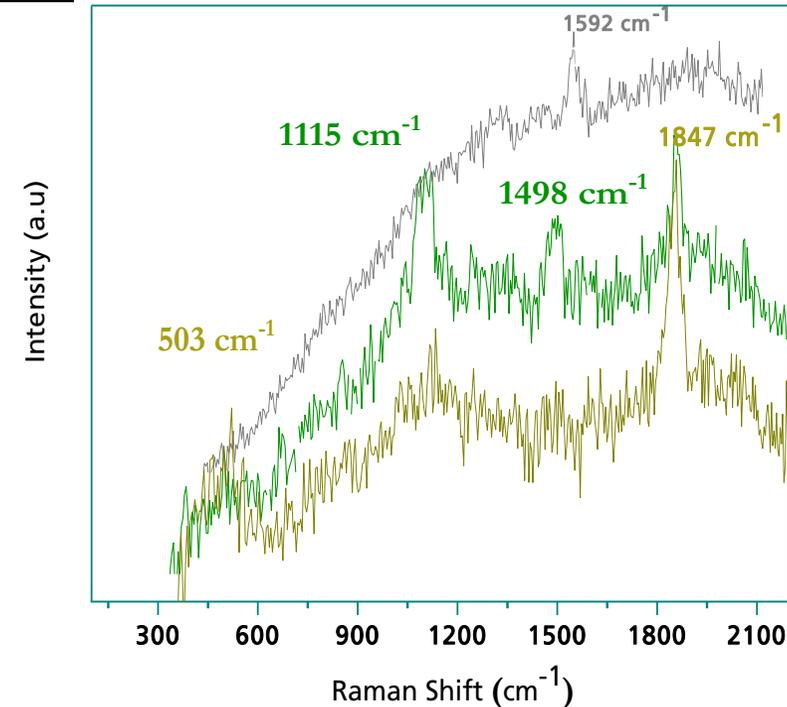
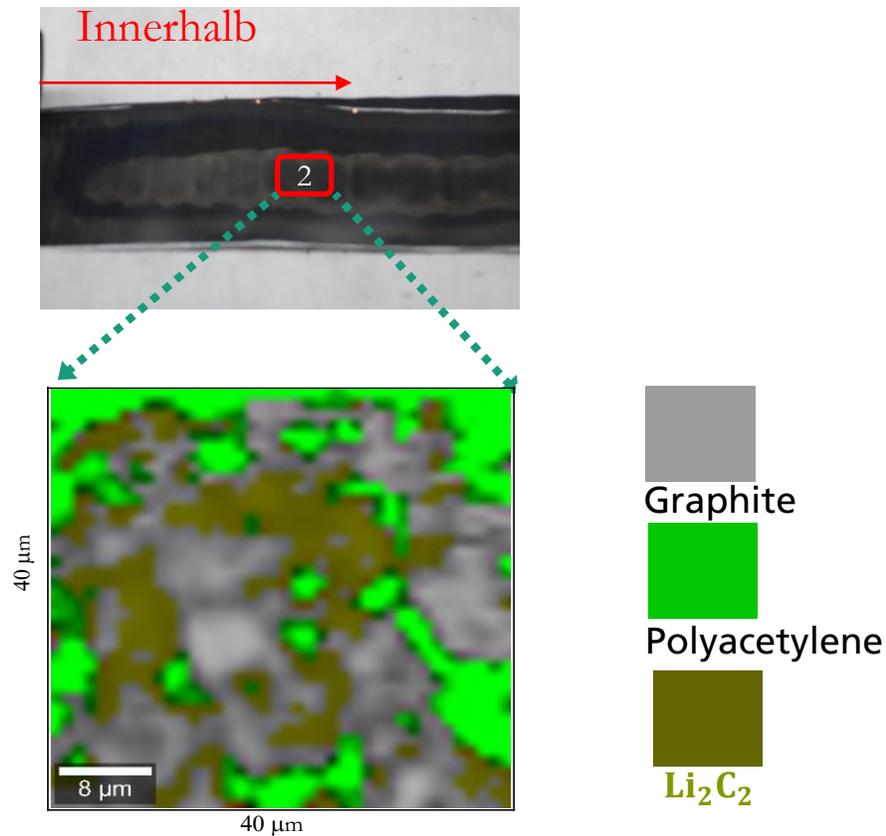
- Raman mapping of graphite anode in the edge position



➔ Start of aging: presence of polyacetylene

Raman results of aged graphite anode – 100 cycles

- Raman mapping of graphite anode at the mitte position



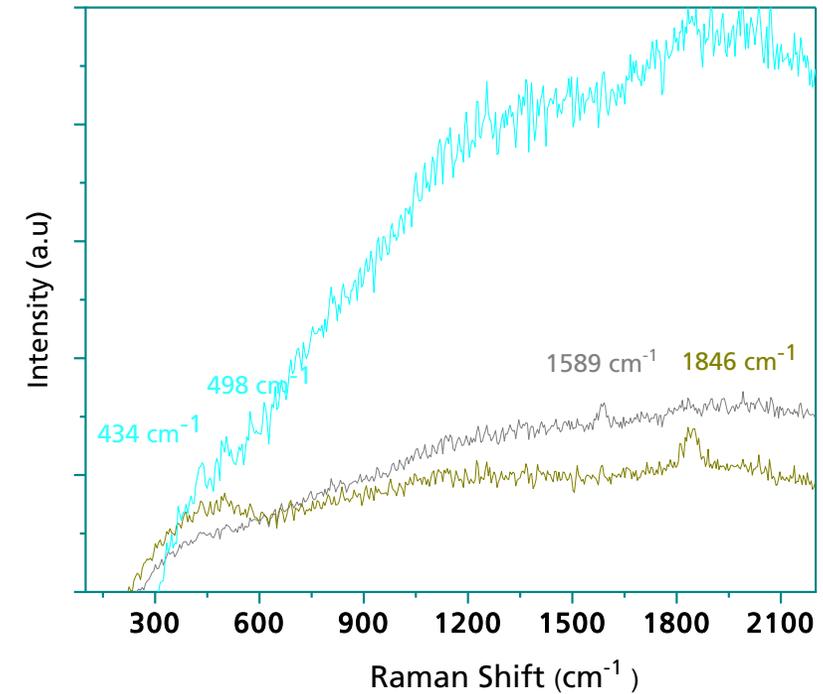
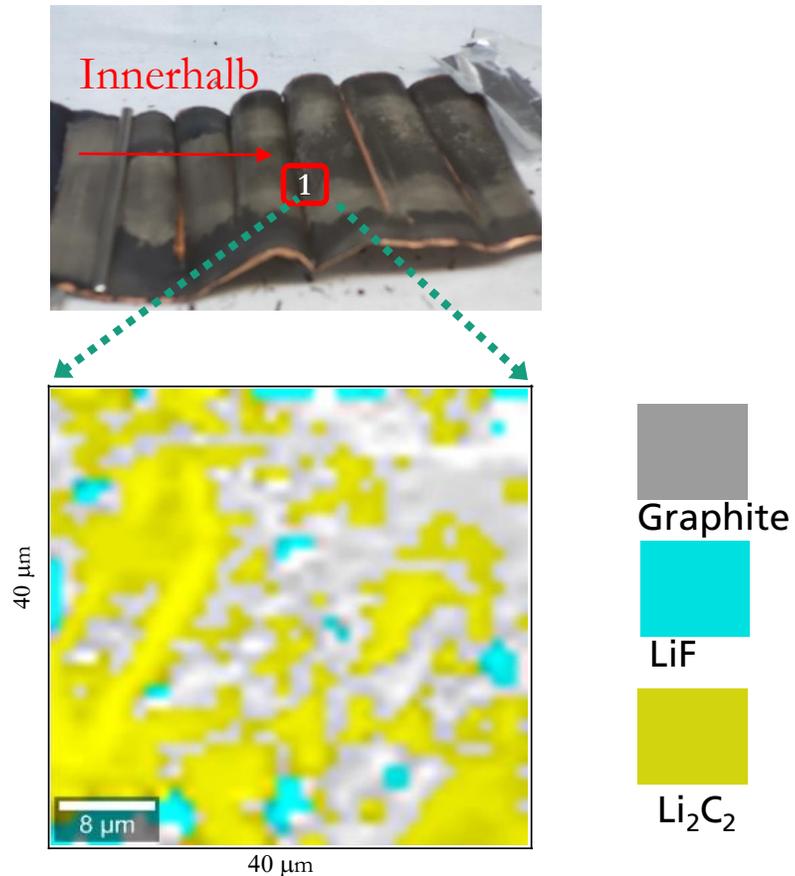
Most aging in the middle position

Stronger presence of polyacetylene

Presence of Li_2C_2

Raman results of aged graphite anode – 250 cycles

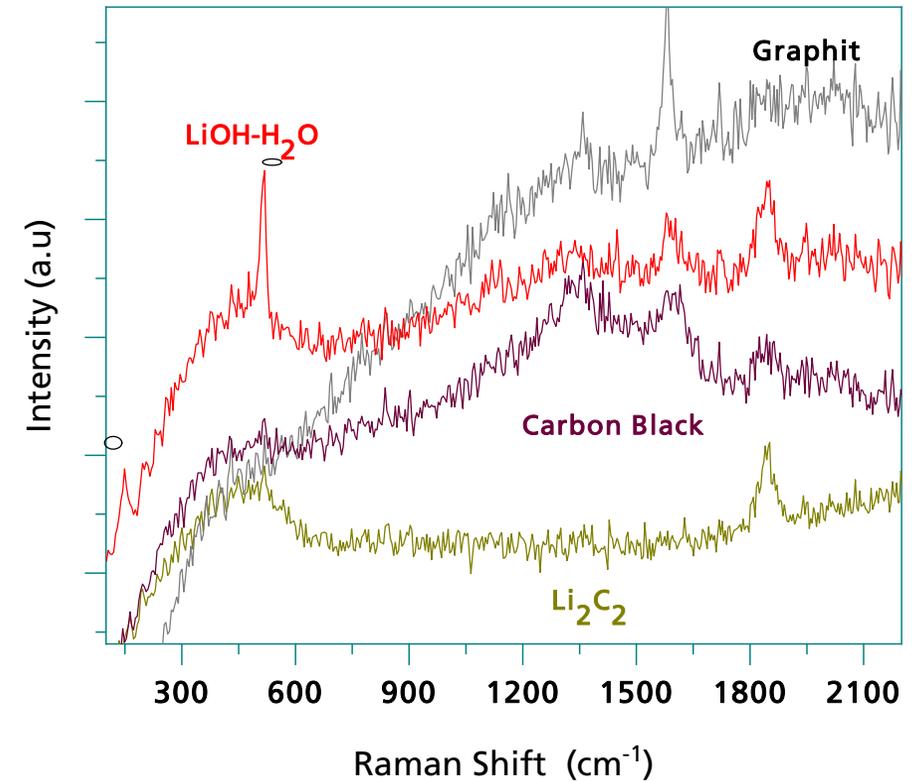
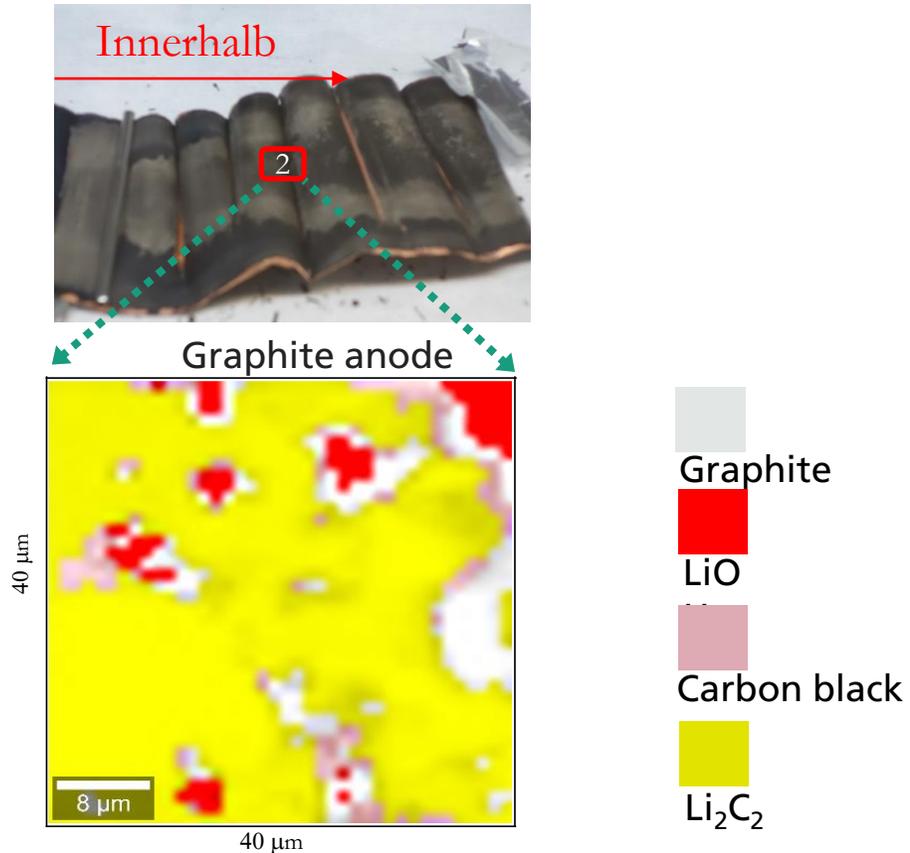
- Raman mapping of graphite anode at the edge position



➔ Appearance of lithium carbide at 1846 cm^{-1}

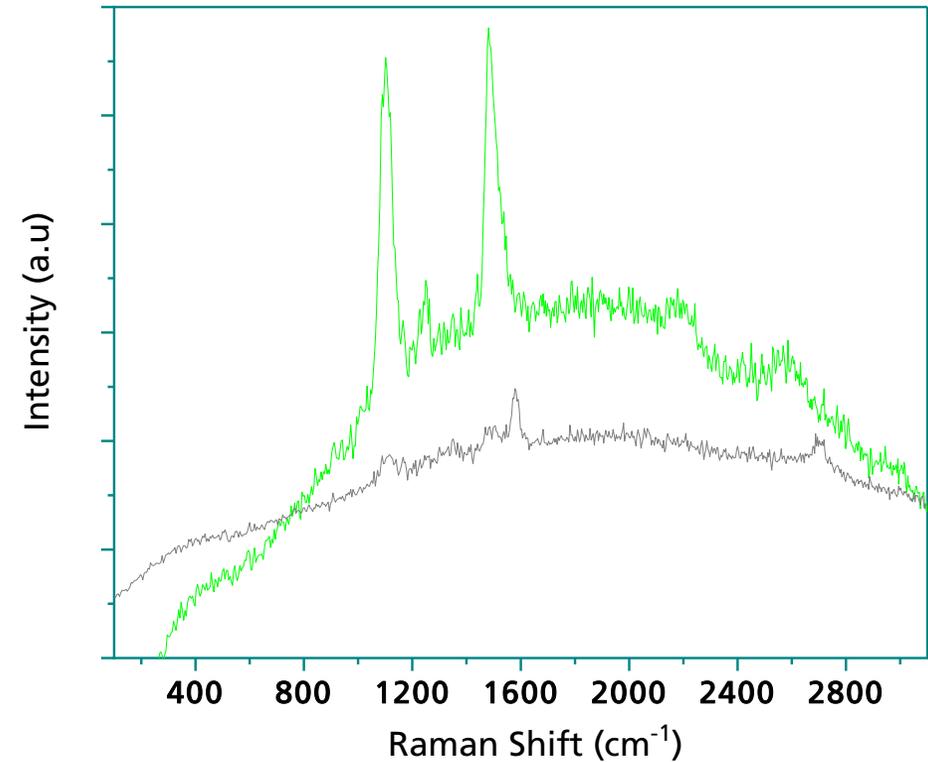
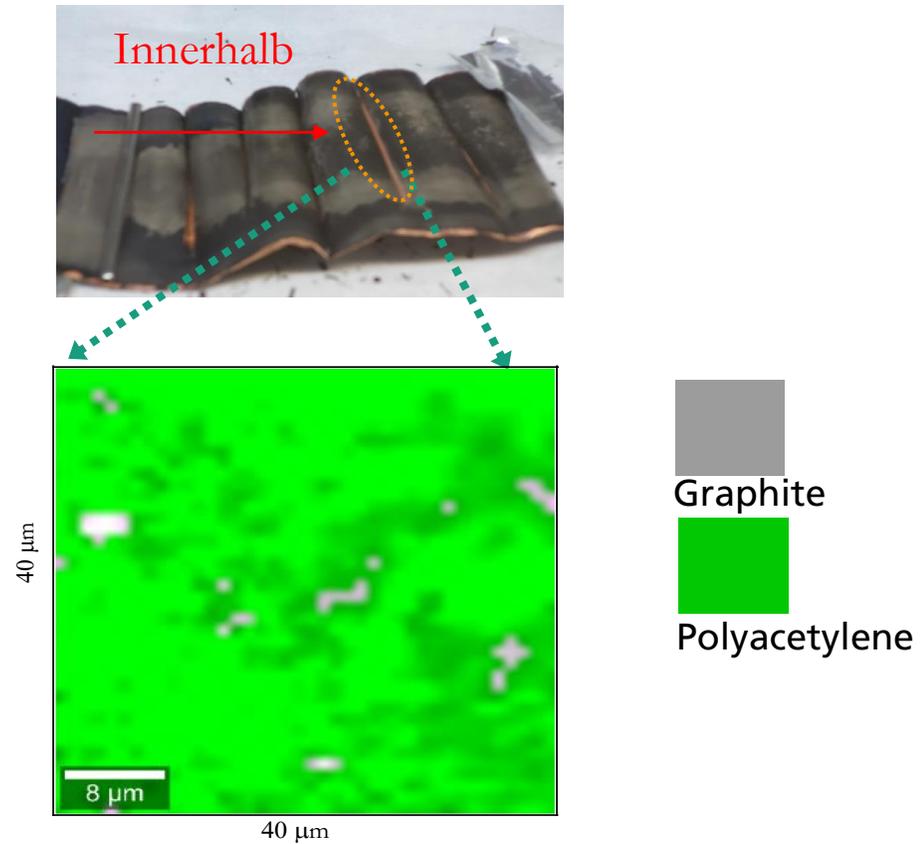
Raman results of aged graphite anode – 250 cycles

■ Raman mapping of graphite anode at the middle position



Raman results of aged graphite anode – 250 cycles

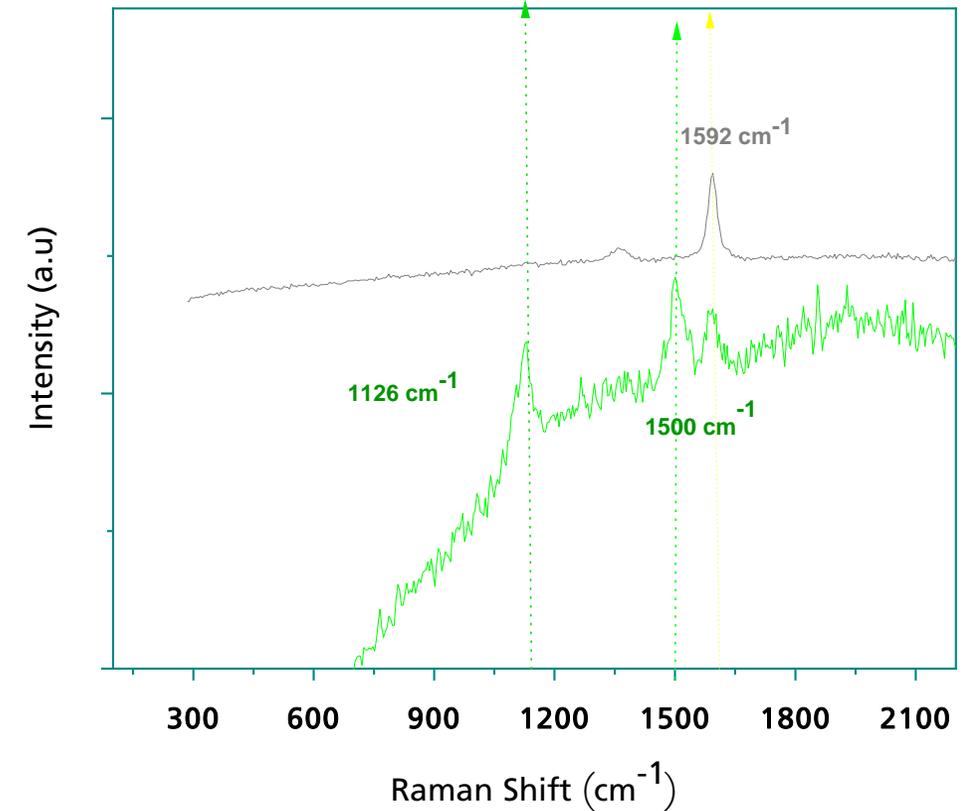
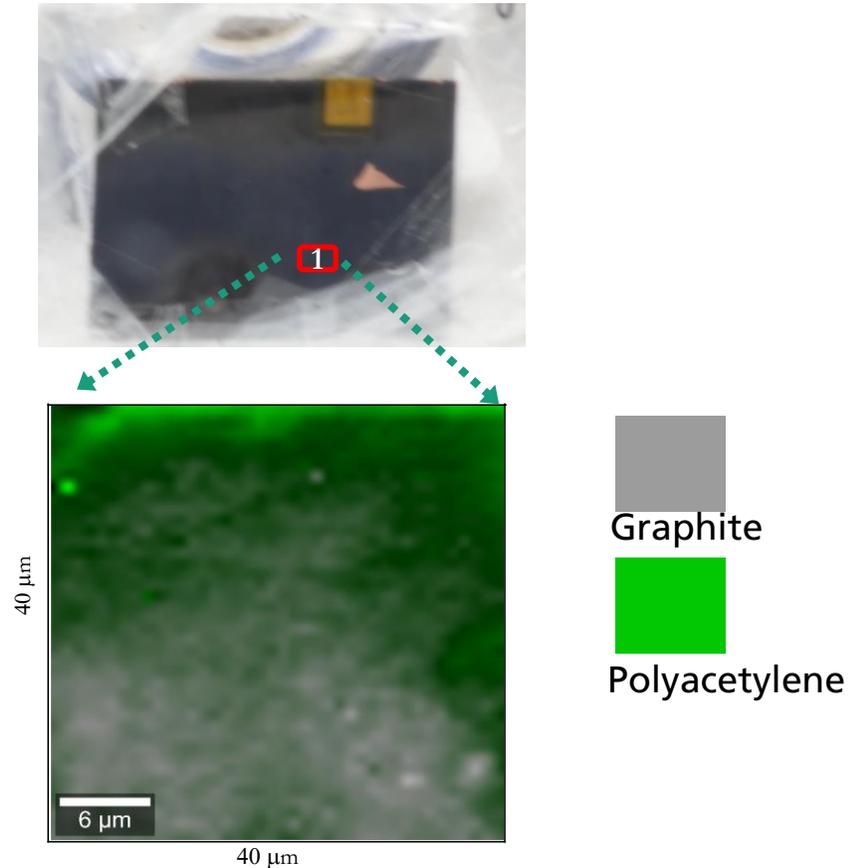
■ Raman mapping of copper foil



➔ Appearance of polyacetylene layer on the copper

Raman results of aged graphite anode next to the cathode tab – 250 cycles

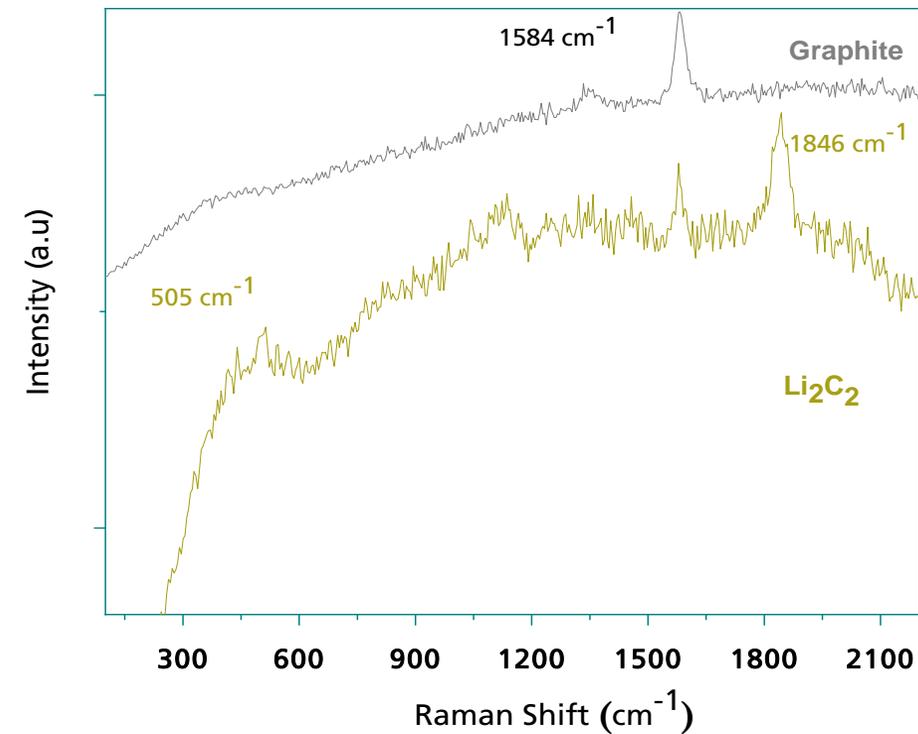
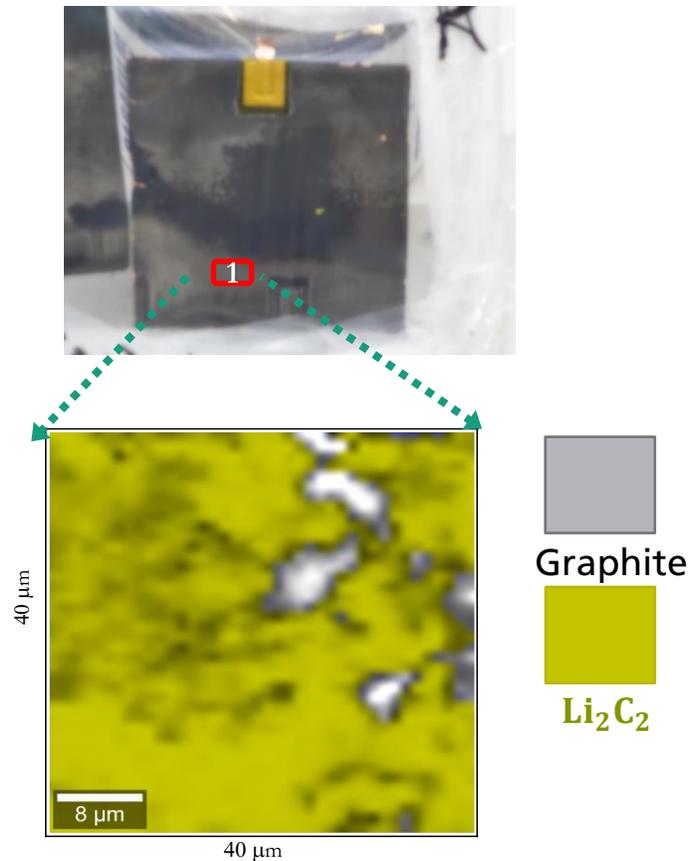
- Raman mapping image at the edge position



➔ Starting of aging with the appearance of polyacetylene

Raman results of aged graphite anode next to the tab – 250 cycles

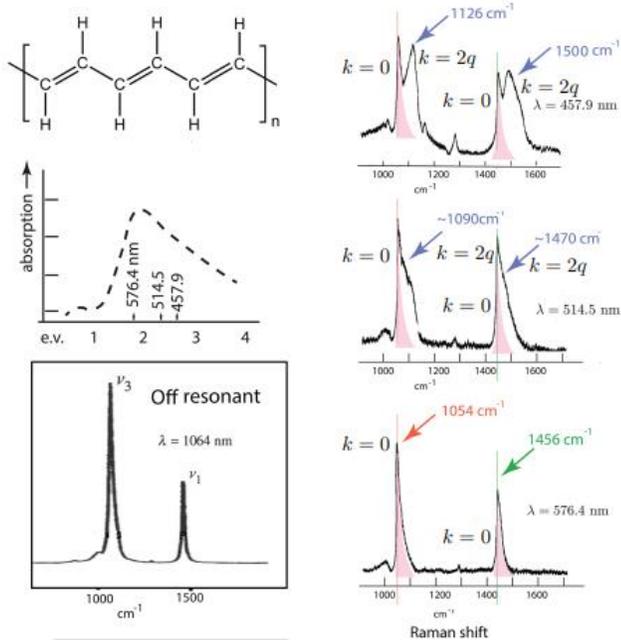
- Raman mapping at the edge position



➔ Starting of aging with the appearance of Li_2C_2

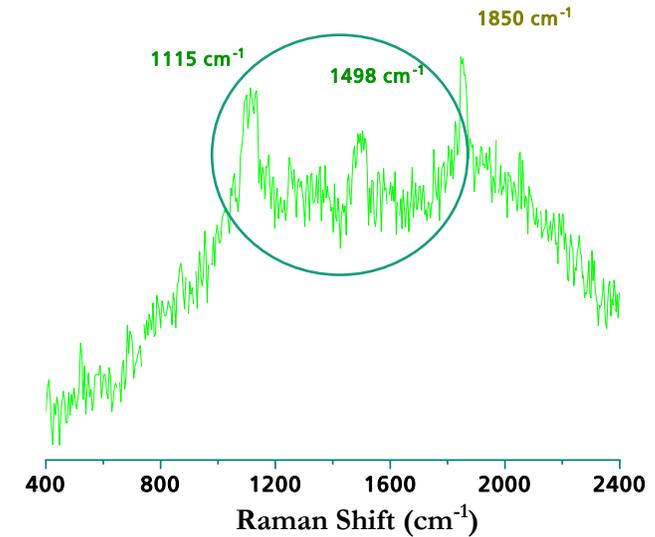
Polyacetylene on the anode

Literature

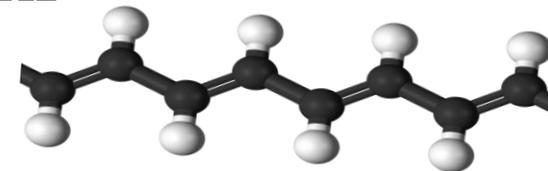


HELLER et al arXiv preprint arXiv:1410.8795, 2014.

Presence of polyacetylene



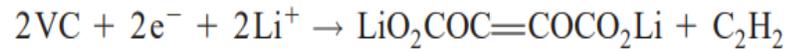
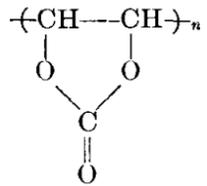
C_2H_2



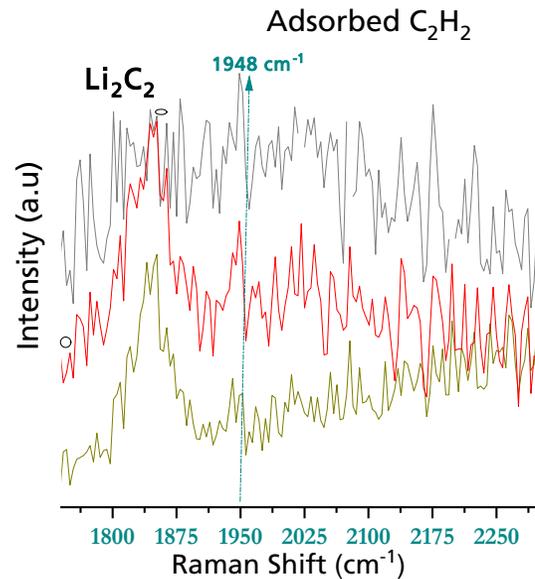
<https://www.chemistryworld.com/podcasts/polyacetylene/6506.article>

Possible origin of polyacetylene

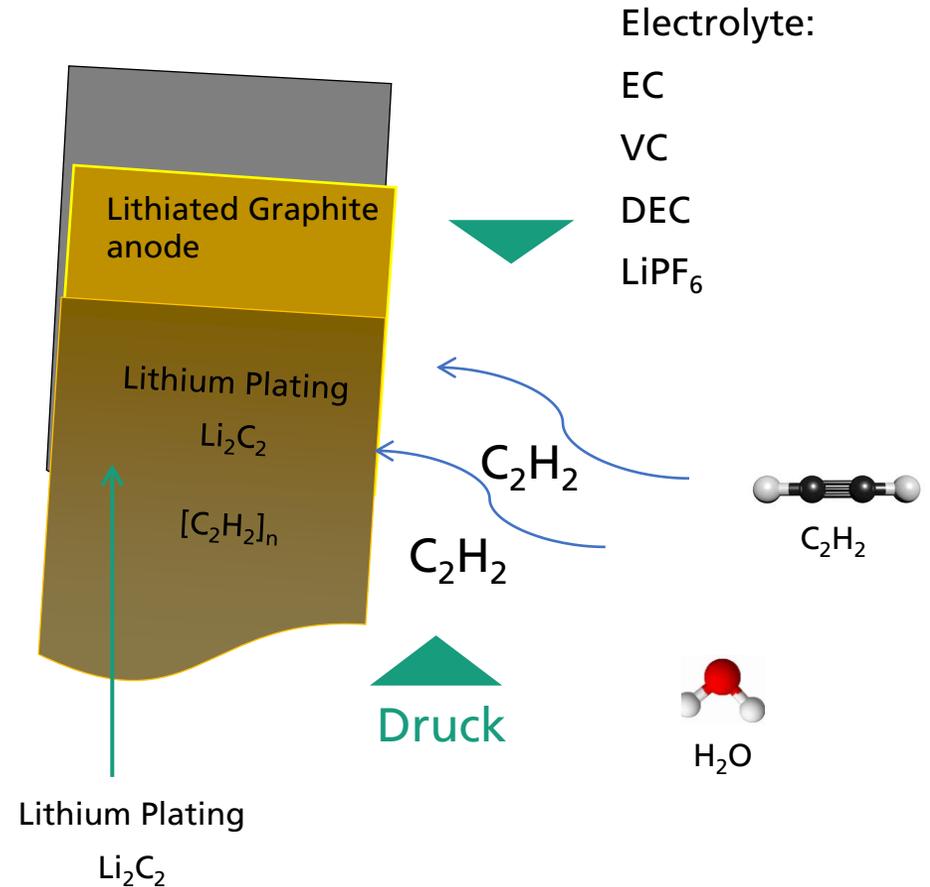
Electrolyte degradation



Journal of Physical Chemistry C, 123(33), 20084-20092.



Presence of polyacetylene



Conclusion

- Raman investigation of aged electrodes of Li-ion battery cells without air contact
- Mapping of chemical distribution on the surface of battery components
- Detection of lithium plating as Li_2C_2

- Common aging of anode:
 - Cracks
 - Delamination of graphite from current collector
 - Separator pores covered by graphite

- New aging mode:
 - Presence of polyacetylene on the surface of the aged anode

Thank You for Your Attention!

Slaheddine Jabri

www.ise.fraunhofer.de

slaheddine.jabri@ise.fraunhofer.de

Luciana.pitta.bauermann@ise.fraunhofer.de

