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HIGH RESOLUTION IMAGING OF LI-ION ELECTRODES BY MICRO-LIBS (LASER-INDUCED BREAKDOWN SPECTROSCOPY)

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The improvement of Li-ion batteries is a major challenge for the decarbonization of individual means of transport. Their behavior and performance mainly differs by the nature of their electrode materials, some of which are still in development. In order to fit with electrochemical models, the elemental distribution of lithium in electrodes needs to be measured at micrometric resolution. Nowadays, few techniques (e.g. MRI (Magnetic Resonance Imaging)) are able to characterize lithium. These techniques are generally time consuming and are difficult to apply in routine due to technical constraints. Furthermore, other approaches such as SEM (Scanning Electron Microscopy) or TEM (Transmission Electron Microscopy) combined to EDS (Energy Dispersive Spectroscopy) can image most of the elements with a high spatial resolution ($\sim \mu\text{m}$) [1, 2] but cannot detect lithium with enough sensitivity due to its low atomic number.

In this work we propose to apply the micro LIBS-based imaging approach for the characterization of the lithium distribution in various types of electrodes. Thanks to its high sensitivity for light elements and the possibility to focus the laser beam on very small surfaces, LIBS is very promising for this application [3-5]. However, there are several major obstacles to overcome. Firstly, the measurement resolution must be comparable to that of SEM – EDS ($\sim 1 \mu\text{m}$). Achieving this resolution is indeed essential to observe properly lithium grains of a few micrometers in size. Secondly, given the small amount of material ablated per shot ($\sim \text{pg}$), it is essential to work with a high sensitivity and optimized detection system. In this presentation, we will describe an original LIBS microscope using a high numerical aperture objective ($\times 50$ magnification), a UV laser beam (266 nm) shaped to achieve an M^2 close to 1, and a detection system optimized for measurement in the visible range. With this instrument, the lithium distribution has been imaged with a resolution of $3 \mu\text{m}$ (cf. figure 1), as well as other elements of interest, such as C, Co, Ni, Cu and Al. Charged and discharged NMC type electrodes with different lithiation states will be shown. To the best of our knowledge, this is the first time that such type of LIBS analysis is performed.

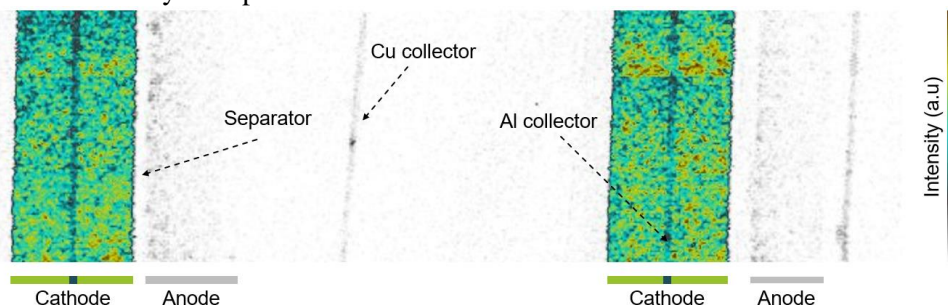


Figure 1 : Lithium image at $3 \mu\text{m}$ spatial resolution on a sample composed of a formed and discharged NMC type commercial battery.

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- [5] Susumu Imashuku, Hiroyuki Taguchi, Shun Fujieda, Shigeru Suzuki, and Kazuaki Wagatsuma, *Electrochimica Acta*, 293 :78–83, January 2019.

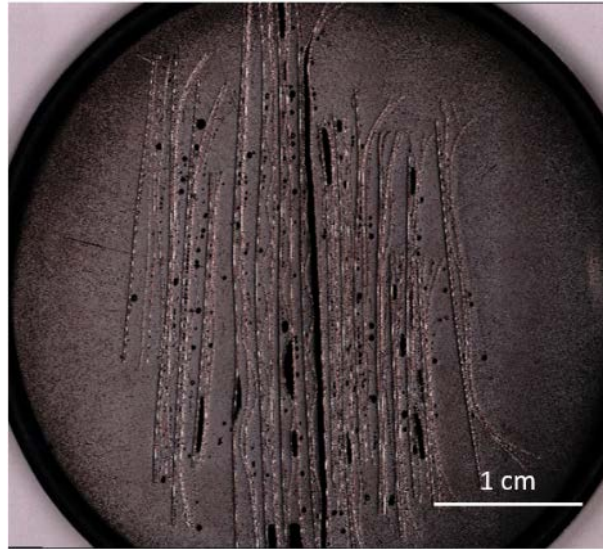
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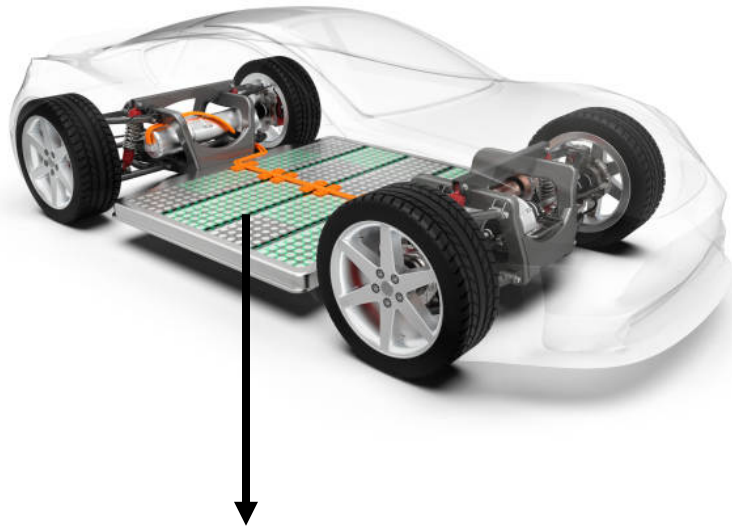
¹*Institut Lumière Matière UMR5306, Université Lyon 1 – CNRS, Université de Lyon, 69622 Villeurbanne, France*

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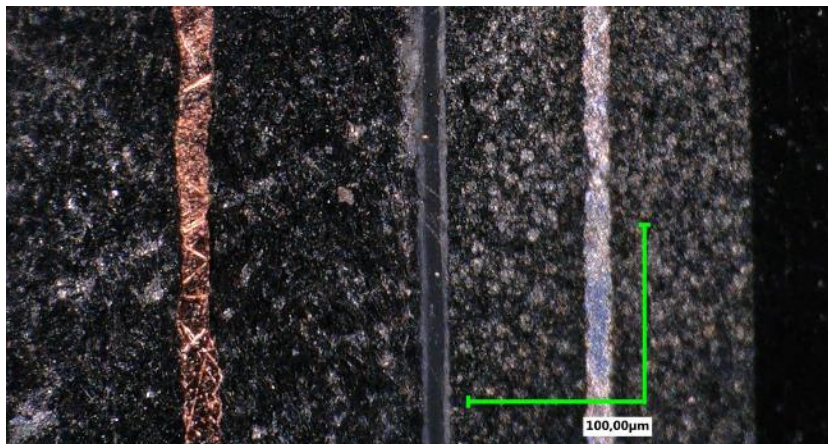
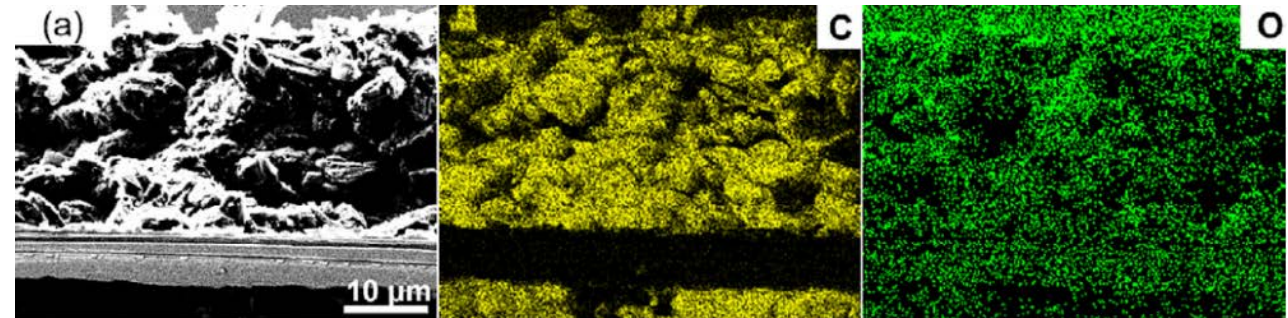
e-mail : jordan.fernandes@univ-lyon1.fr



Context



Scanning Electron Microscopy - Energy Dispersive Spectroscopy (SEM - EDS)

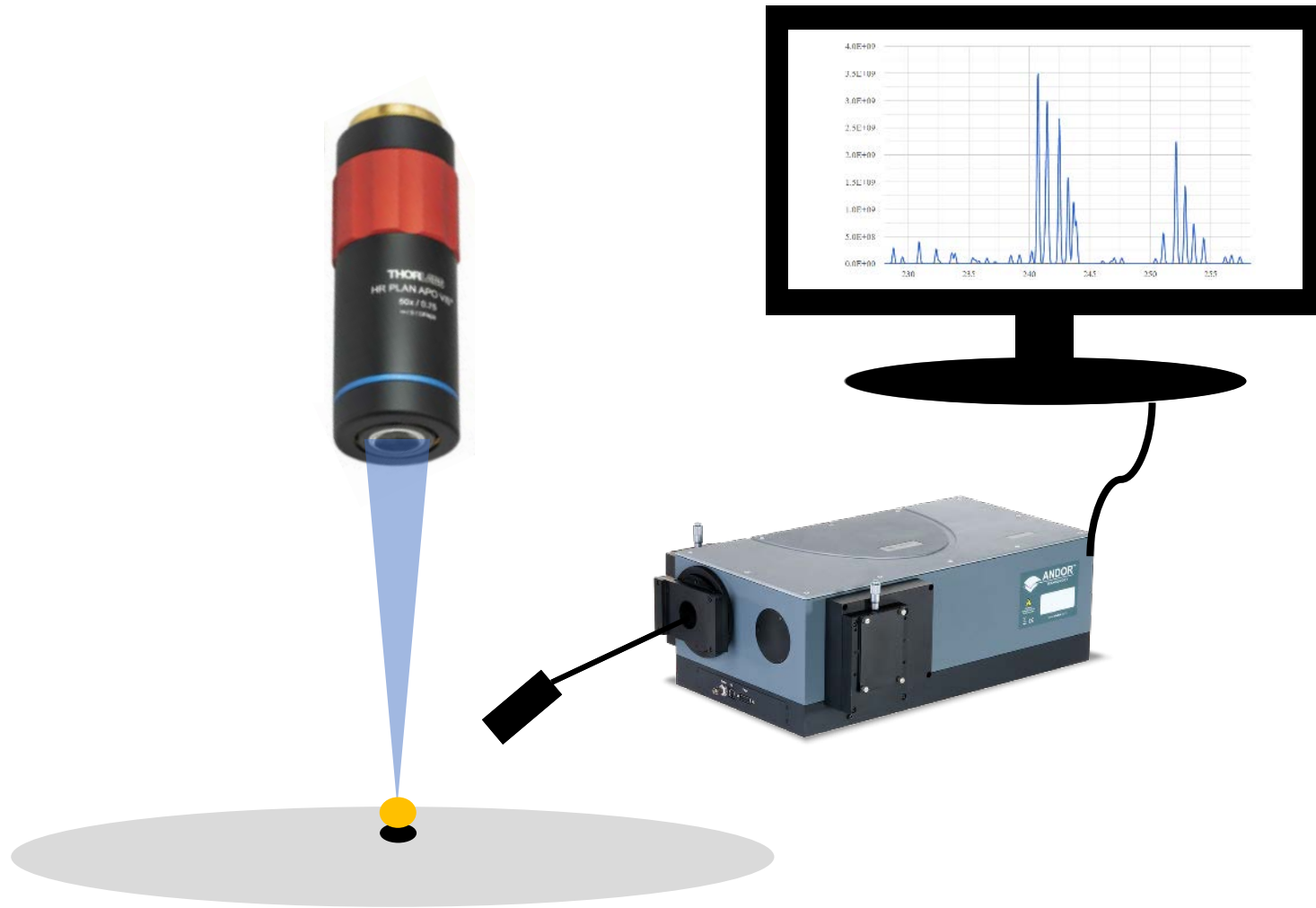


Guo, Jia, Yaqi Li, Jinhao Meng, Kjeld Pedersen, Leonid Gurevich, et Daniel-Ioan Stroe. 2022. « Understanding the Mechanism of Capacity Increase during Early Cycling of Commercial NMC/Graphite Lithium-Ion Batteries ». *Journal of Energy Chemistry* 74 (novembre): 34-44. <https://doi.org/10.1016/j.jechem.2022.07.005>.

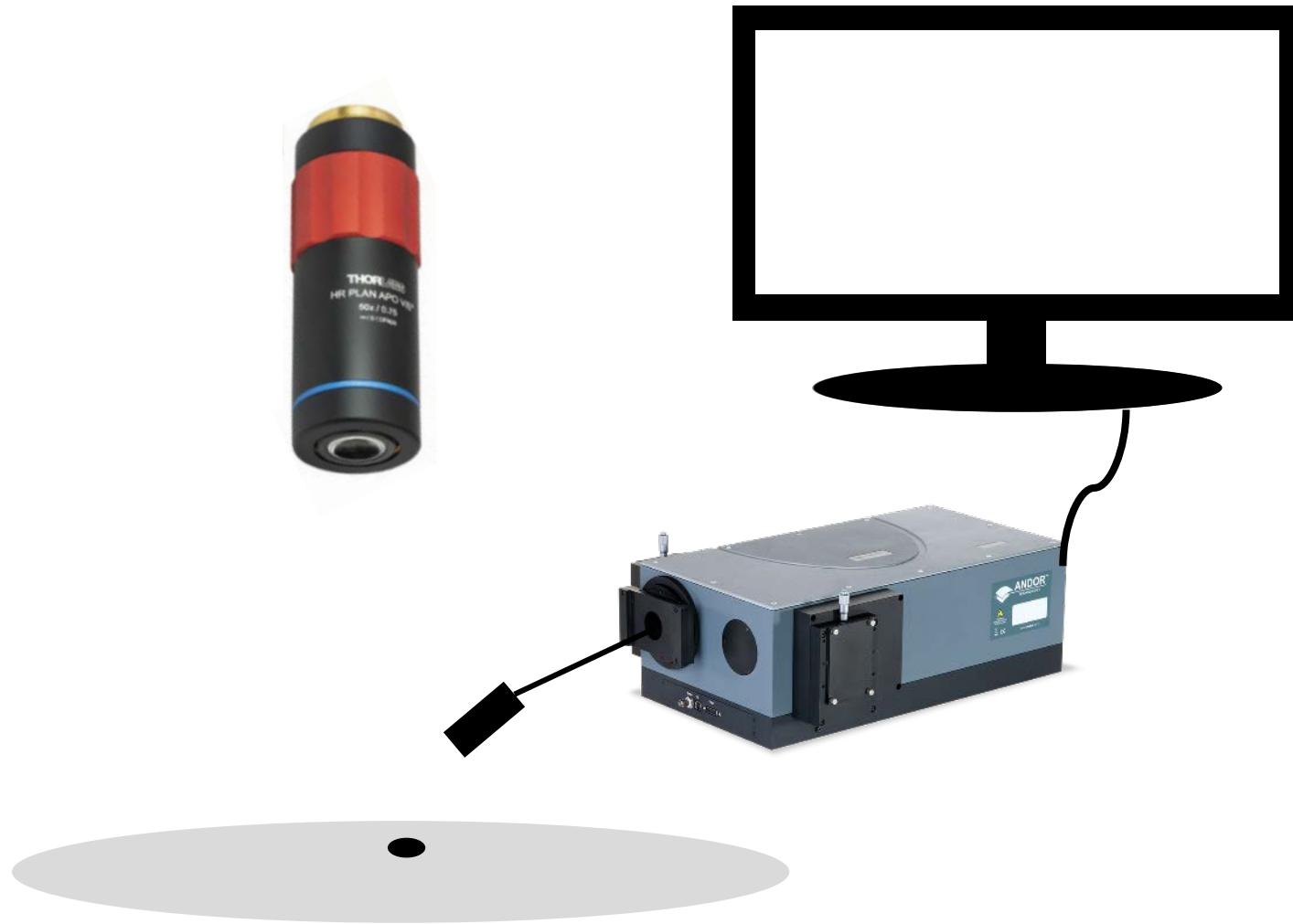
LIBS* is sensitive to Li

*Laser-Induced Breakdown Spectroscopy

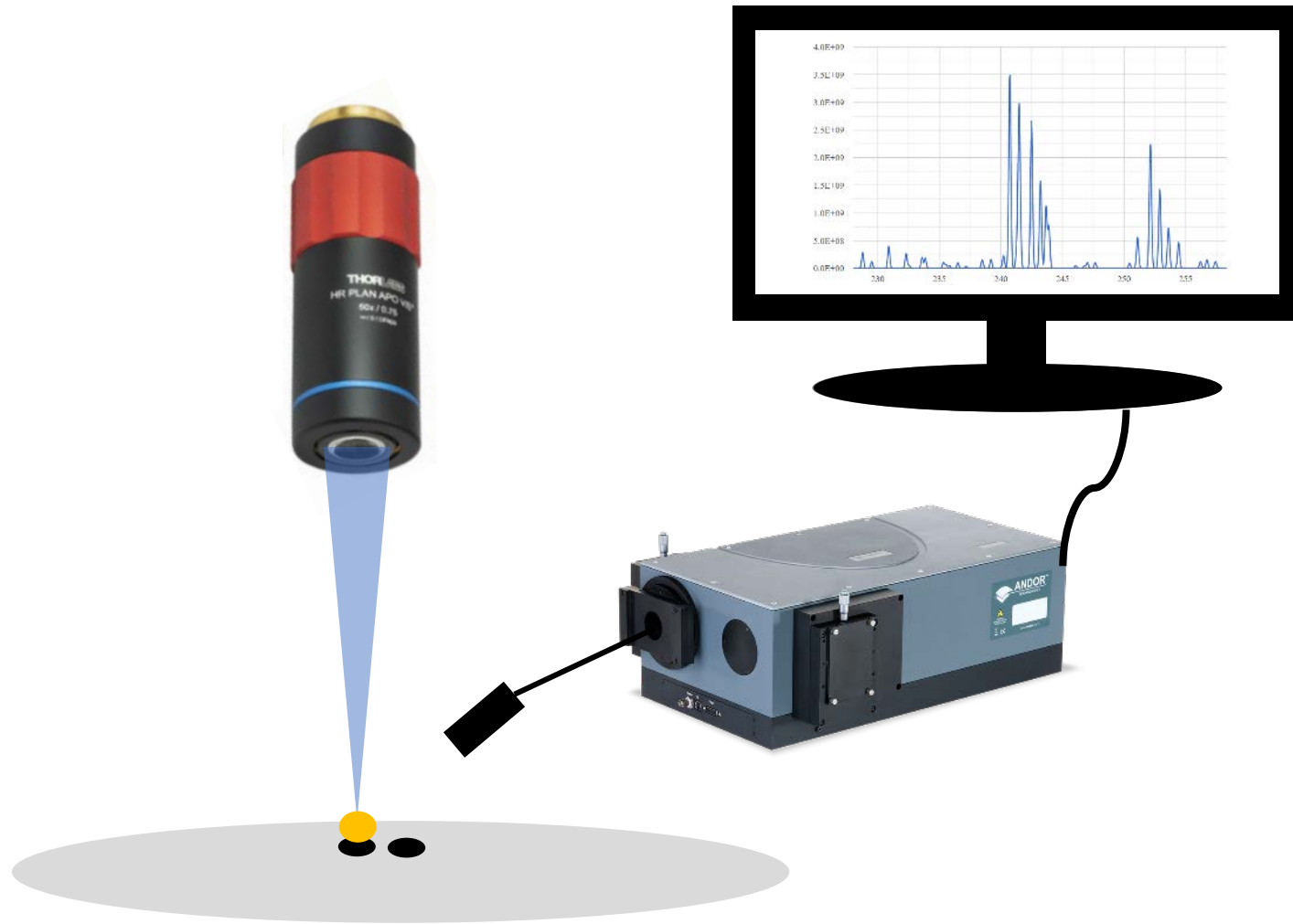
Working principle of LIBS (Laser-Induced Breakdown Spectroscopy) imaging



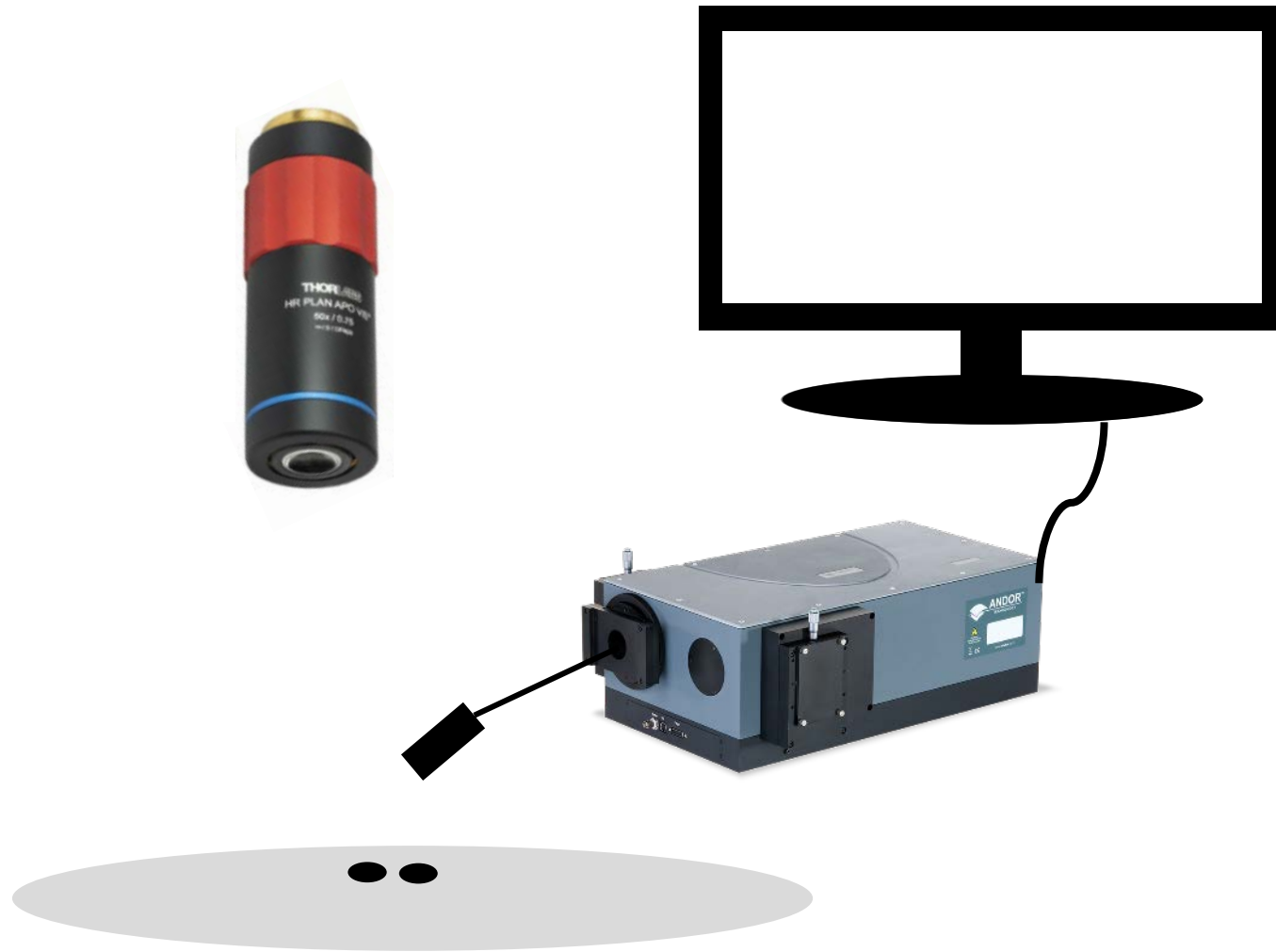
Working principle of LIBS (Laser-Induced Breakdown Spectroscopy) imaging



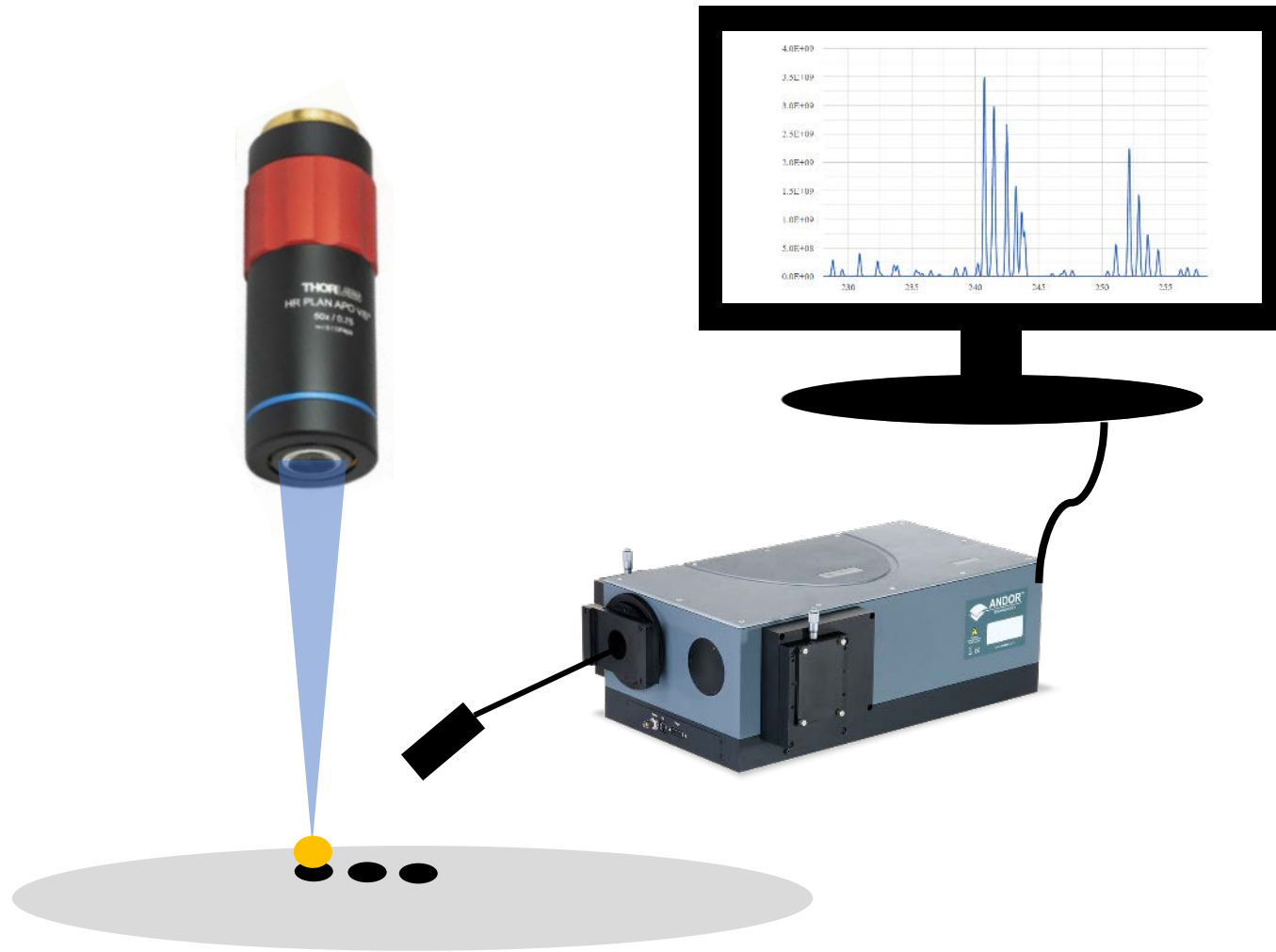
Working principle of LIBS (Laser-Induced Breakdown Spectroscopy) imaging



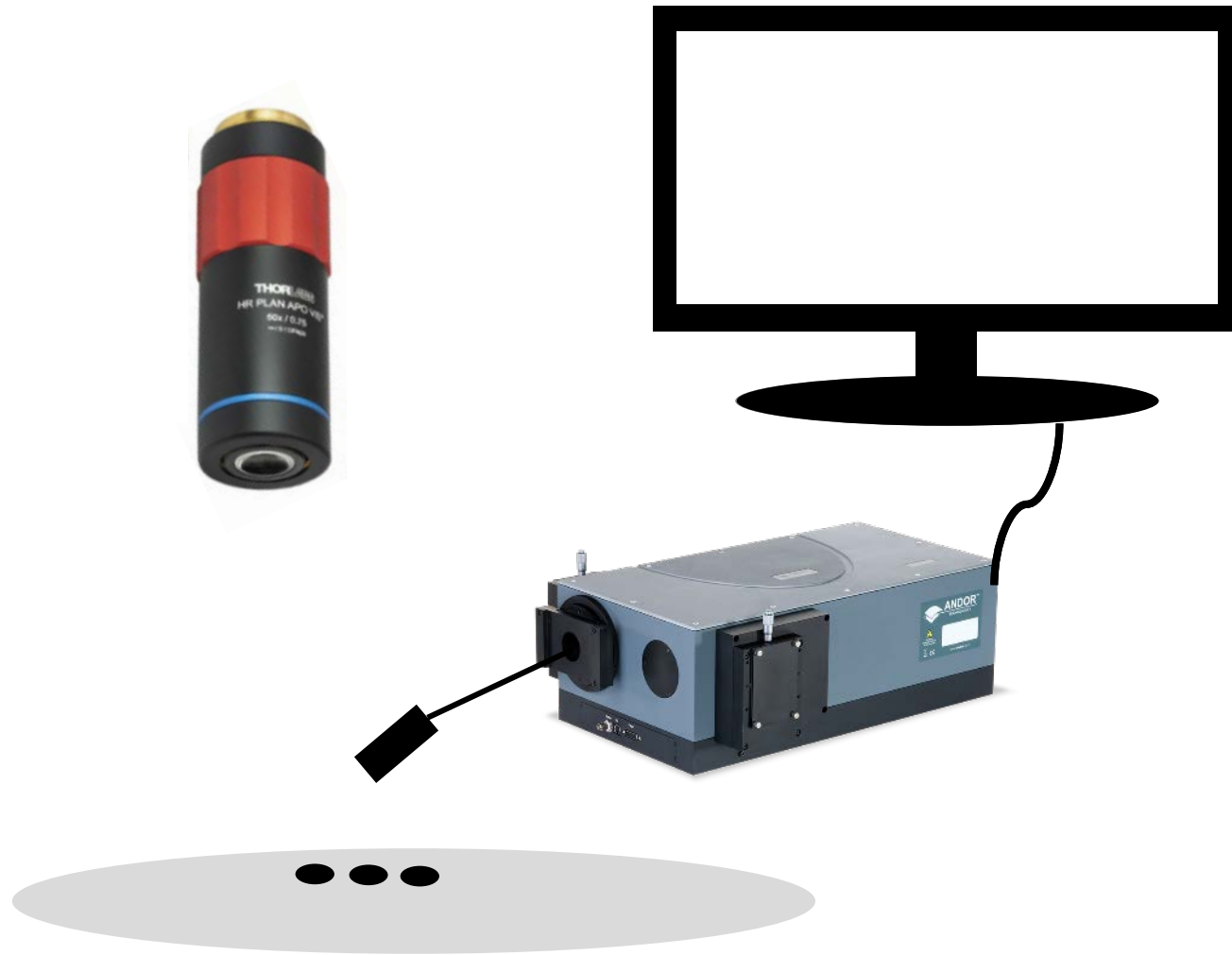
Working principle of LIBS (Laser-Induced Breakdown Spectroscopy) imaging



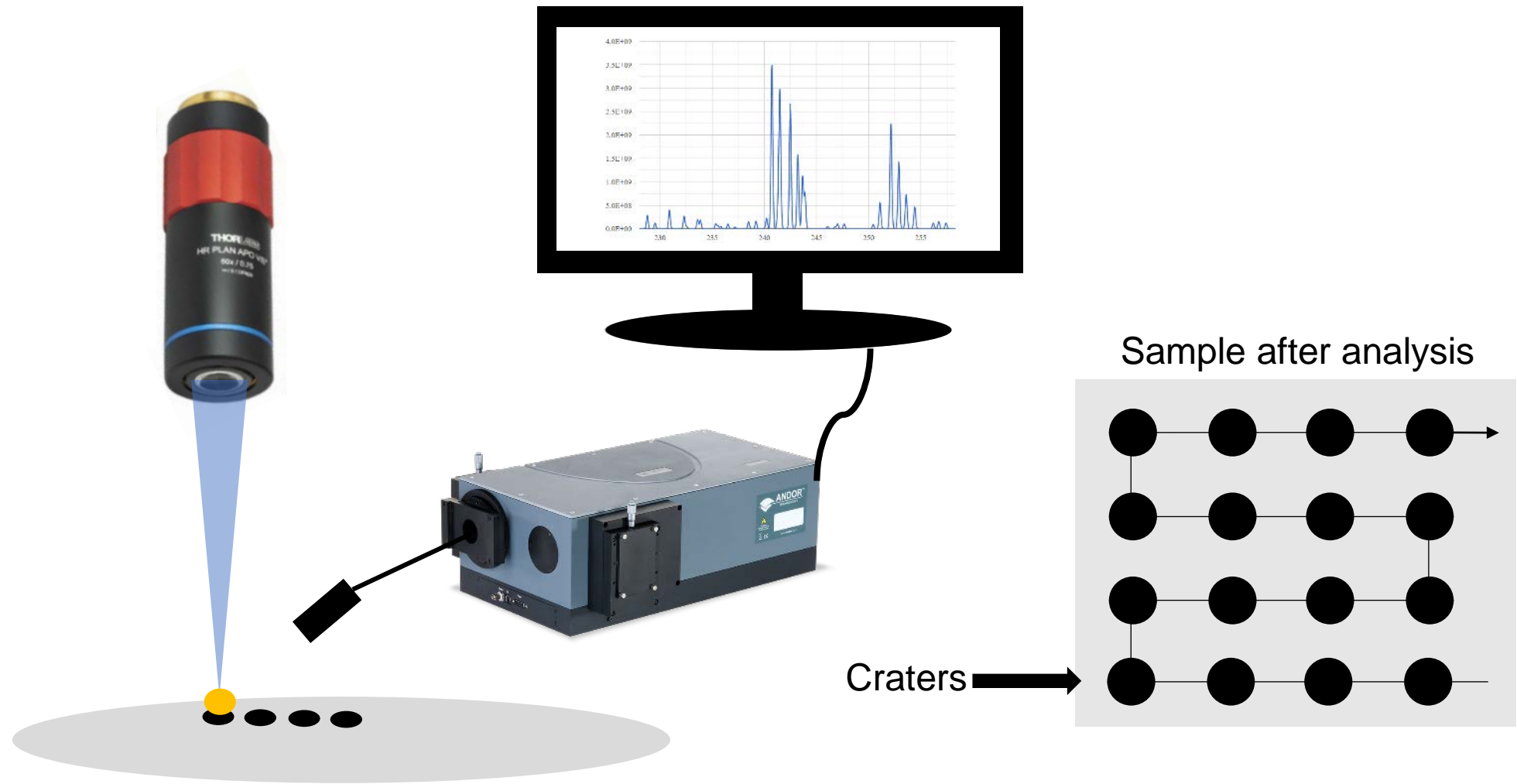
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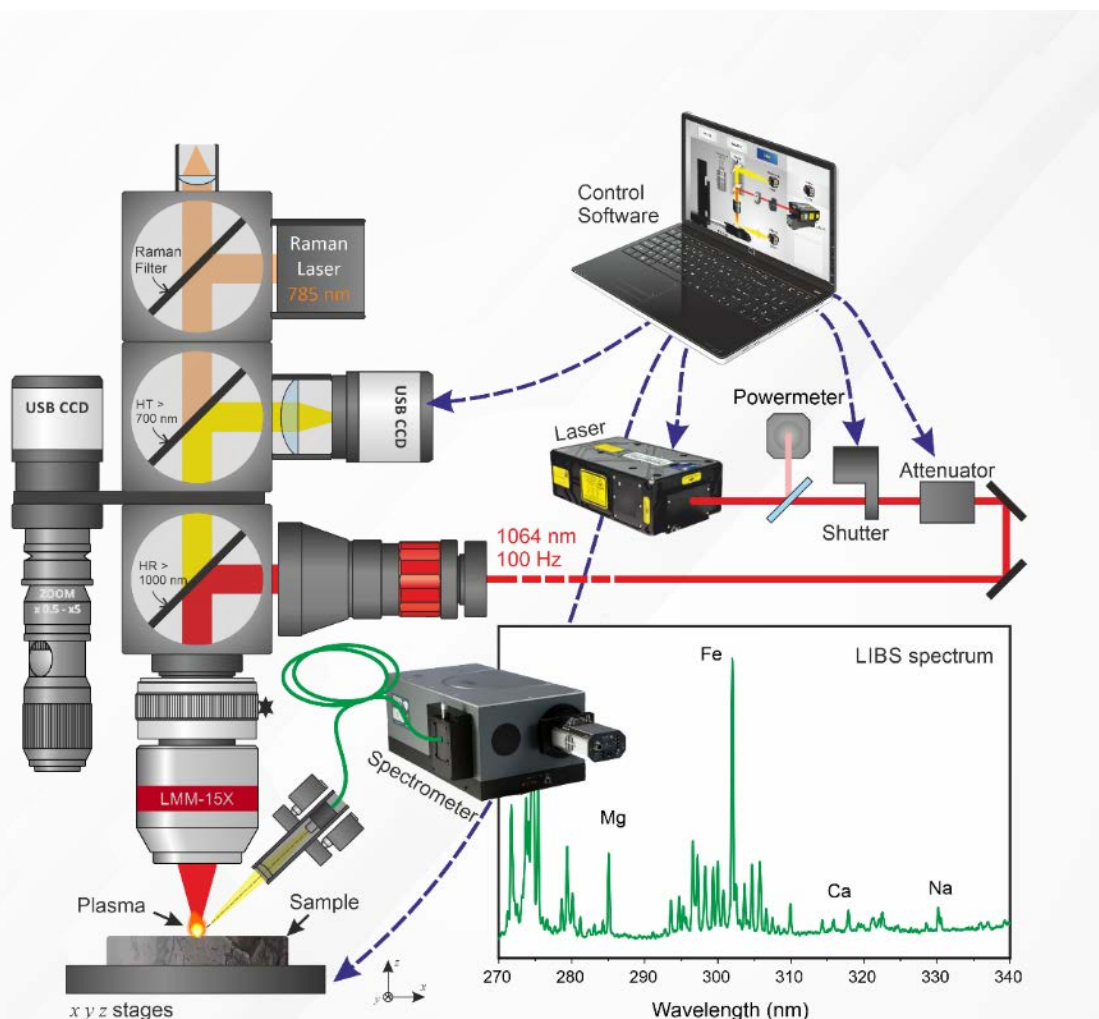
Working principle of LIBS (Laser-Induced Breakdown Spectroscopy) imaging



Working principle of LIBS (Laser-Induced Breakdown Spectroscopy) imaging

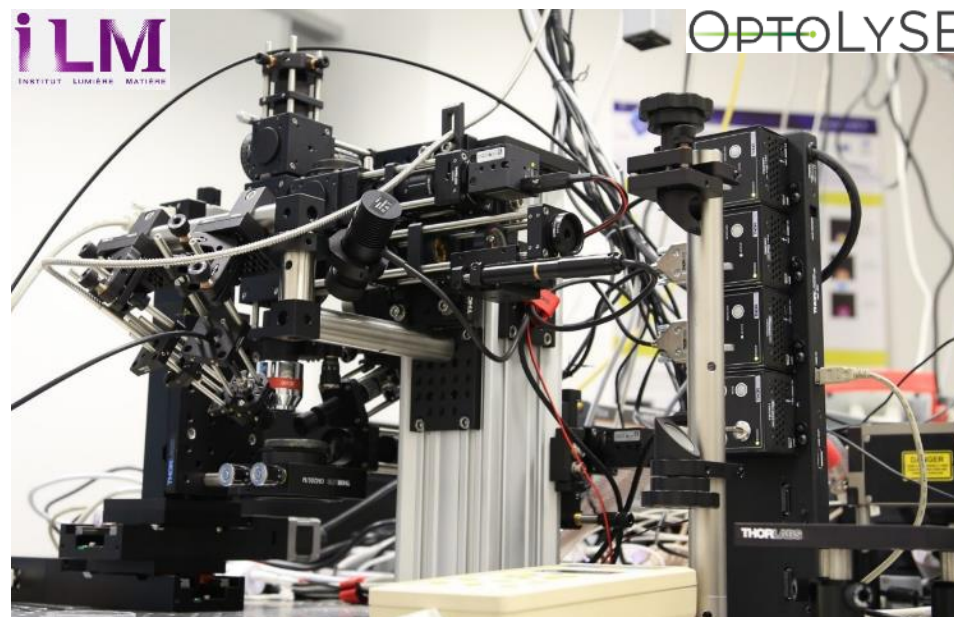


State of the art of the 100 Hz routine device

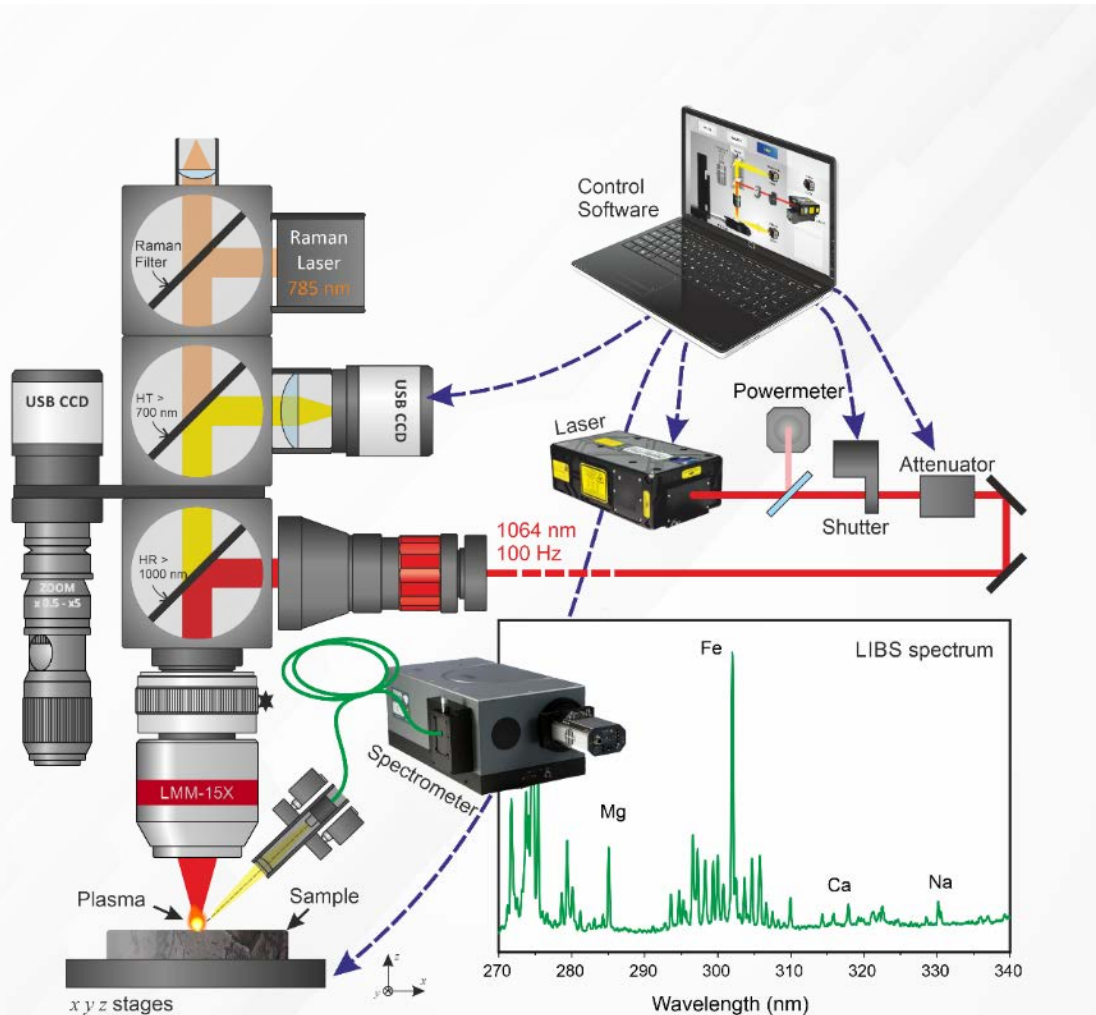


Performances :

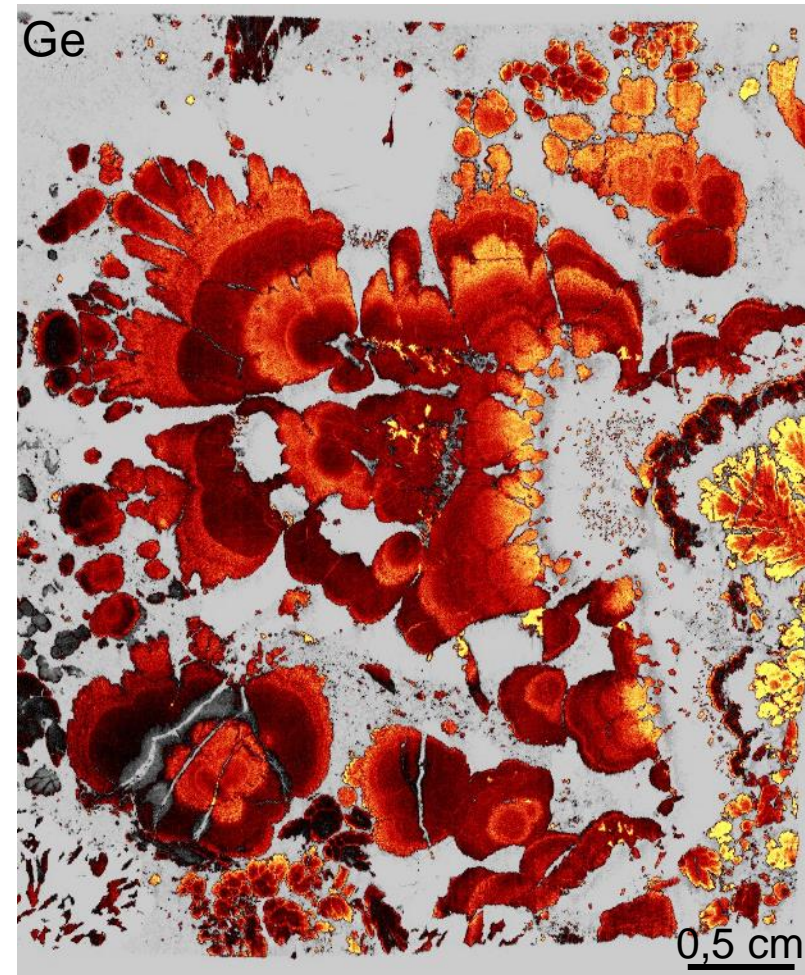
- ▶ Laser Nd:Yag 1064 nm, 100 Hz
- ▶ Ar flow
- ▶ 3 Spectrometers : 2 Czerny-Turner & ICCD et 1 compact spectrometer
- ▶ 360 000 pixels per hours (100 Hz)
- ▶ Scan of 50 mm at 10 μ m spatial resolution



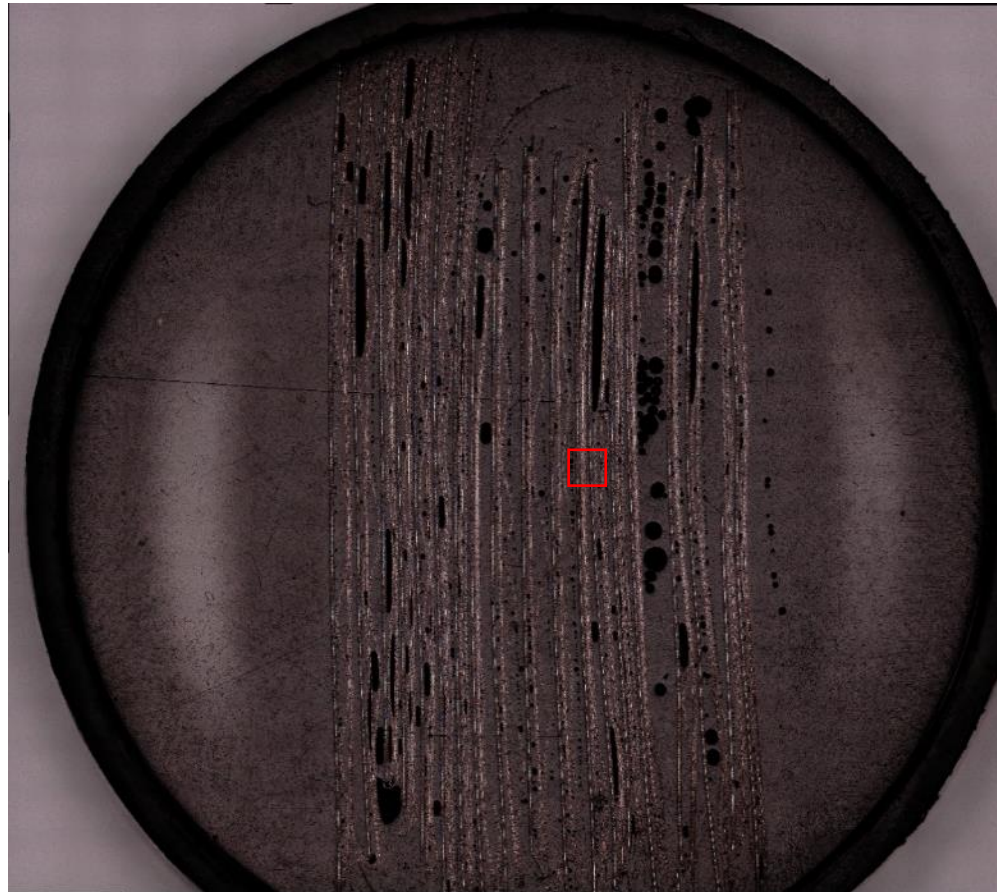
State of the art of the 100 Hz routine device



Sphalerite

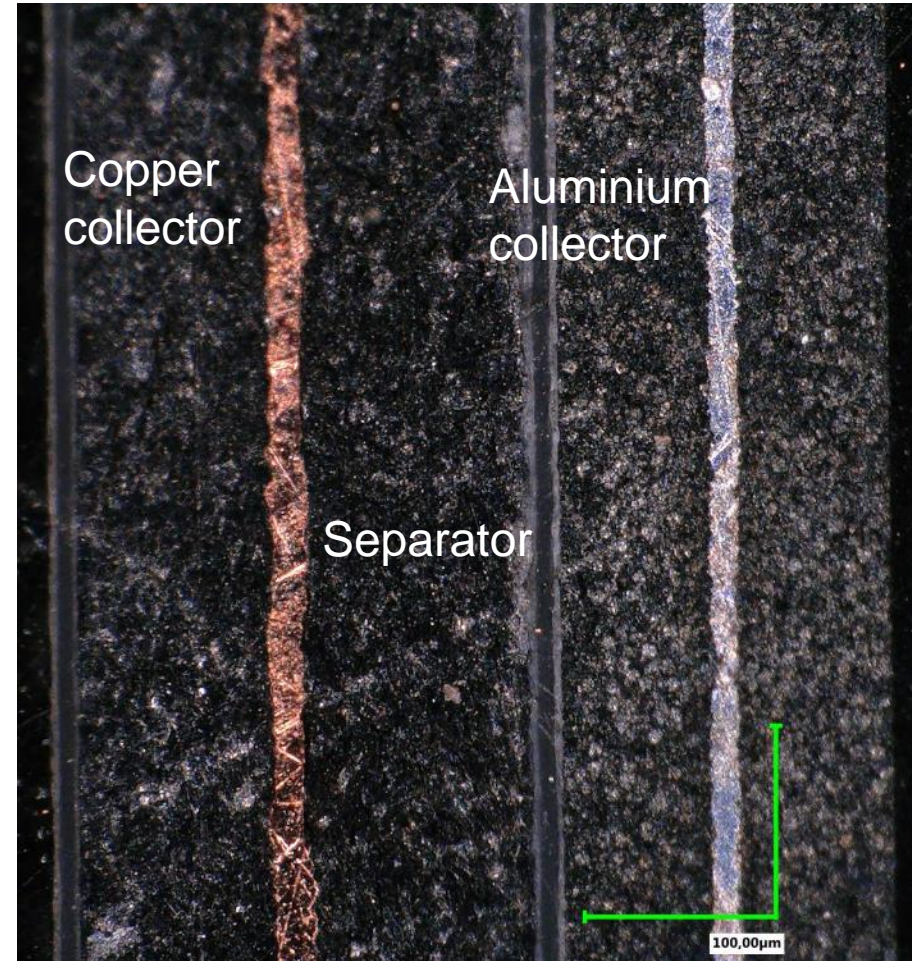


Sample of analysis



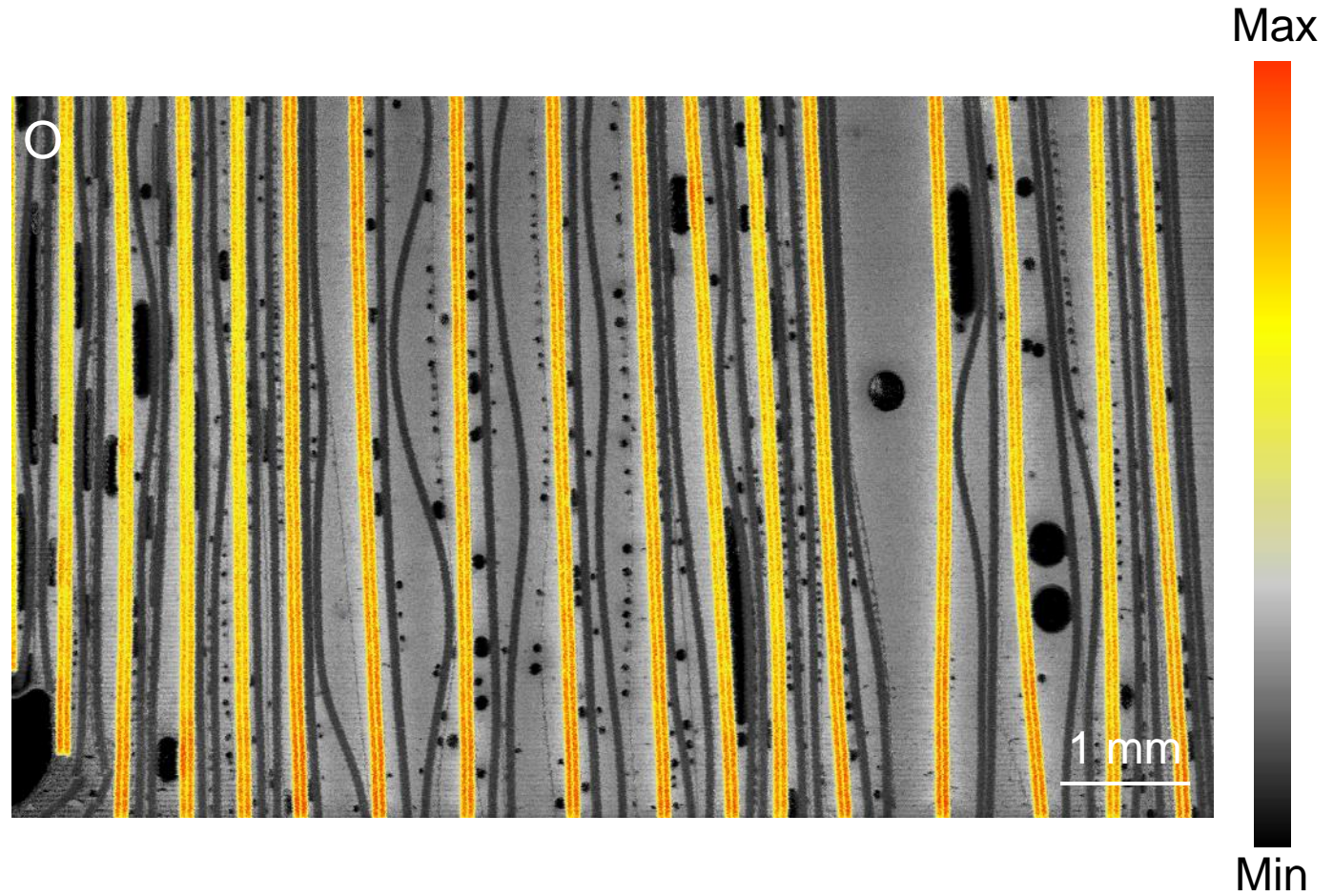
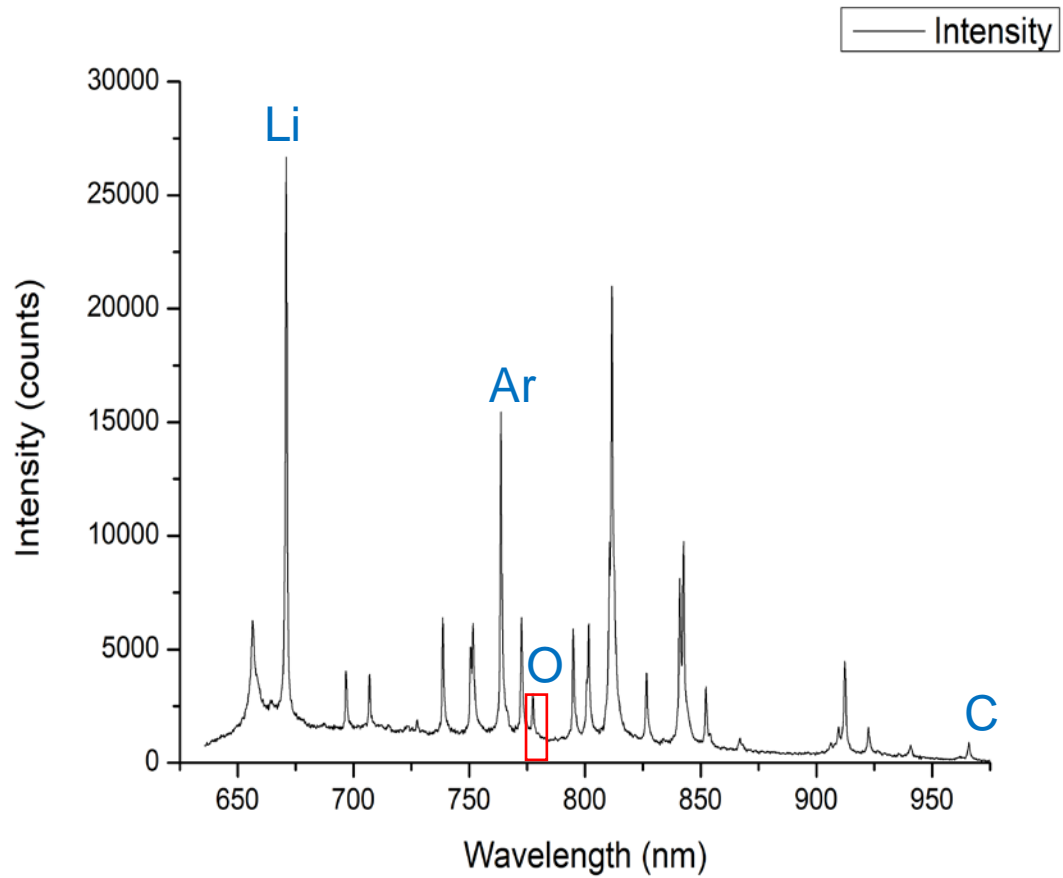
Stack of positive electrode (NMC) – separator – negative graphite electrode at the discharged state

Active matter graphite Active matter NMC

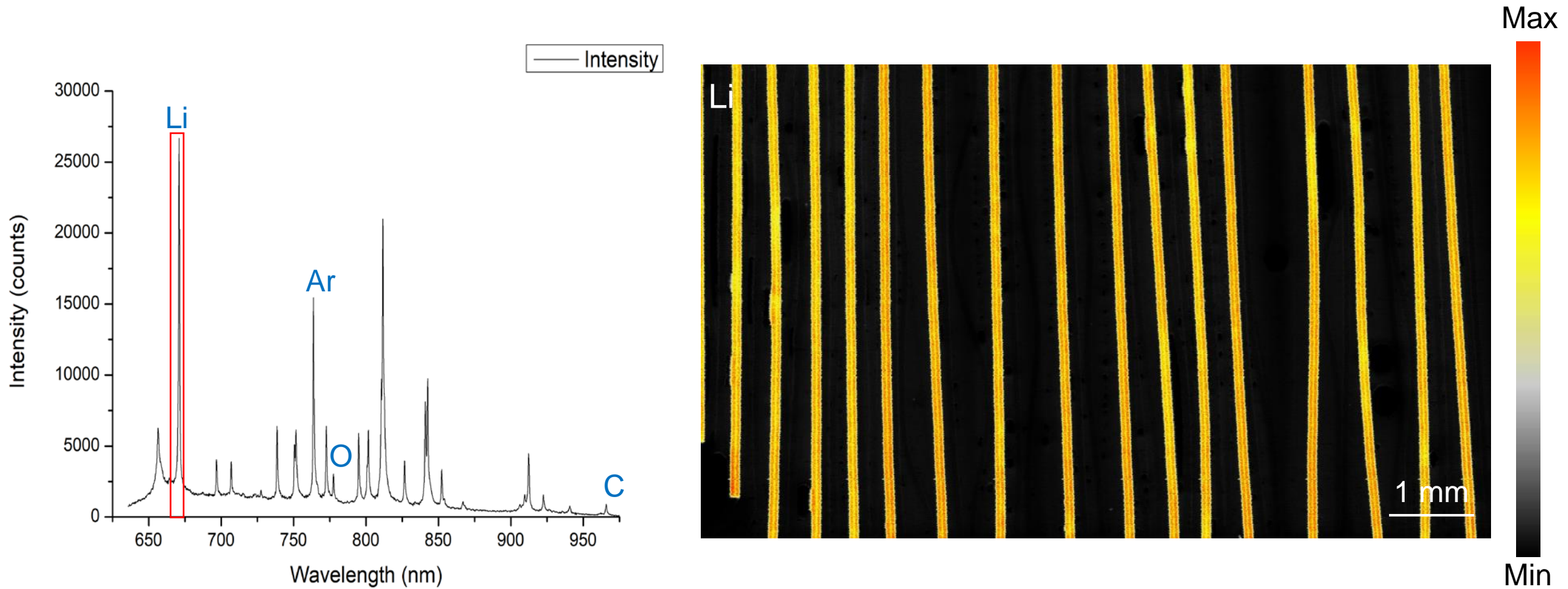


Zoom (in the rectangular part)

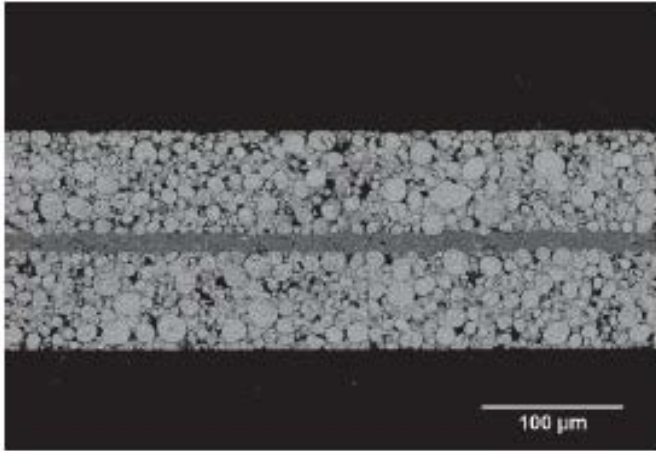
10 μm oxygene elemental map



10 μm lithium elemental map



Spatial resolution ?



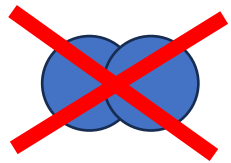
SEM image of the
cross-section

Our objective is to achieve a spatial resolution of 1 μm

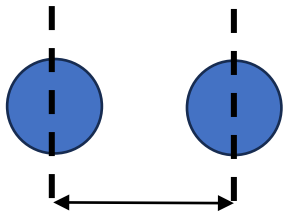
How to improve the spatial resolution in LIBS ?

Surface of a scanned sample

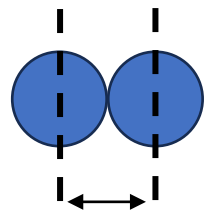
Beam radius after focusing



Non reproducible analysis



Reproducible analysis but not ultimate resolution



Reproducible analysis and ultimate resolution

Step size

$$I = \propto f(m_{ablated})$$

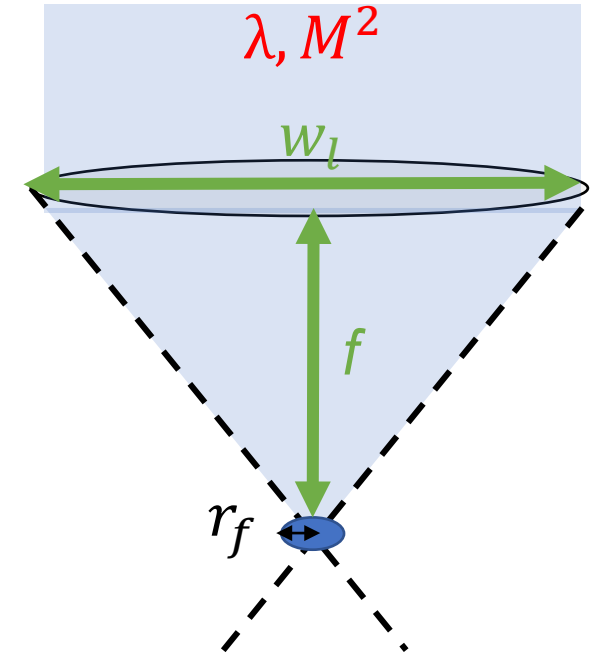
$$r_f = \frac{\lambda f M^2}{\pi w_l}$$

 Laser

 Focusing instrument

Laser energy

- Thermic diffusion
- Shockwave generation



Improving the spatial resolution is at the expense of sensitivity

Reducing the ultimate spatial resolution by 10 is decreasing the sensitivity by 1000

Experimental device

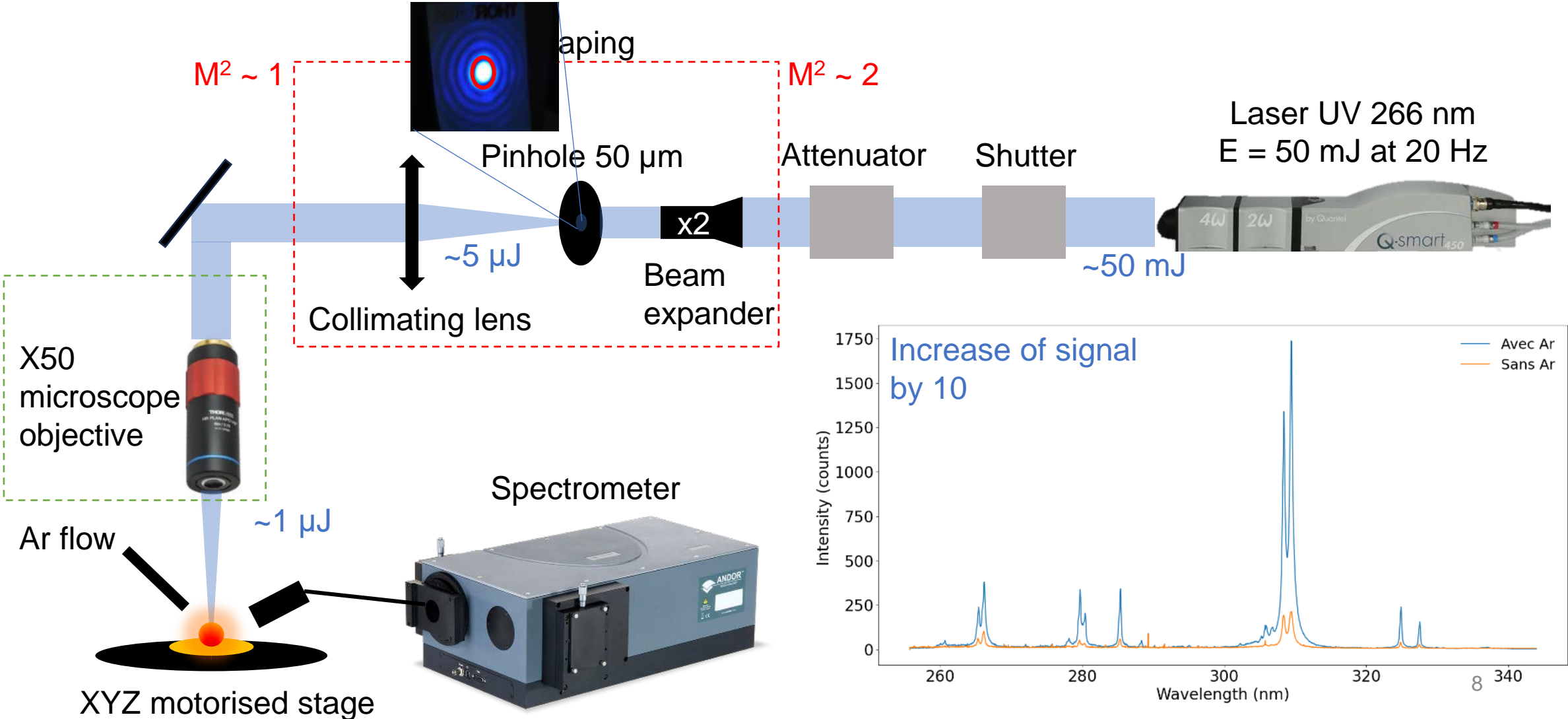
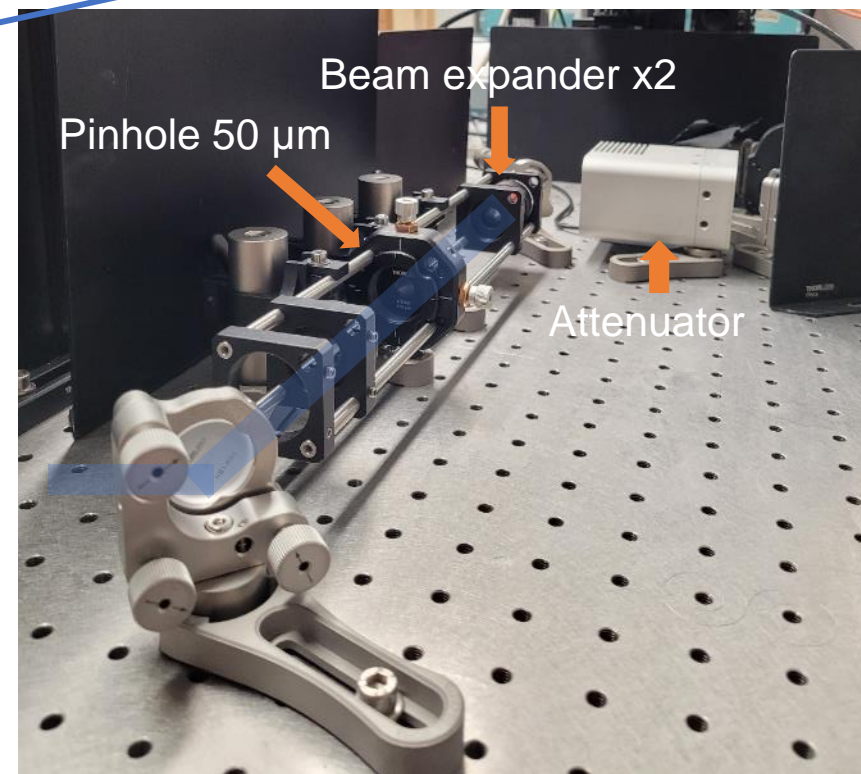
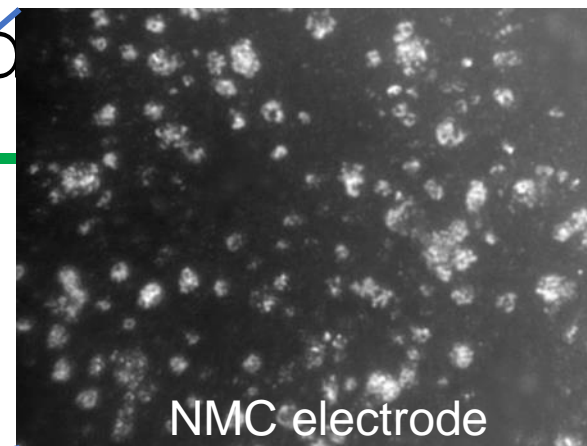
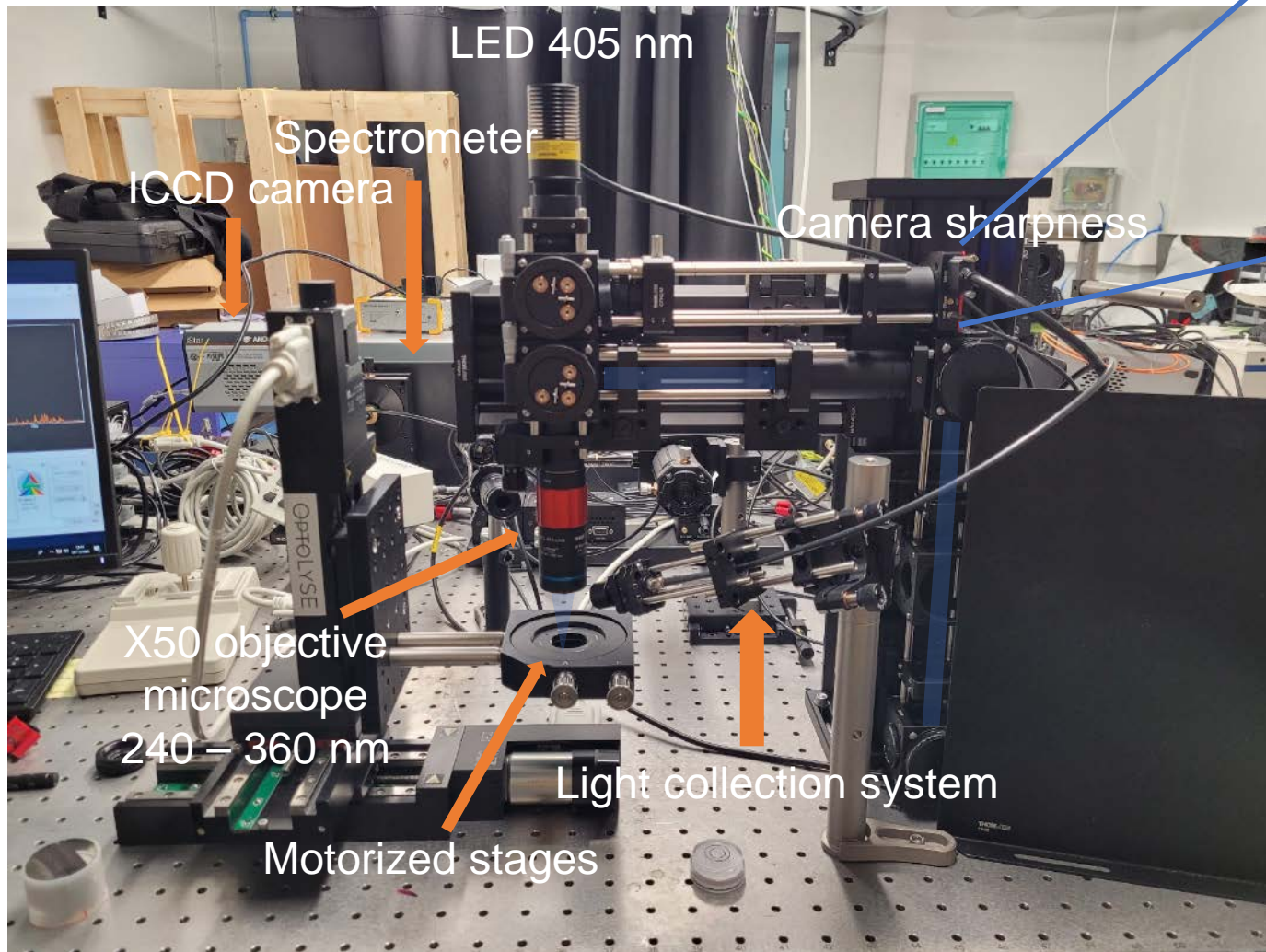
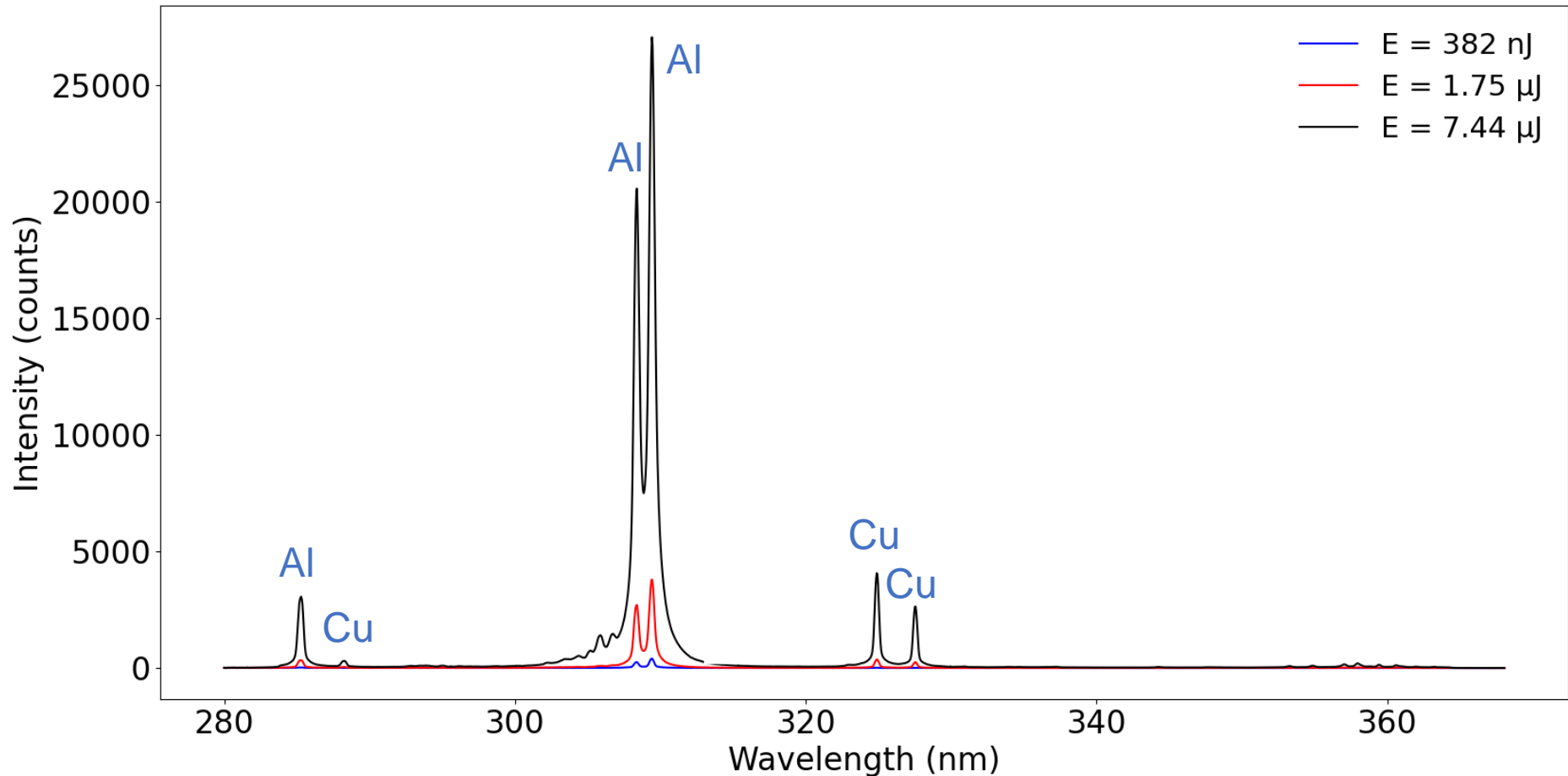


Image of the mounted

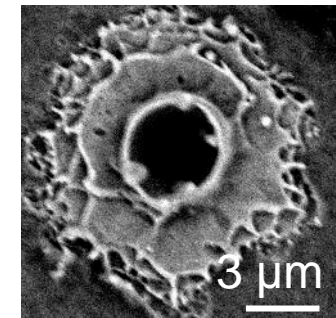


Study of the impact of laser energy on the amount of signal collected and the size of craters

Average spectrum of 1000 laser shots fired on a sample of Al



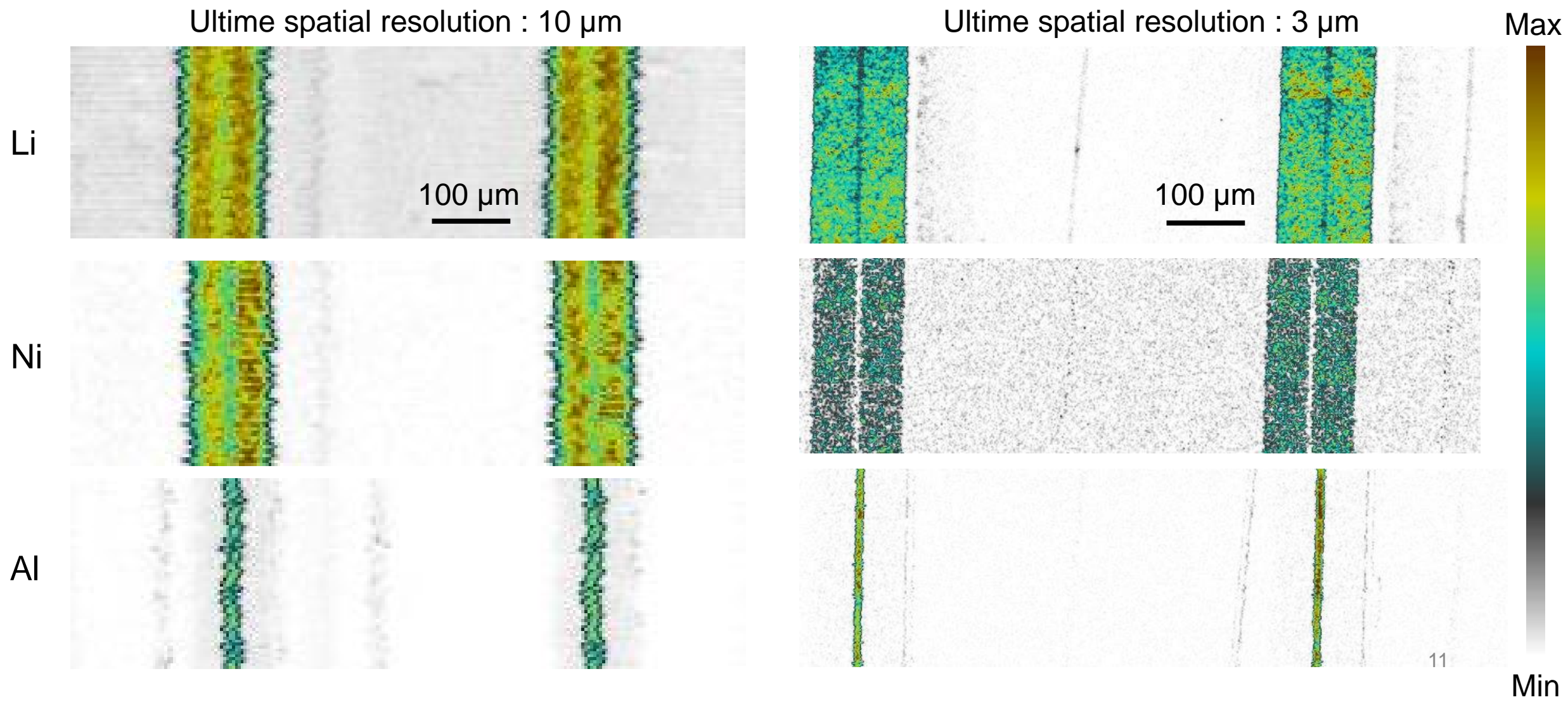
$E = 1.75 \text{ }\mu\text{J}$



$E = 382 \text{ nJ}$

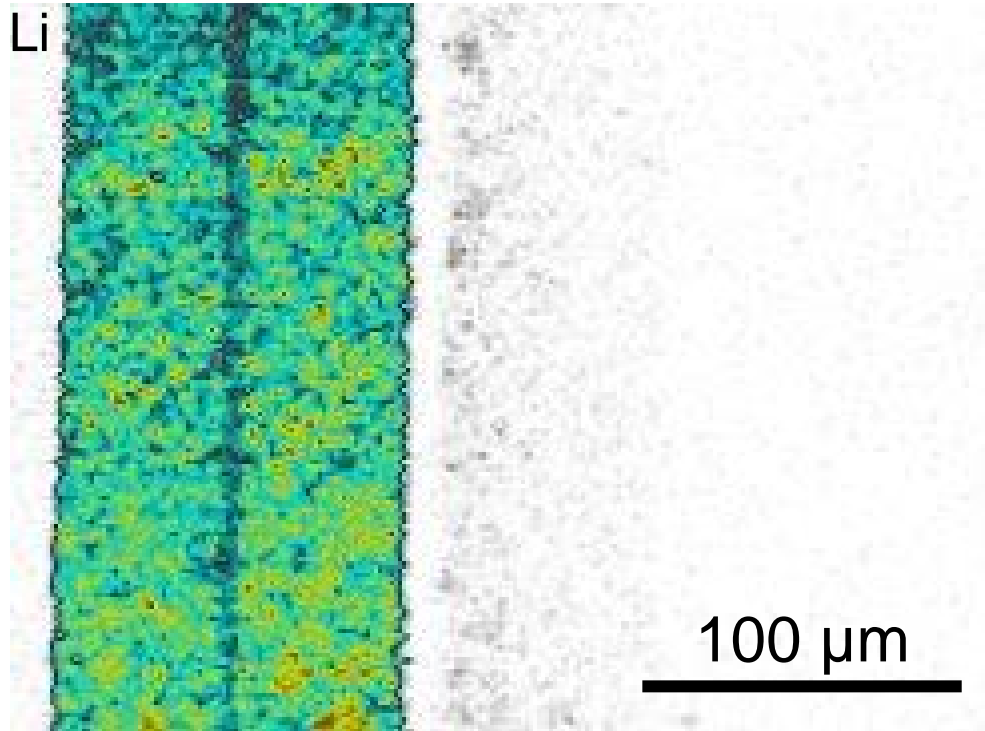


Elemental maps of NMC cathode

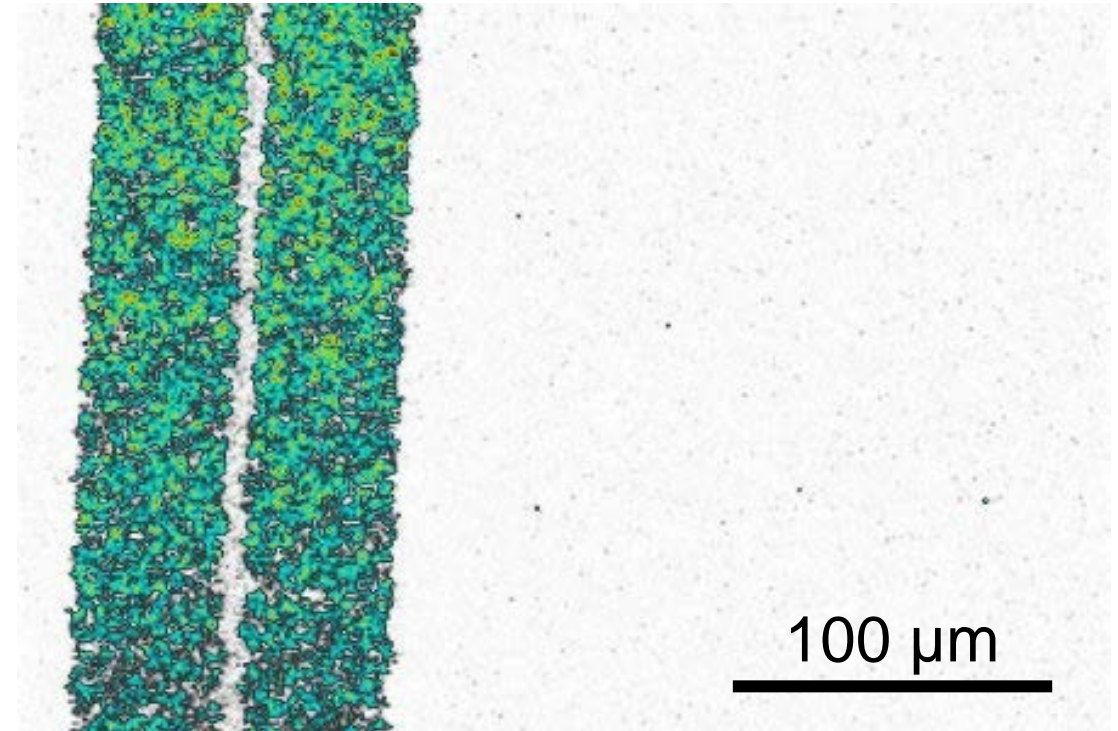


Lithium elemental maps of NMC cathode

Ultimate spatial resolution : 3 μm



Ultimate spatial resolution : 2 μm



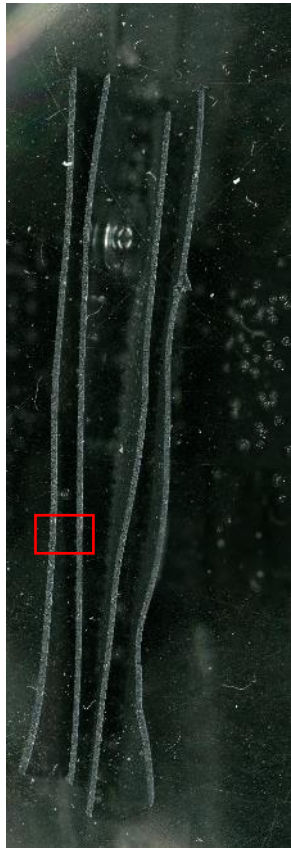
Max



Min

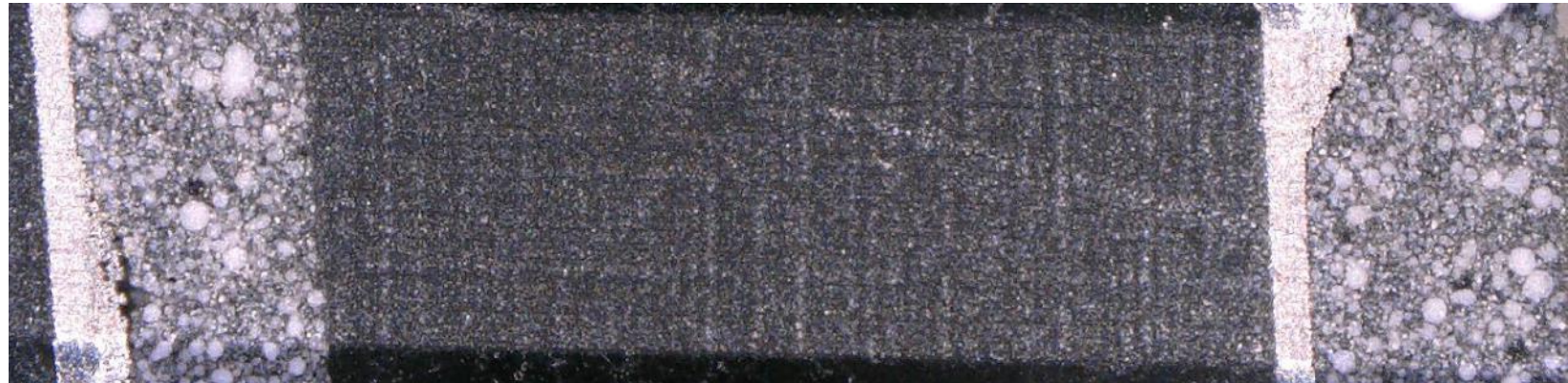
Li mapping at 2 μm ultimate spatial resolution of a pristine LFP electrode

LFP

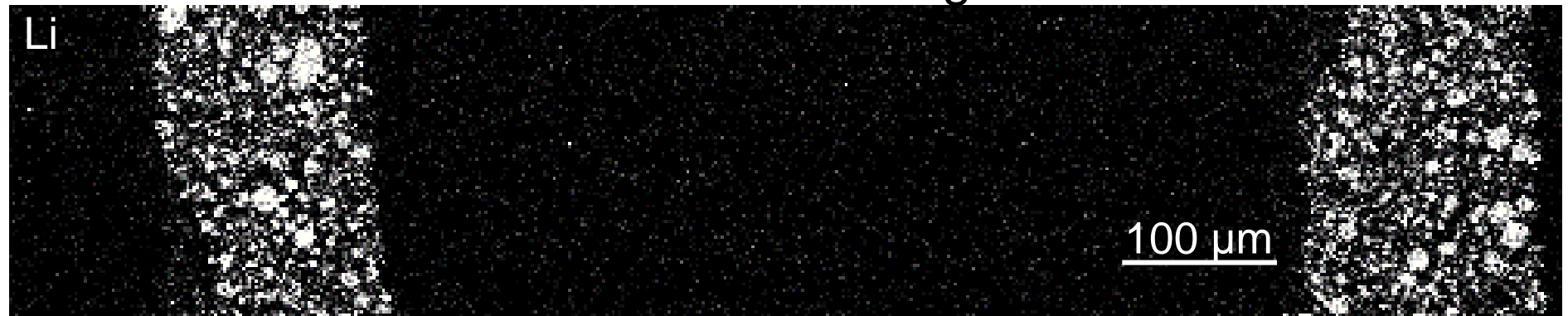


Pristine positive electrode at the discharged state

Optical image



Micro-LIBS image



High

Low

Conclusion

- In 1 year, improve the spatial resolution by 5 : $10\ \mu\text{m}$ \longrightarrow $2\ \mu\text{m}$



- This resolution makes it possible to study the distribution of lithium at the microstructure level

Outlook

Increase of the sensitivity

- ❑ Assist LIBS with LIF (Laser-Induced Fluorescence)

Working on calibration models for lithium

- ❑ Creation and quantification by ICP of standard sample
- ❑ Elaboration of univariate and/or multivariate models

Thank you for your attention



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