THERMAL TOMOGRAPHY FOR MICROSCALE ENERGY CONVERSION DEVICES

Stéphane CHEVALIER

HDR Defense - April 11th, 2024

Committee Members

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	Annie COLIN	-	Professor, ESPCI
	Helcio ORLANDE	-	Professor, Federal University of Rio
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	Ivan IORDANOFF	-	Professor, ENSAM
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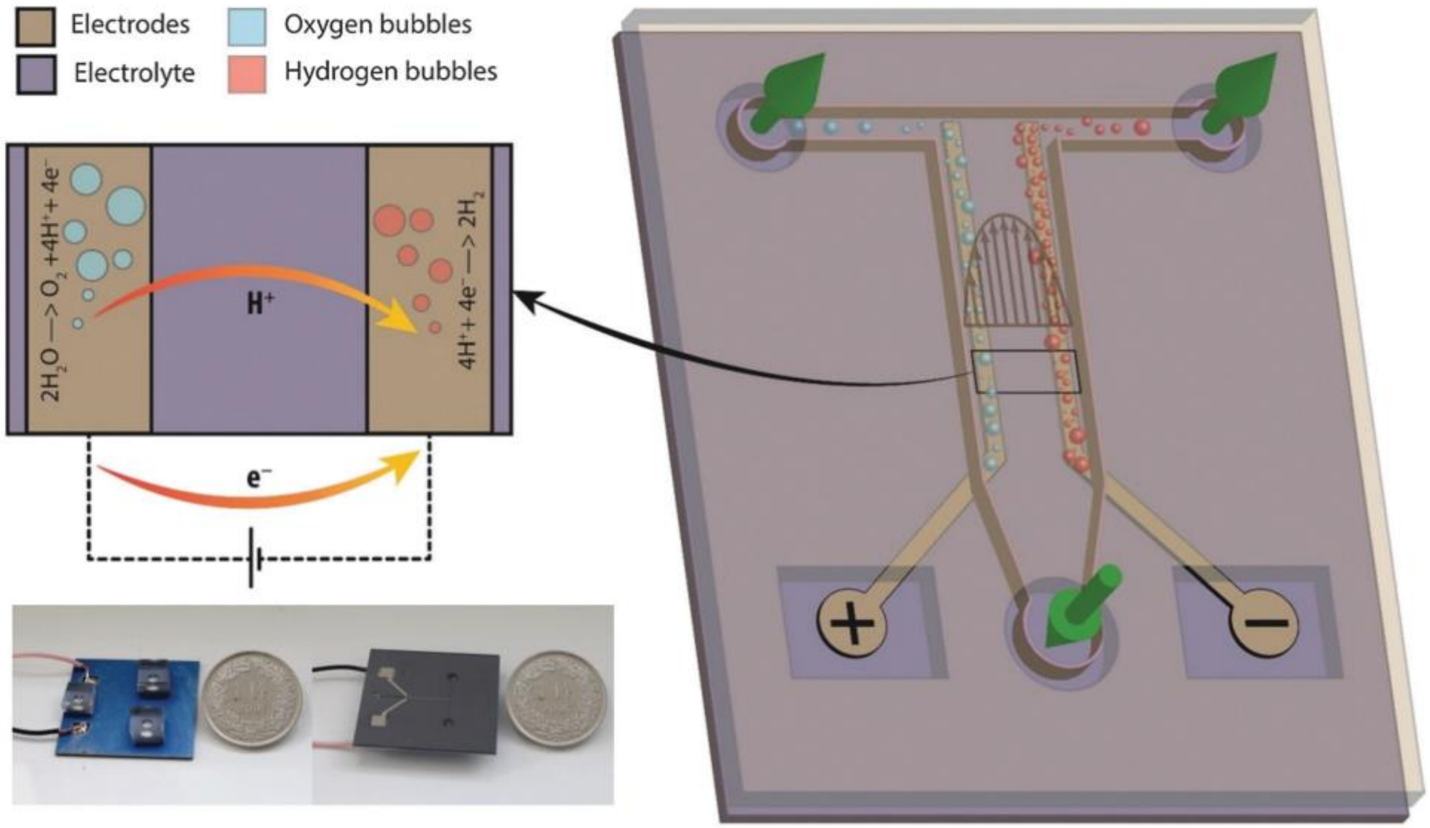
Guest :	Jean-Noël TOURVIEILLE	-	PhD, SYENSQO

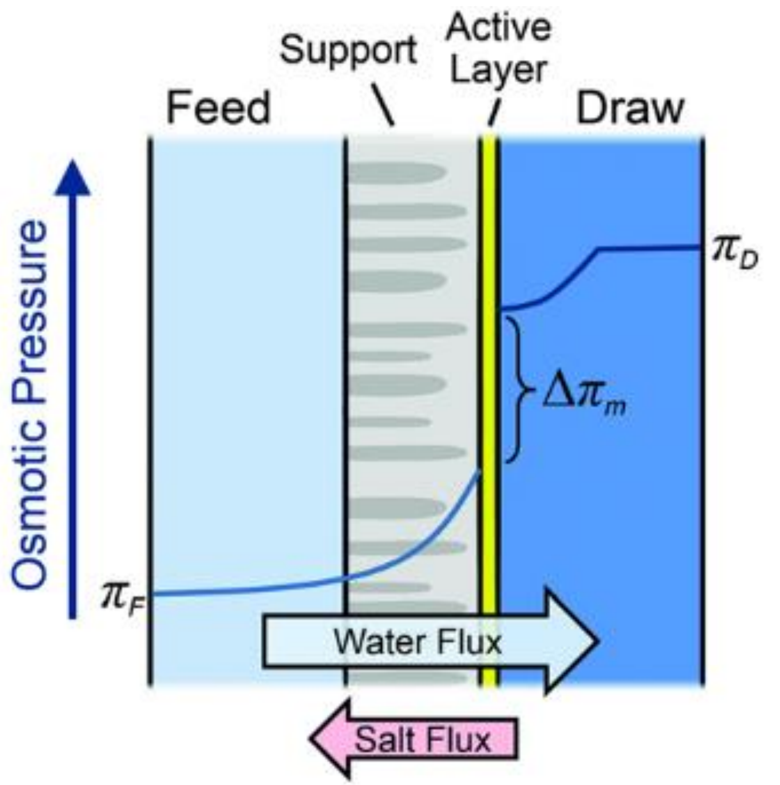
I2M BORDEAUX INSTITUT DE MÉCANIQUE ET D'INGÉNIERIE

Arts et Métiers Sciences et Technologies

Energy Transfers in Microscale Energy Conversion Devices



H. Hashemi, S. et al. *Energy Environ. Sci.* **2015**, *8* (7), 2003–2009.

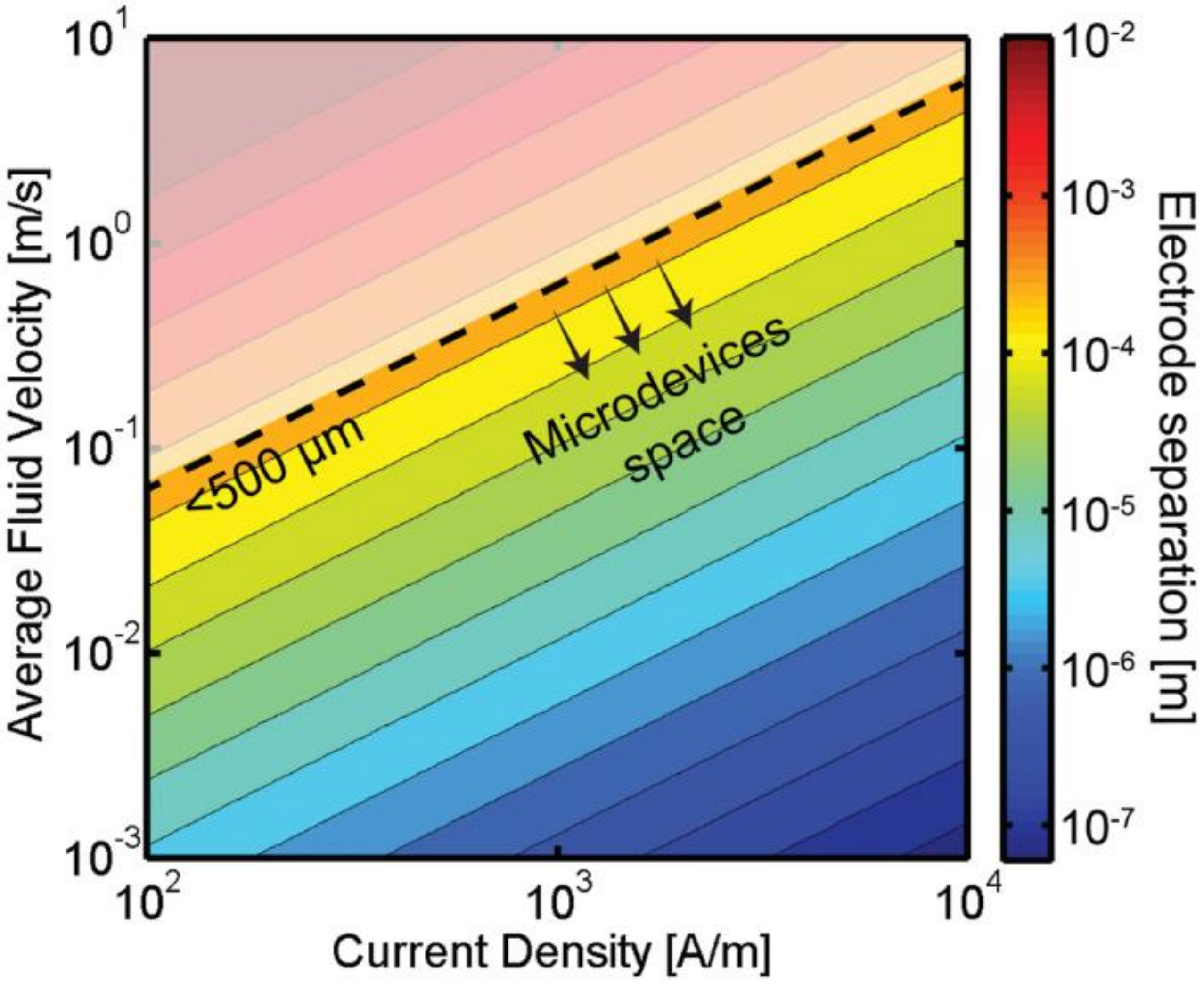


Wu, N. et al. *Lab Chip* **2023**, *23* (5), 1034–1065.

→ Electrochemical energy conversion devices!

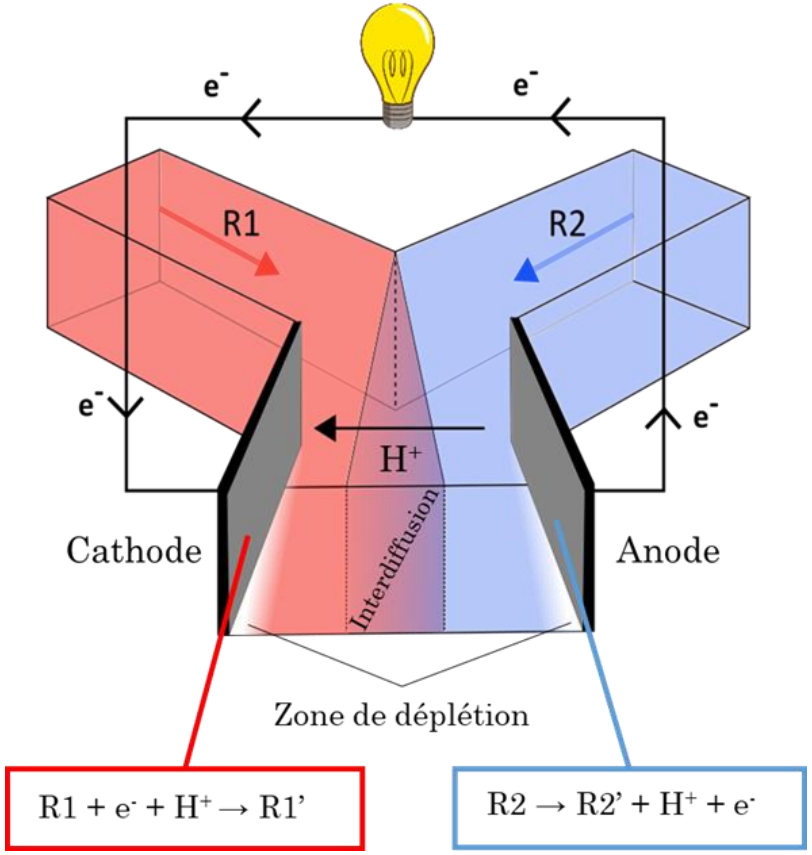
Microscale is good for energy transfers!

Modestino, M. A. et al. *Energy Environ. Sci.* **2016**, *9* (11), 3381–3391.



→ Power density increases with downsizing

WHAT IS ENERGY TRANSFER?



M. Garcia, PhD Thesis 2024

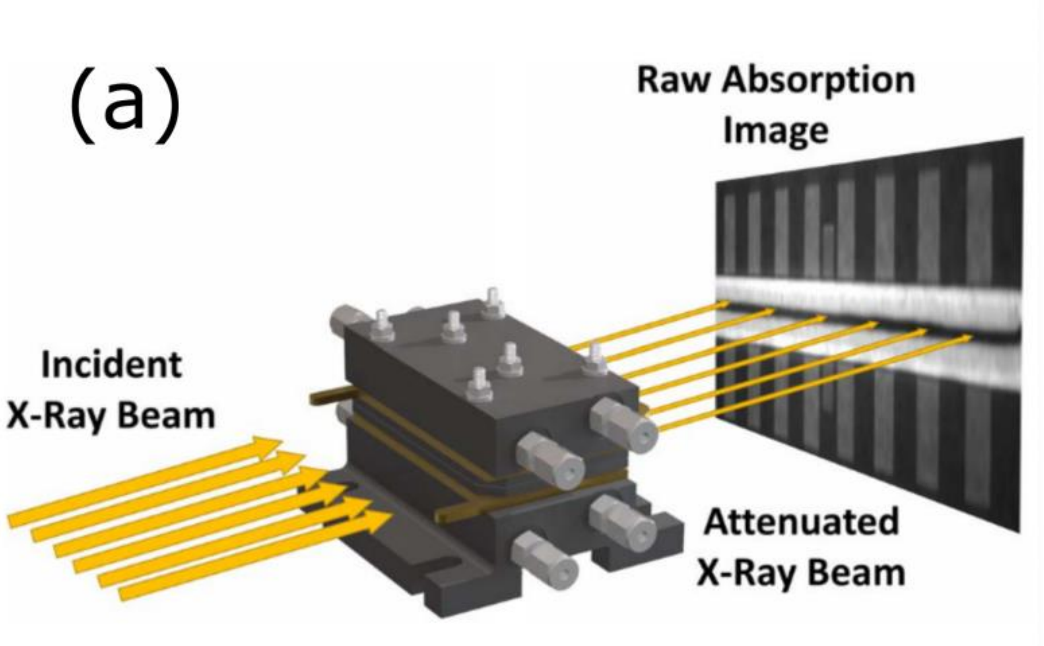
Energy transfer = heat and mass transfer

$$R_1 + e^- + H^+ \rightarrow R_{1'} + \Delta h$$

Mass Charge Heat

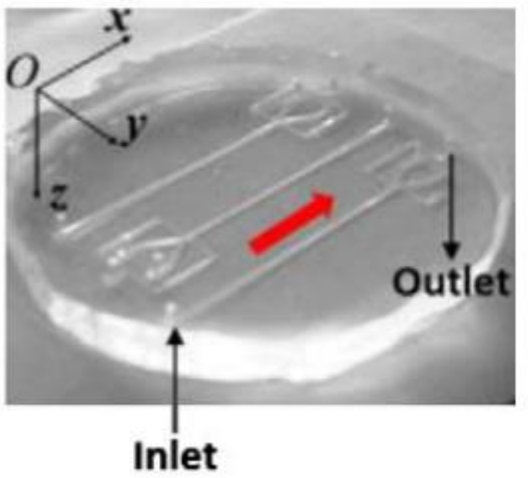
How to measure heat and mass transfer in MECD?

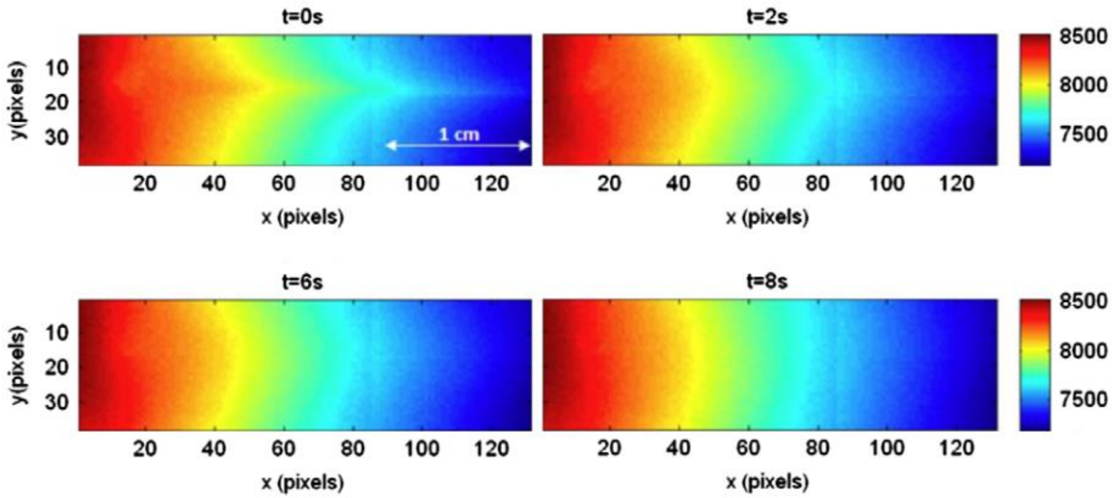
Opaque systems
Field properties



Shrestha P. et al., Electrochimica Acta, **2023** 142810

Diffusivity [m^2/s]

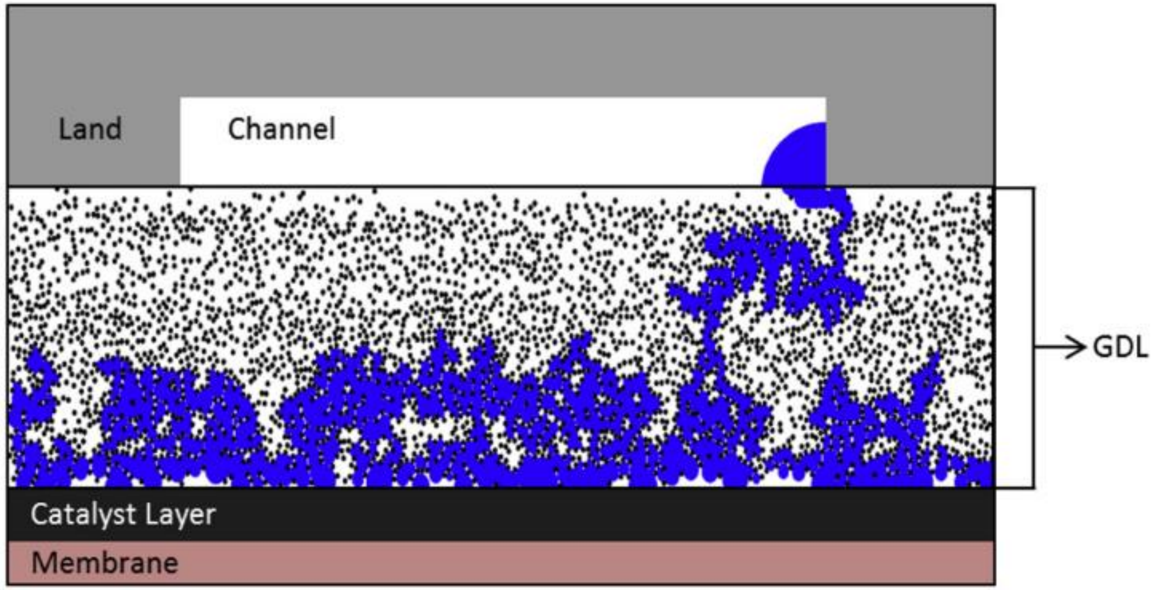




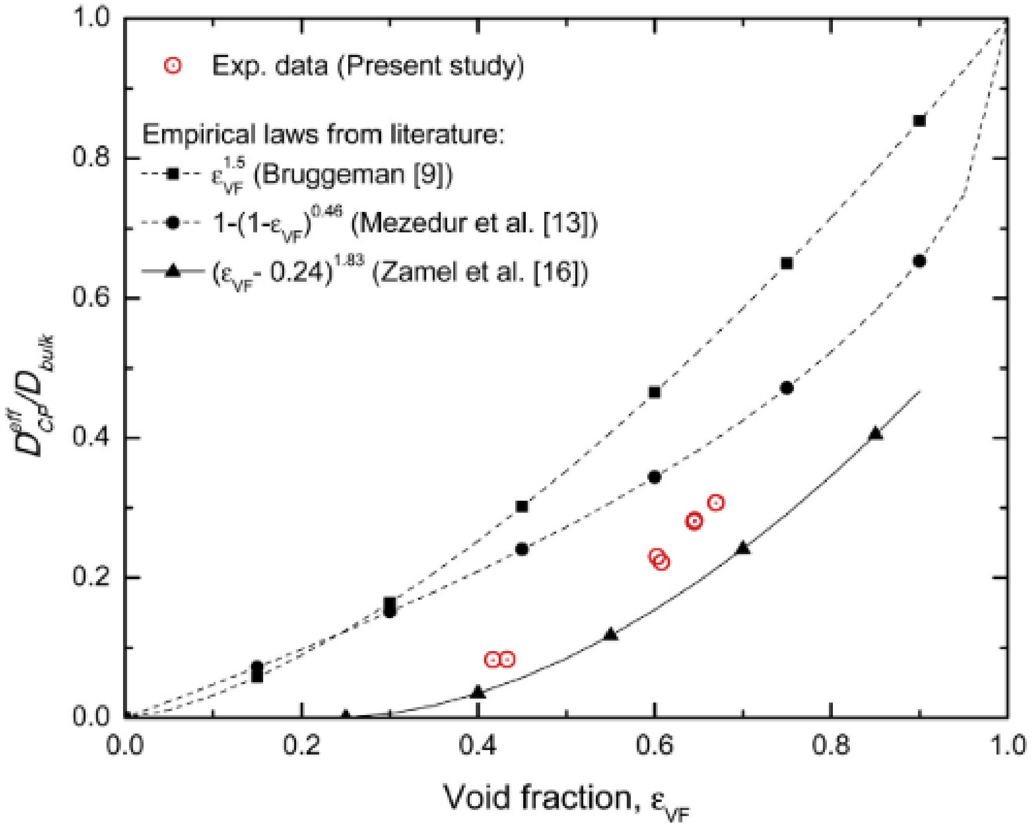
Ravey, C. et al. *Quant. Infrared Thermogr. J.* **2012**, *9* (1), 79–98.

What are operando heat and mass transfer properties in MEDC?

Example: two-phase flow in fuel cell gas diffusion layer



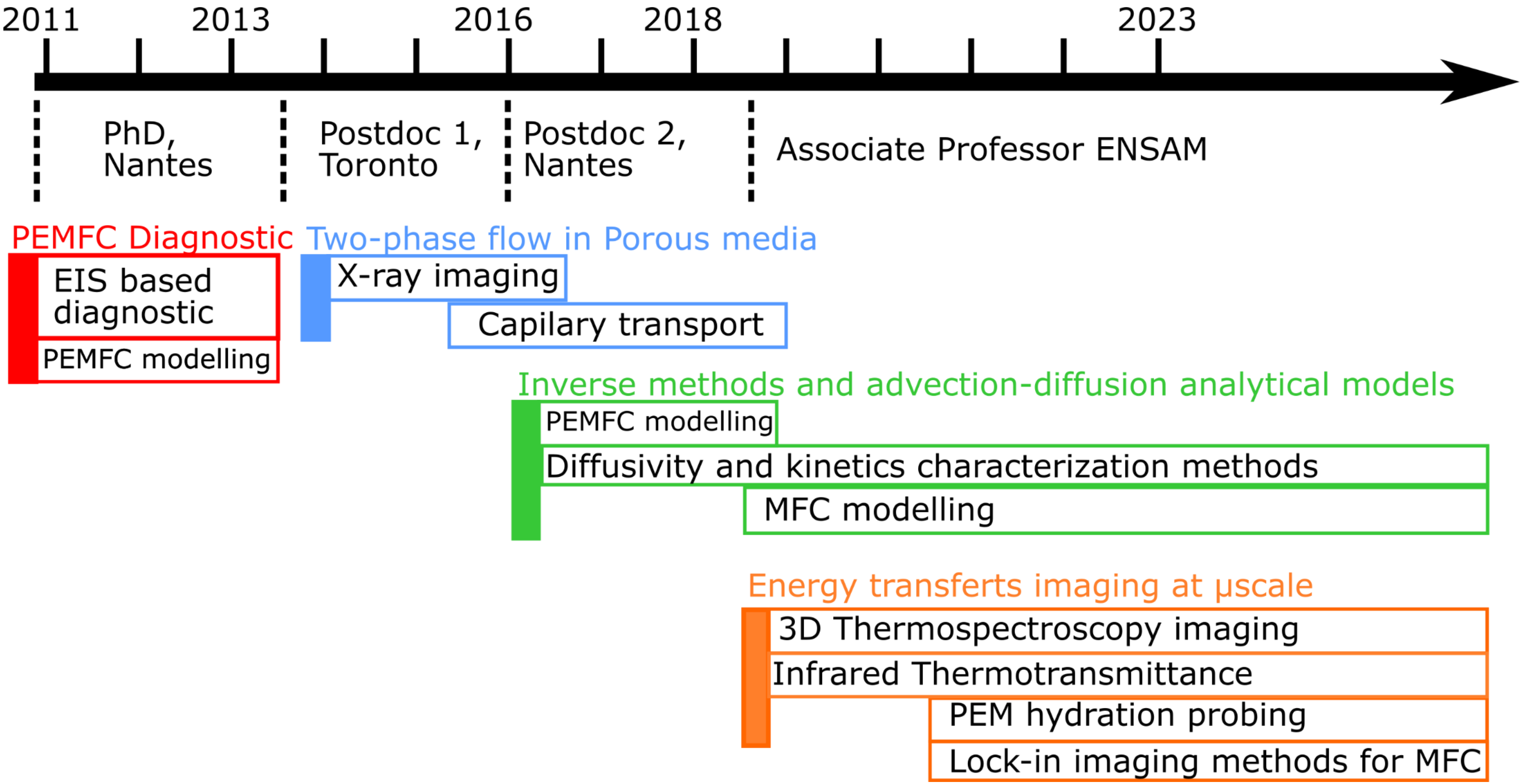
Lee, J. et al. *J. Power Sources* **2013**, *227*, 123–130.



Chevalier, S. et al. *Electrochim. Acta* **2016**, *210* (210), 792–803.

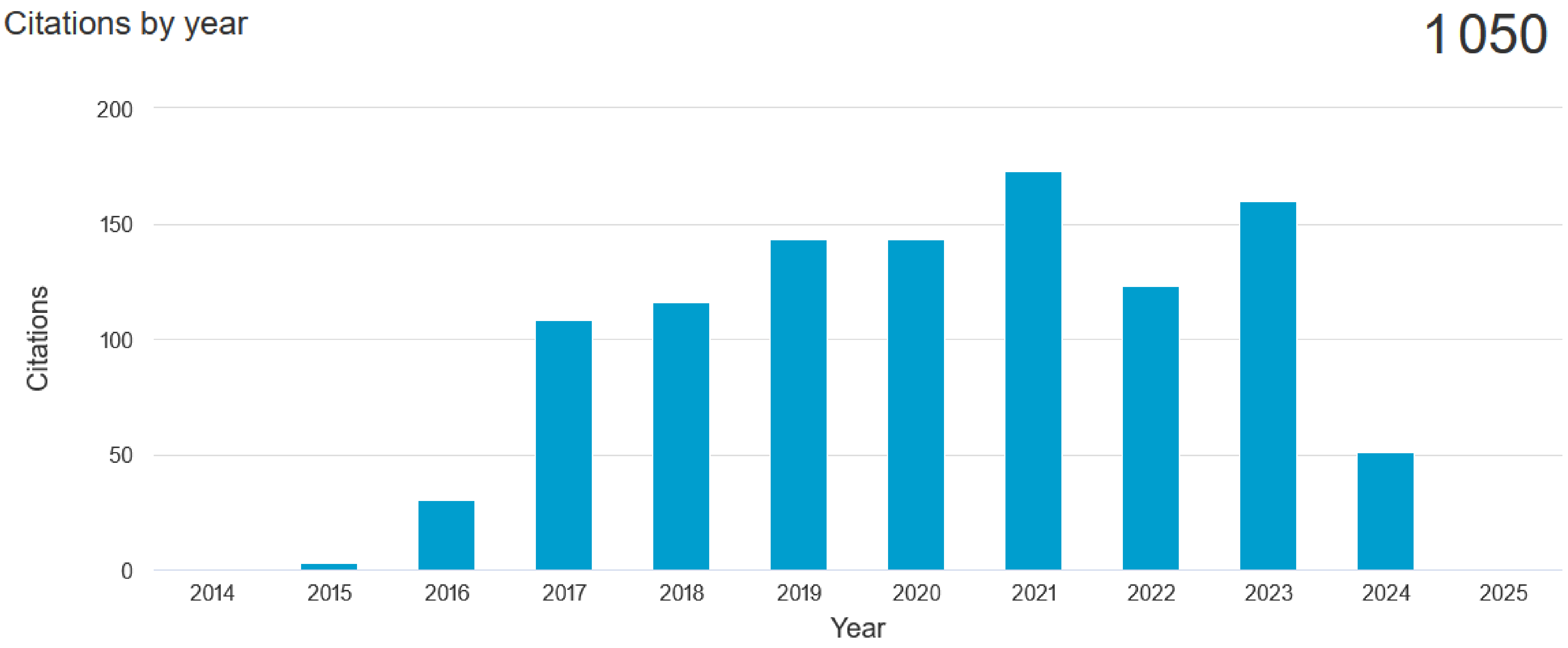
→ Ex situ properties differ from in situ measurements!

These issues have long been important components of my Research !



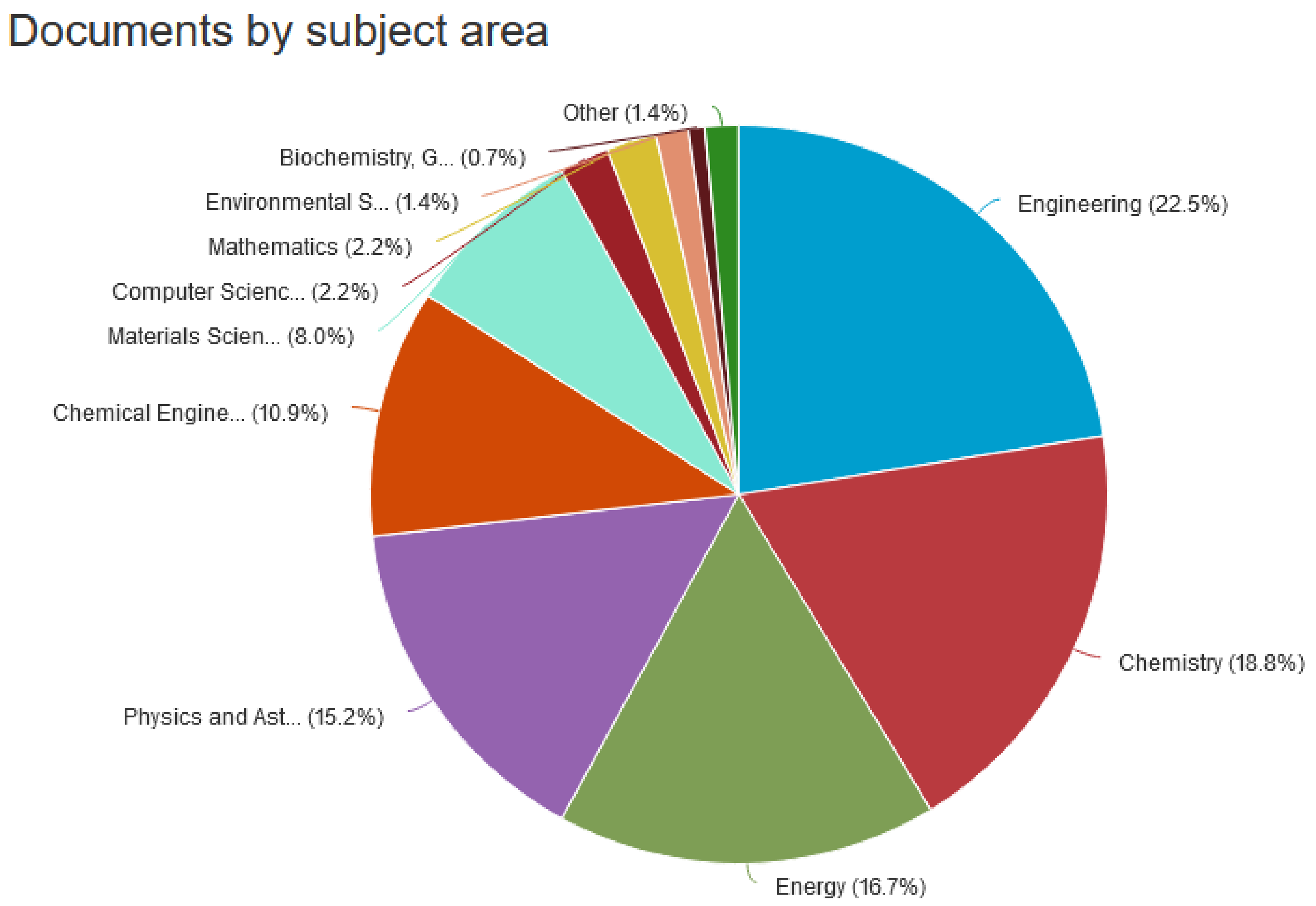
These issues have long been important components of my Research !

→ Answering these questions have led to 49 journal papers
→ More than 1000 citations in 10 years ($h_{index} = 22$)



Source : Scopus le 26/03/24

THESE ISSUES HAVE LONG BEEN IMPORTANT COMPONENTS OF MY RESEARCH !



→ Confluence of Engineering, Chemistry, Energy and Physics (heat transfers, optics, signal processing…)

RESEARCH TASK FORCE

Over the last 10 years:

→ 6 PhD students (4 graduated and 2 undergoing)

→ 7 Master 2 students

→ 1 M€ of funding

2 CNRS Joint PhD programs

Nouvelle Aquitaine Region Funding

MSCA funding

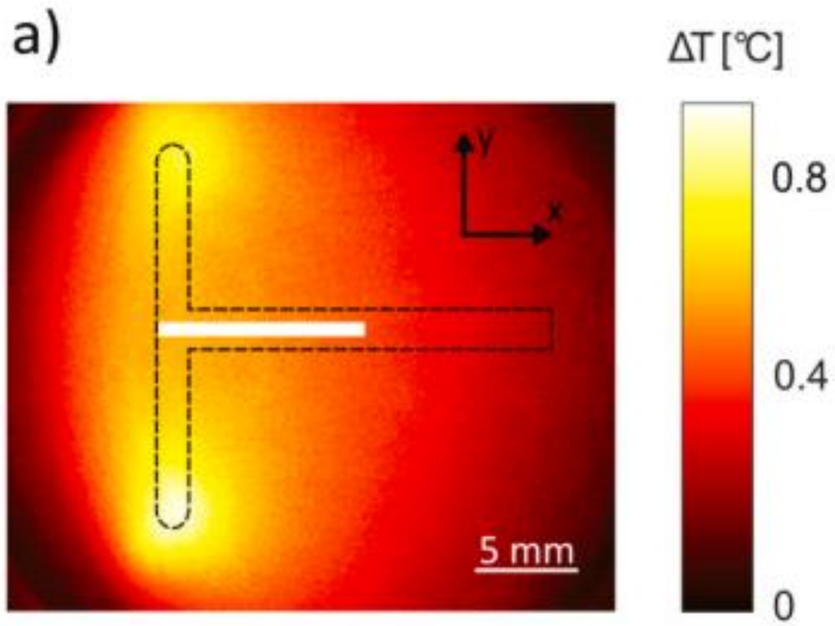
ANR JCJC

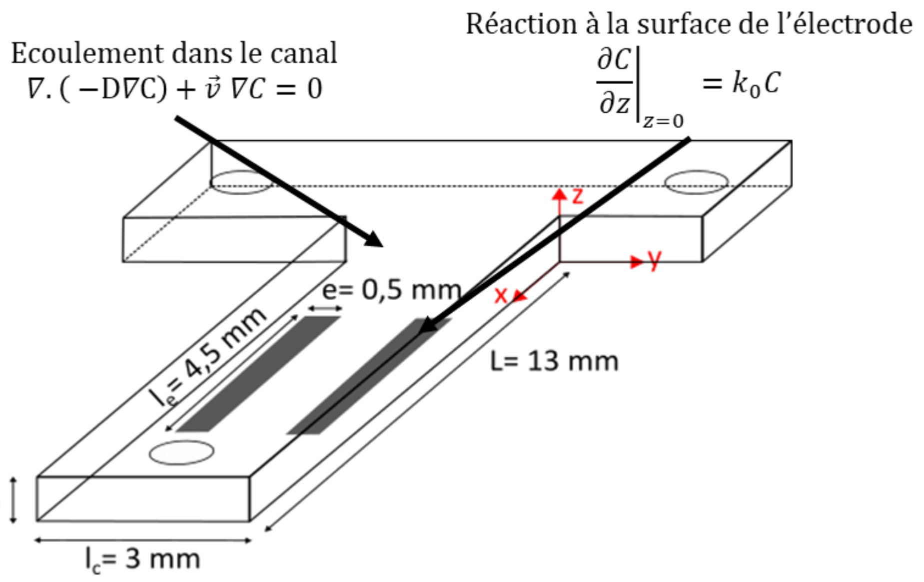
Carnot Institute ART hydrogen program

Industrial Contracts

How to measure heat and mass transfer in MECD?

What are the operando heat and mass transfer properties in MEDC?



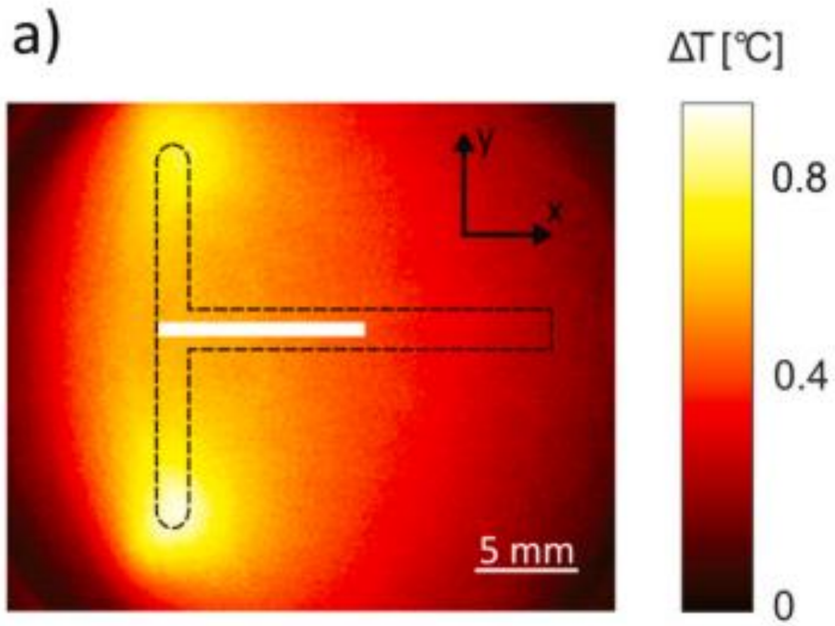


➔ Imaging µscale heat transfer in semi-transparent media using thermo-transmittance

➔ A new spectroelectrochemical microsopy for operando electrochemical kinetics measurement in microfludic fuel cells

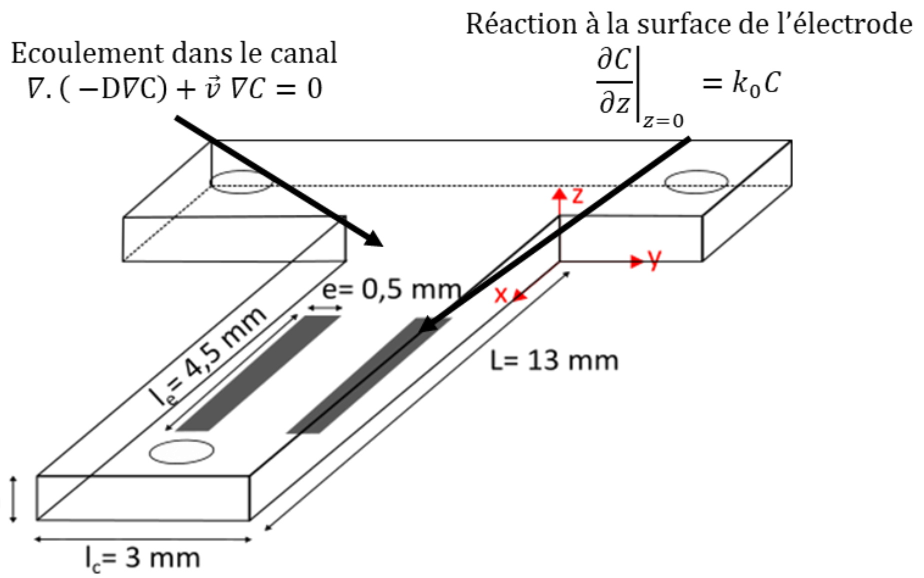
Main outcomes

How to measure heat and mass transfer in MECD?



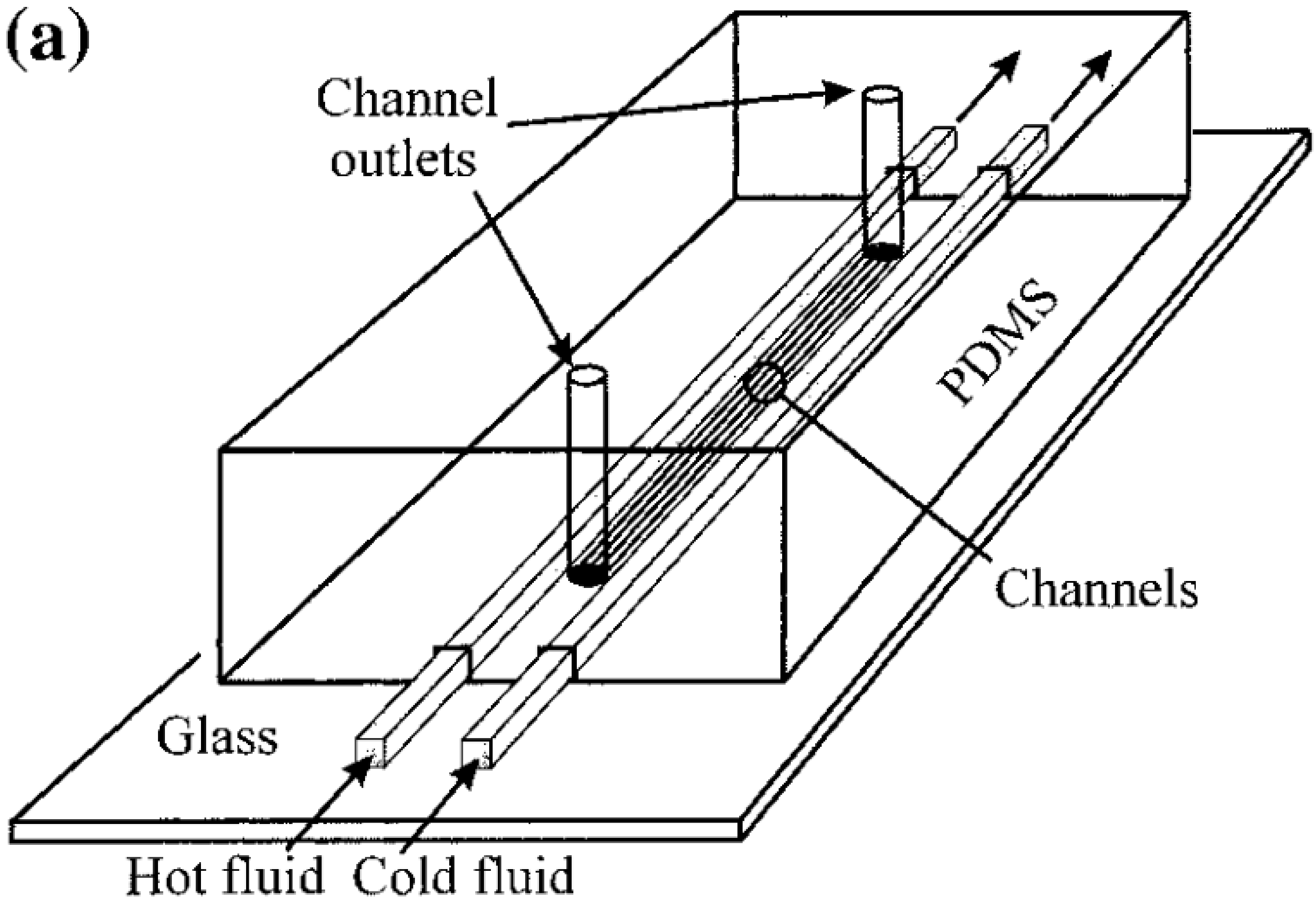
➔ Imaging µscale heat transfer in semi-transparent media using thermo-transmittance

What are the operando heat and mass transfer properties in MEDC?



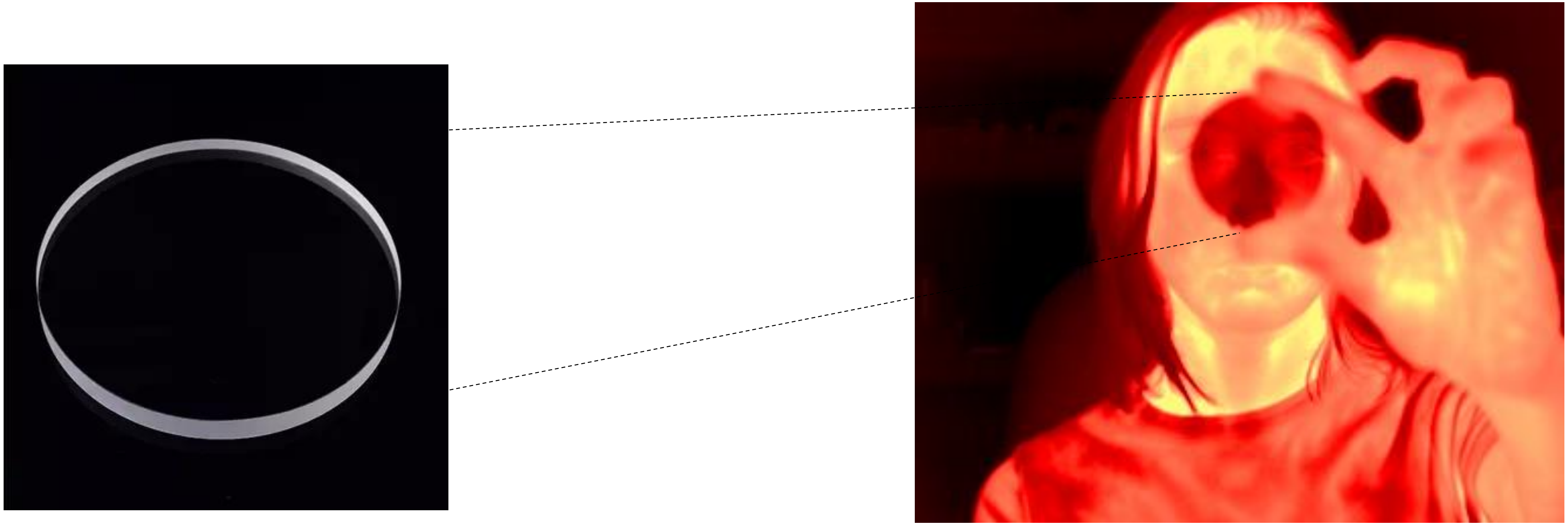
➔ A new spectroelectrochemical microsopy for operando electrochemical kinetics measurement in microfludic fuel cells

Example : high temperature control required for biological applications



Mao, et al. *J. Am. Chem. Soc.* **2002**, *124* (16), 4432–4435.

What happen if we use a camera ?



Existing expertise in the group

Pradere, C. et al., *J. Appl. Phys.* **2017**, *121* (8), 085102.
Yamashita et al. *Biomed. Phys. Eng. Express* **2018**, *4* (3), 035030.
Ryu, M. et al. *Chem. Eng. J.* **2017**, *324*, 259–265.

→ To avoid the background noise, the main idea is to shed IR lights through the sample to measure the transmission

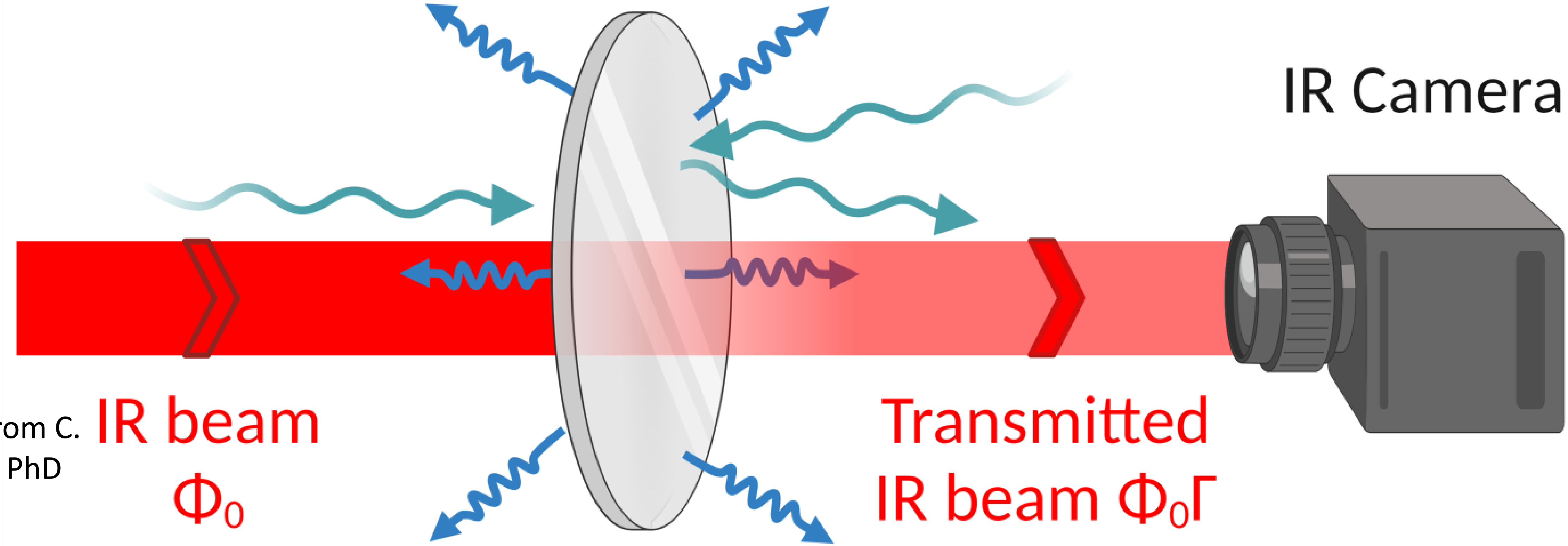
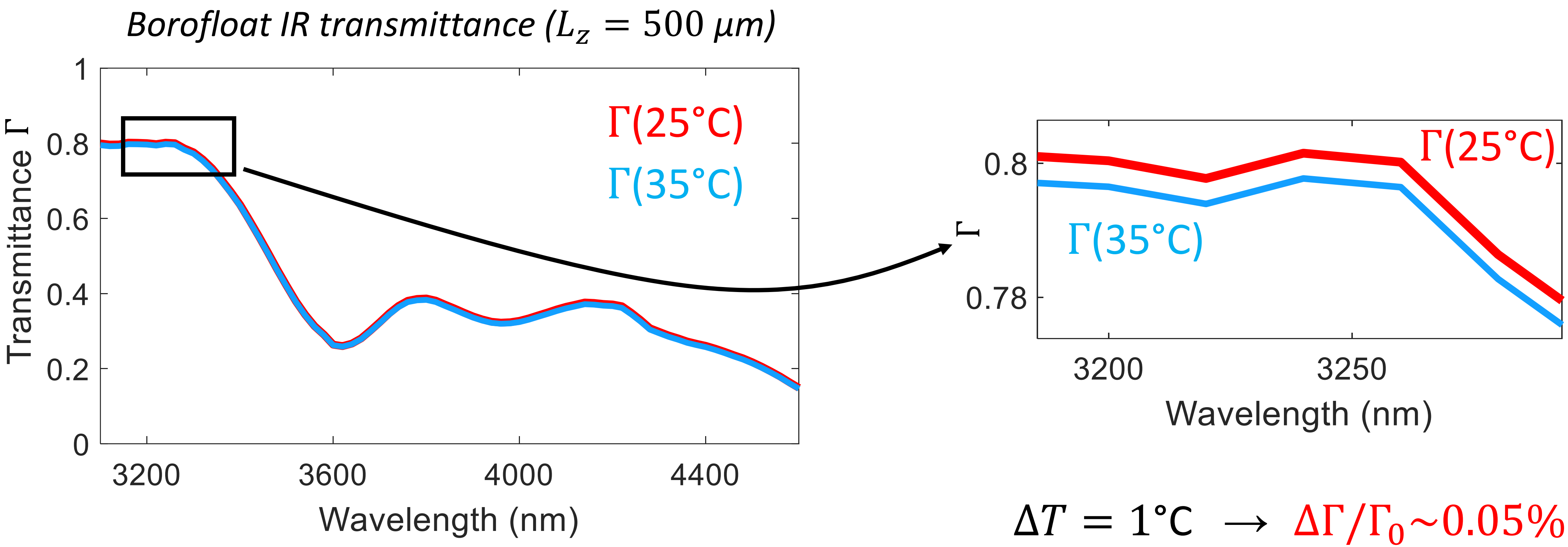


Figure from C. Bourges PhD Thesis



$\Delta T = 1°\mathrm{C} \;\rightarrow\; \Delta\Gamma/\Gamma_0 \sim 0.05\%$

→ **A needle in a haystack** : on a 14 bits camera it is equivalent to detect a change of 8 camera count of out 16384.

Figures from C. Bourges PhD Thesis

Setup developed in C. Bourges PhD (Collab LOMA)

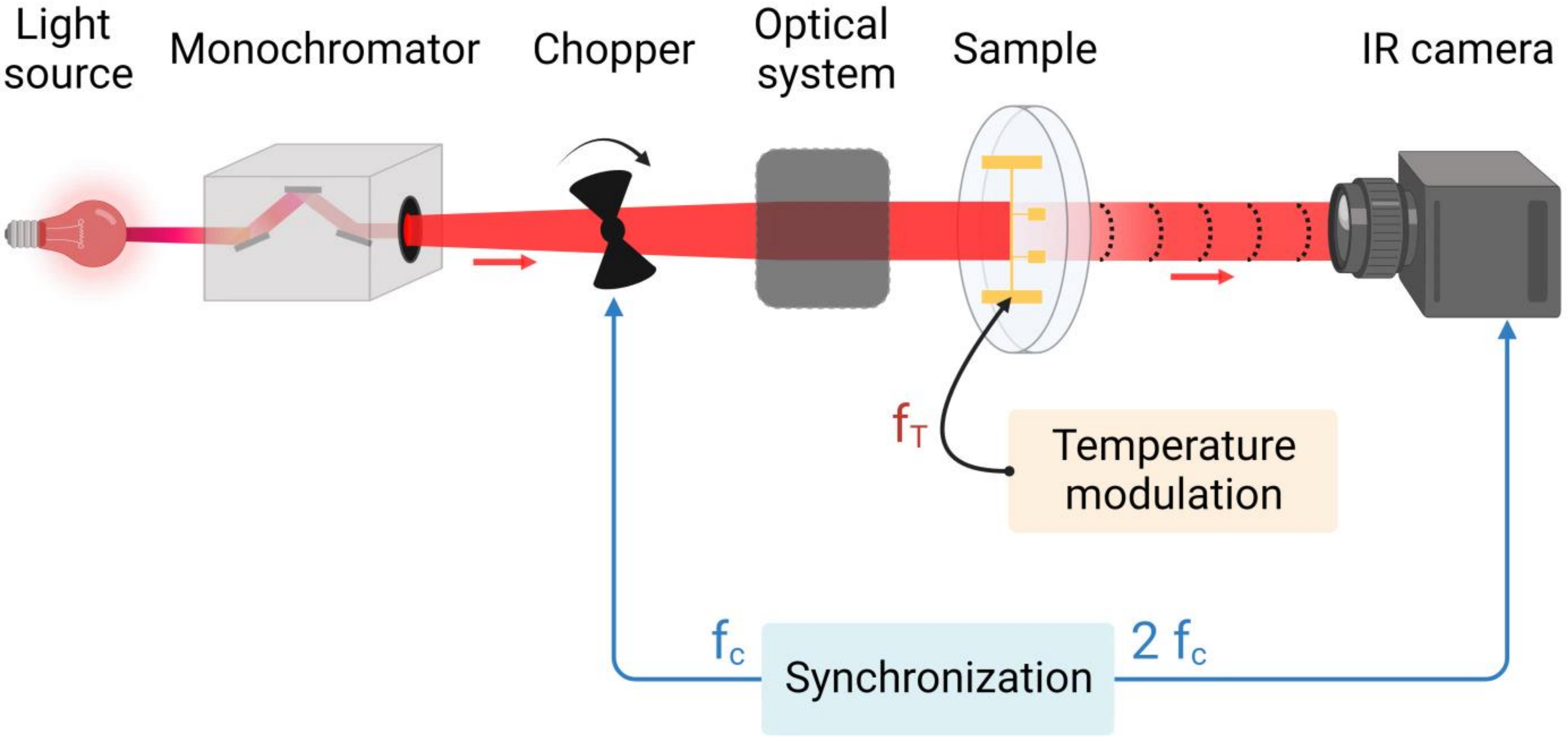
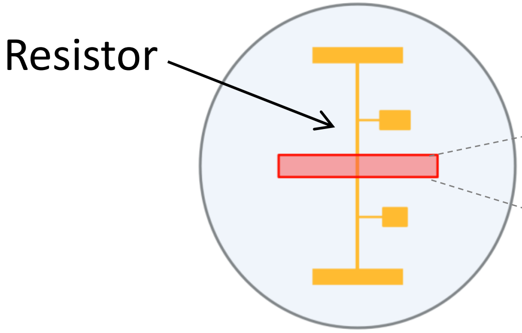
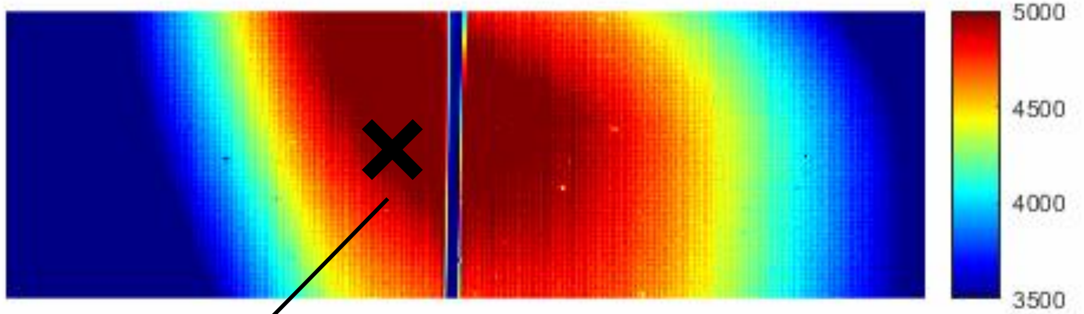


Figure from C. Bourges PhD Thesis

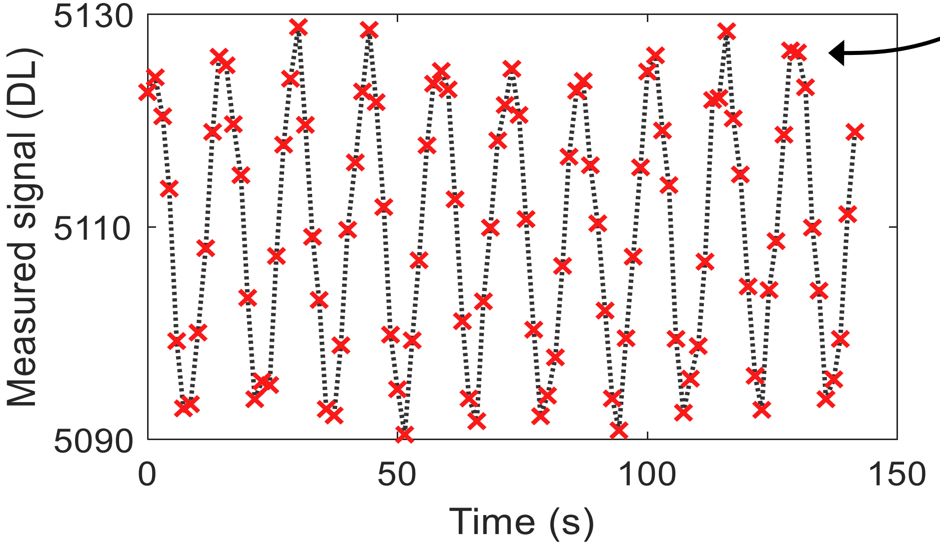
Ok, but how can I measure it?

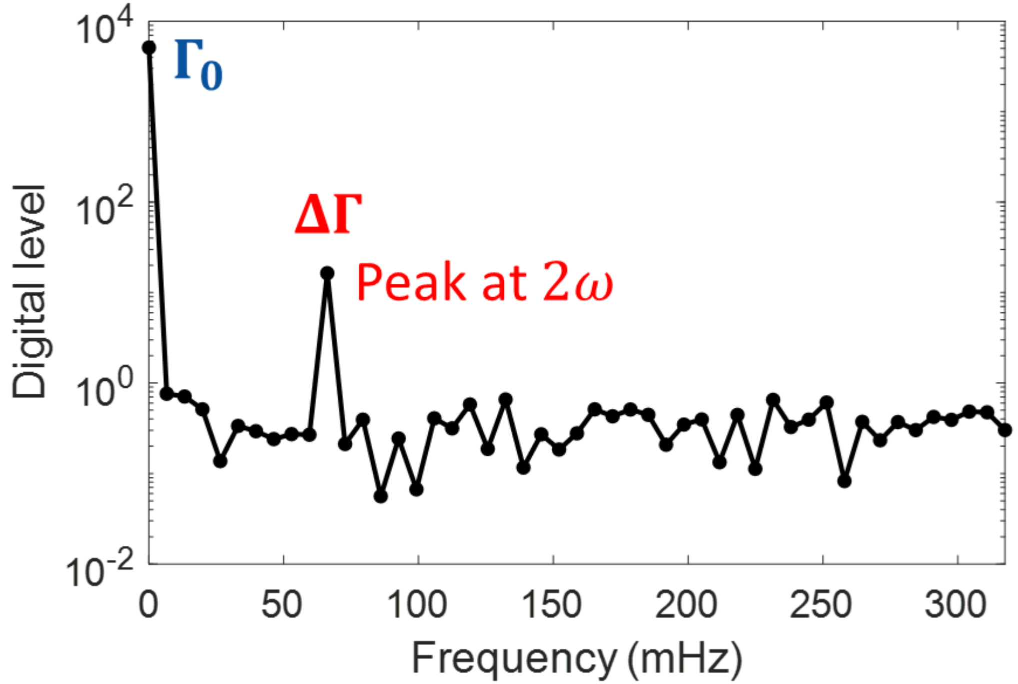


Measured transmitted signal $\Phi_0(\Gamma_0 + \Delta\Gamma)$

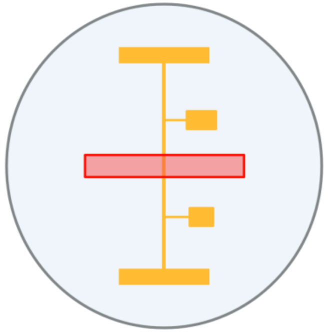


Signal measured by 1 pixel over time



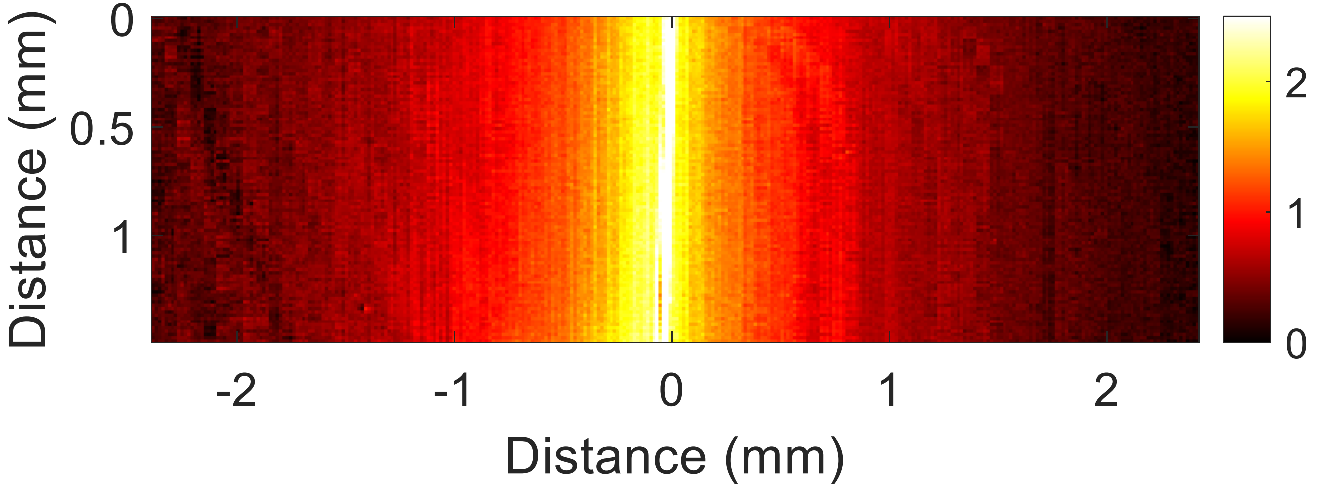


Figures from C. Bourges PhD Thesis



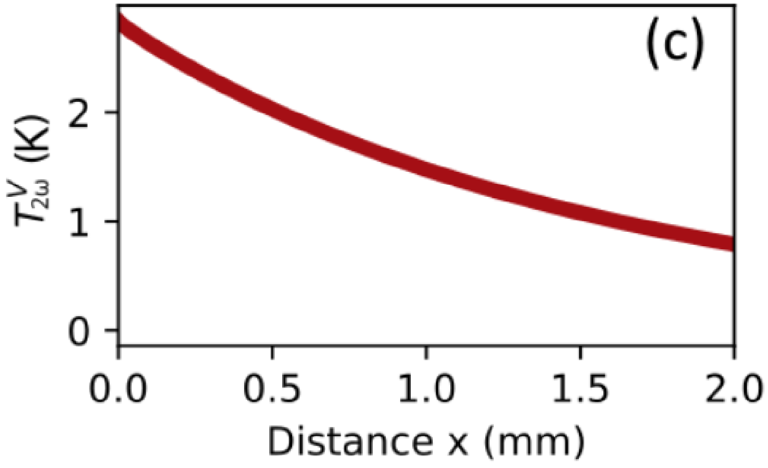
Average temperature field along z

$\langle \Delta T(x,y,z) \rangle_z$



$$\frac{i\omega}{a}\theta = \nabla^2\theta$$

$$-k\frac{\partial\theta}{\partial z} = \delta\phi(x)$$



→ Validation with heat transfer model in Fourier space

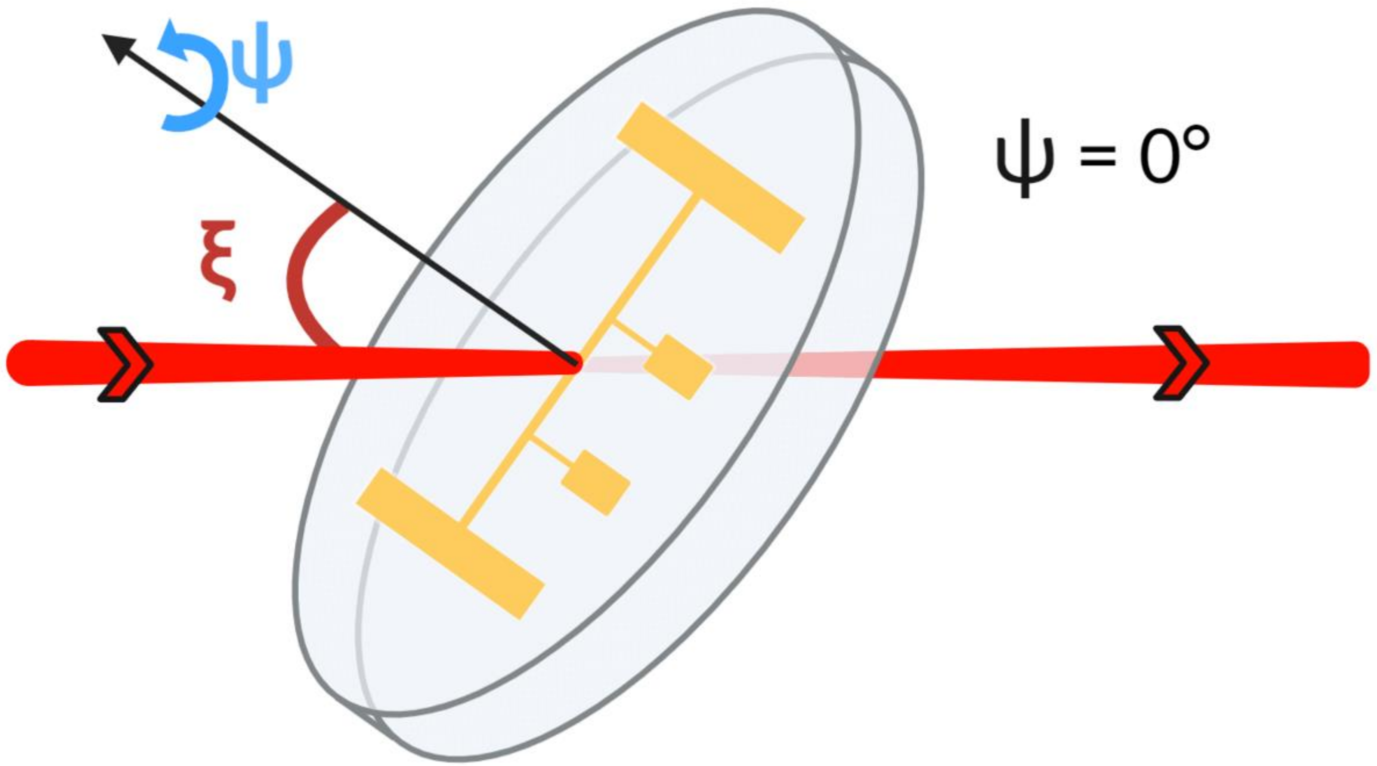
(1) Bourgès, C. *SFT 2023*; Reims, Lauréate !

(2) Bourgès, C. *Rev. Sci. Instrum.* **2023**, *94* (3), 034905.

(3) Bourgès, C *Appl. Phys. Lett.* **2024**, *124* (1).

(4) Bourgès, C *Int. J. Heat Mass Trans.* **2024**, *Submitted*

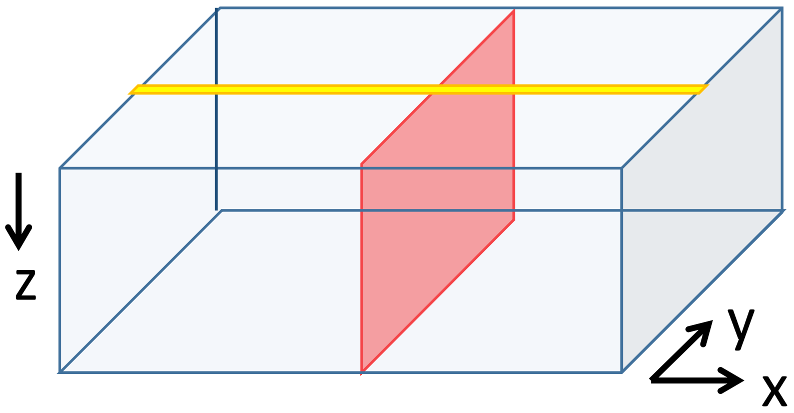
INTERESTING SIDE EFFECT: A DIRECT WAY TO THERMAL TOMOGRAPHY!

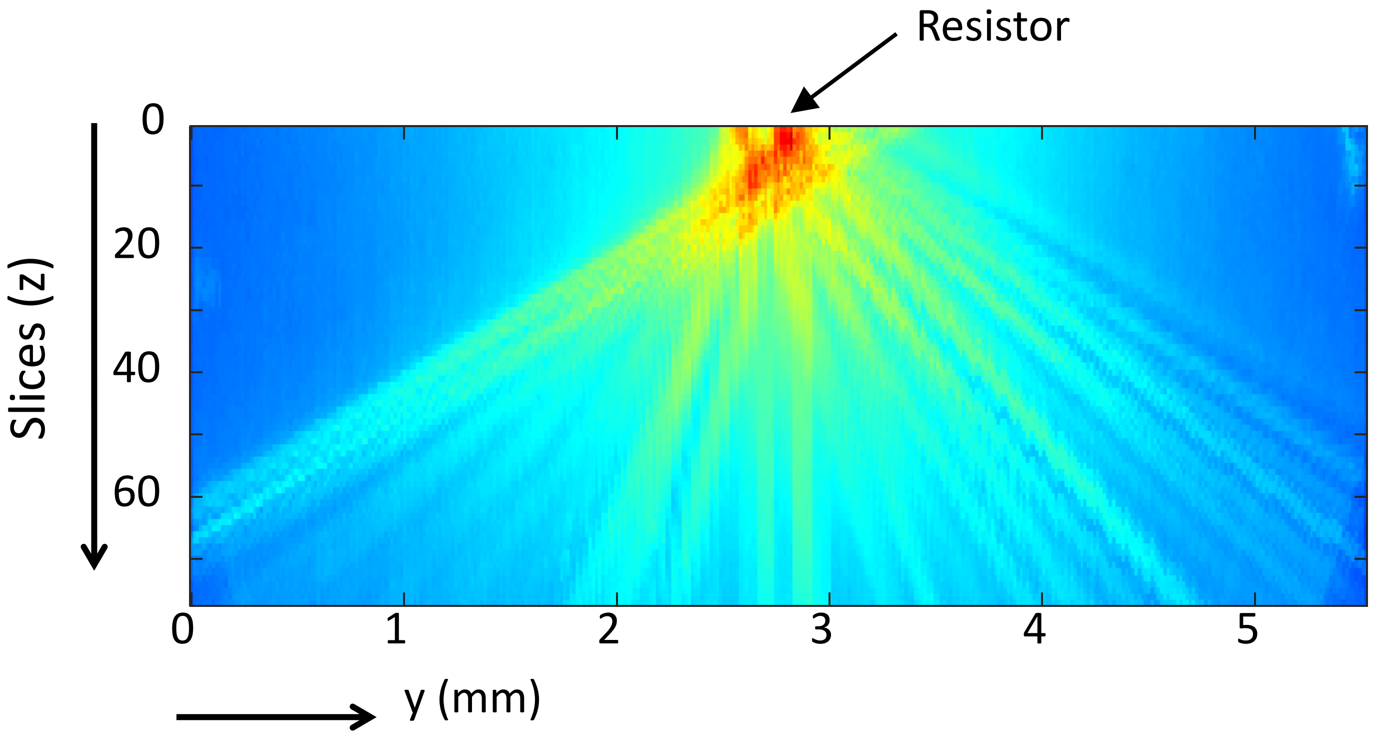


Measured signal:

$$\boxed{\underbrace{\frac{\Delta\Gamma}{\Gamma_0}(u,\mathrm{v})}_{\mathcal{P}(u,v)} = \underbrace{\frac{\kappa}{L_o(\xi,\psi_i)}}_{\text{Multiplying factor}} \int_0^{Lo(\xi,\psi_i)} \underbrace{\Delta T(x,y,z)\, dLo}_{\text{Temperature}}}$$

INTERESTING SIDE EFFECT: A DIRECT WAY TO THERMAL TOMOGRAPHY!





Figures from C. Bourges PhD Thesis

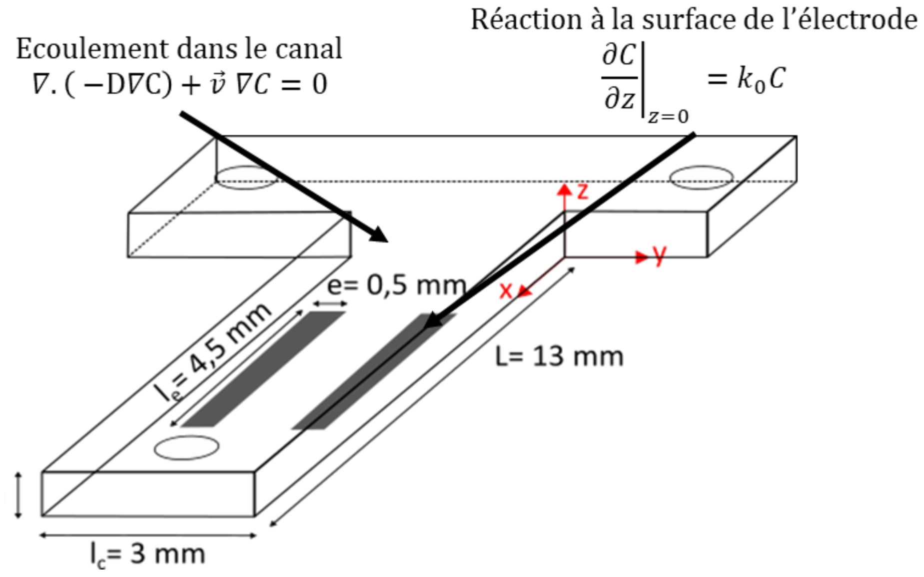
How to measure heat and mass transfer in MECD?

➔Controlling the source is the key to improve the SNR

➔Thermotransmittance is a suitable technique to measure heat transfer in semi-transparent media

➔Proof of concept for tomographic measurement… but a lot to do remain!

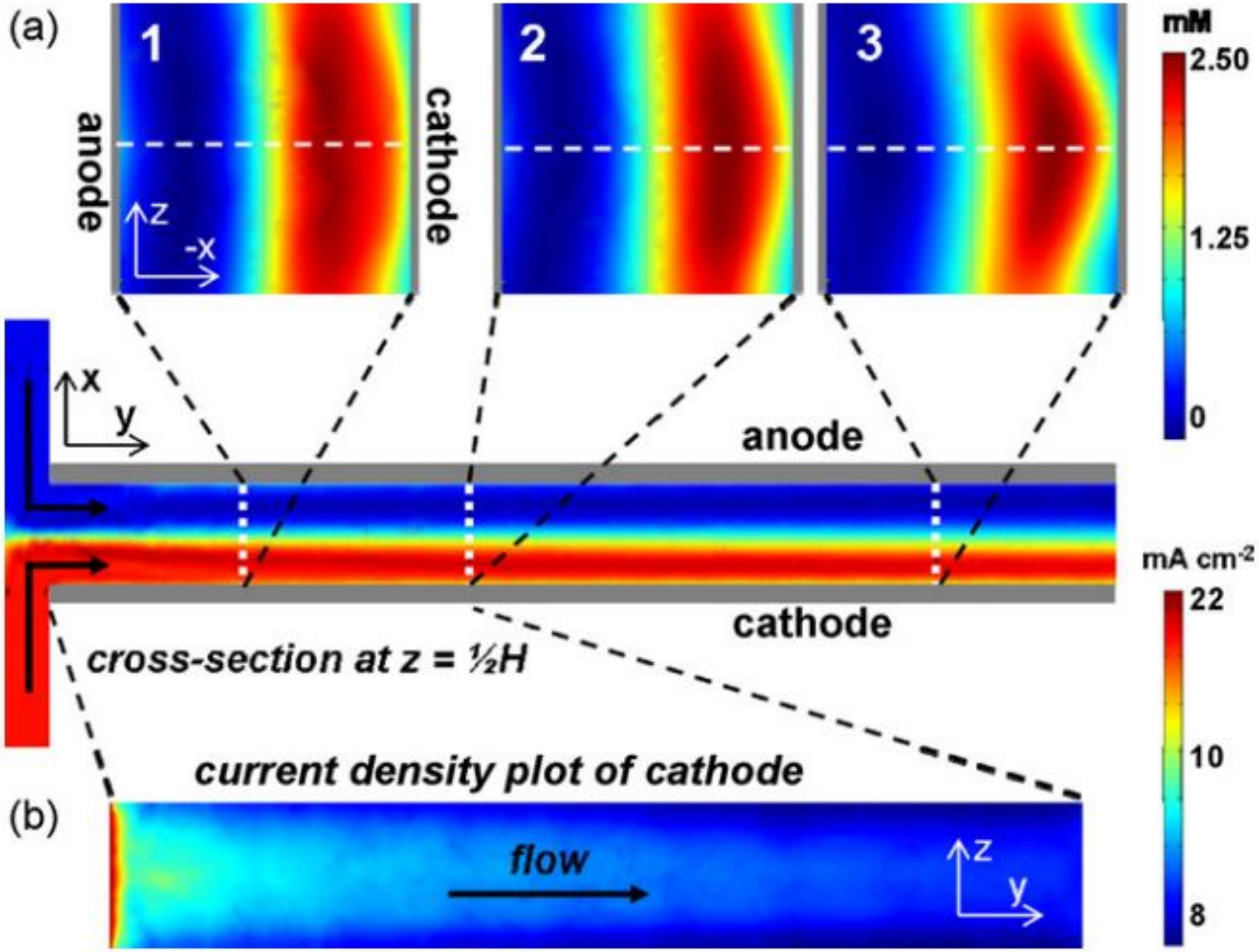
What are the operando heat and mass transfer properties in MEDC?



➔ A new spectroelectrochemical microsopy for operando electrochemical kinetics measurement in microfludic fuel cells

MICROSCALE IS GOOD BUT…

Concentration variations lower to mM

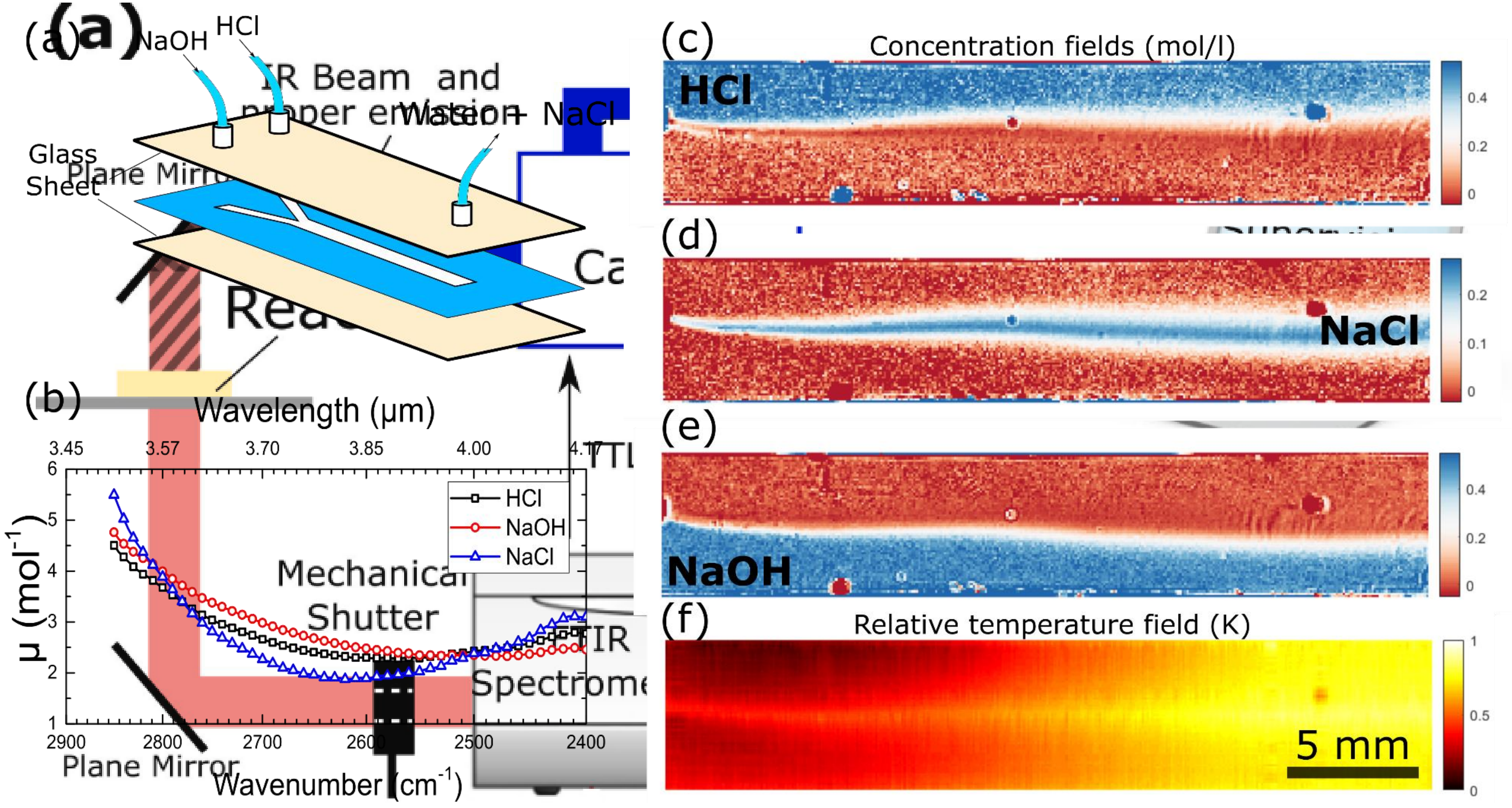


Jayashree et al. *J. Power Sources* **2010**, *195* (11), 3569–3578.

How to measure mmole concentration fields in MECD?

Spectrometry...
Again !!

$$c = -\mu \log_{10} \frac{\Gamma}{\Gamma_0}$$



Chevalier, S. et al. *Chem. Eng. J. Adv.* **2021**, *8*, 100166.

MicroMole measurements… an old trick!

Order of magnitude of the signal: $$\frac{\Delta\Gamma}{\Gamma_0} \approx \kappa c$$

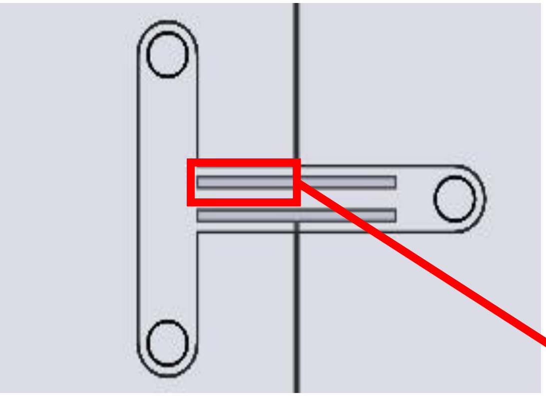
$$\kappa = 1.5 \times 10^{-2}\ \mathrm{mM}^{-1}$$

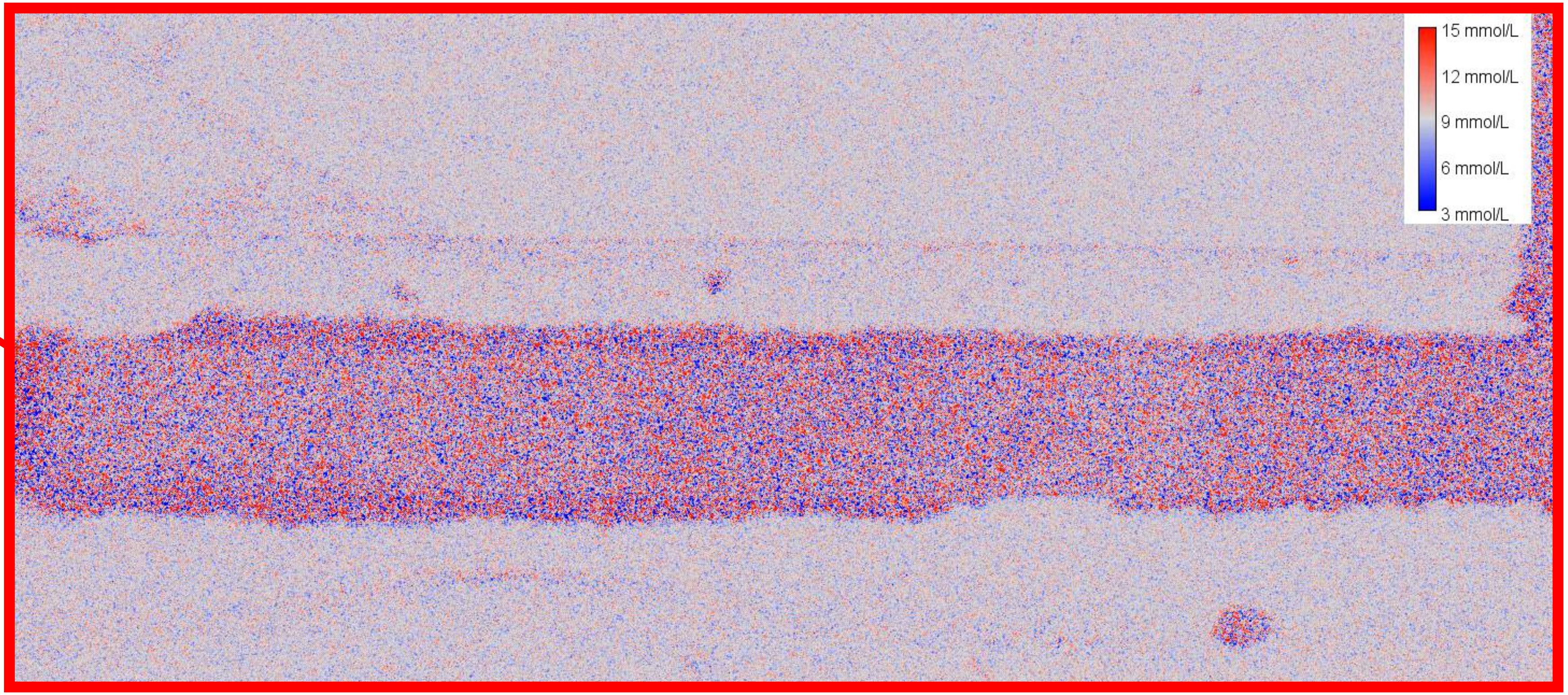
→ To detect $\Delta c \sim 0.1$ mM, a relative transmission variations of less than 0.1% needs to be measured.

→ Similar to thermotransmittance… so same solution → control the source !!

Link between current and concentration : Faraday law

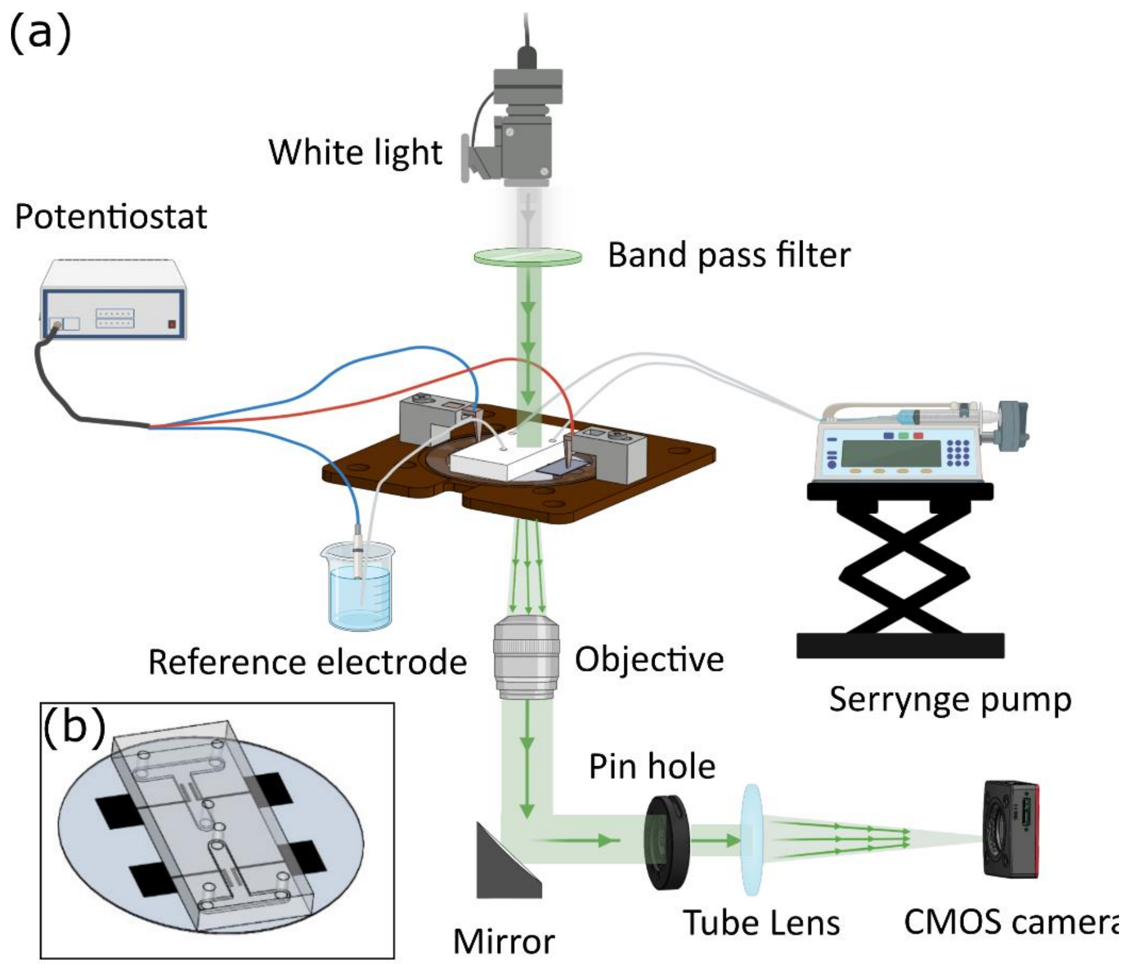
$$\frac{dc}{dx}(t) = \frac{I(t)}{zF} \longleftrightarrow \Delta c(t) \propto I(t)$$

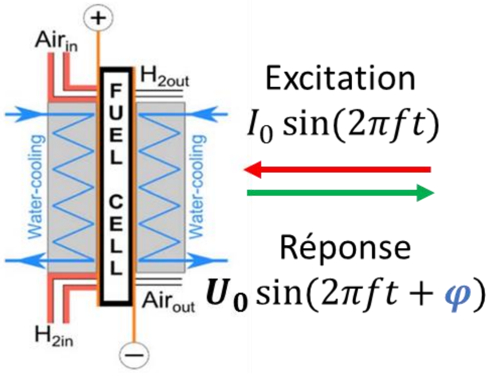


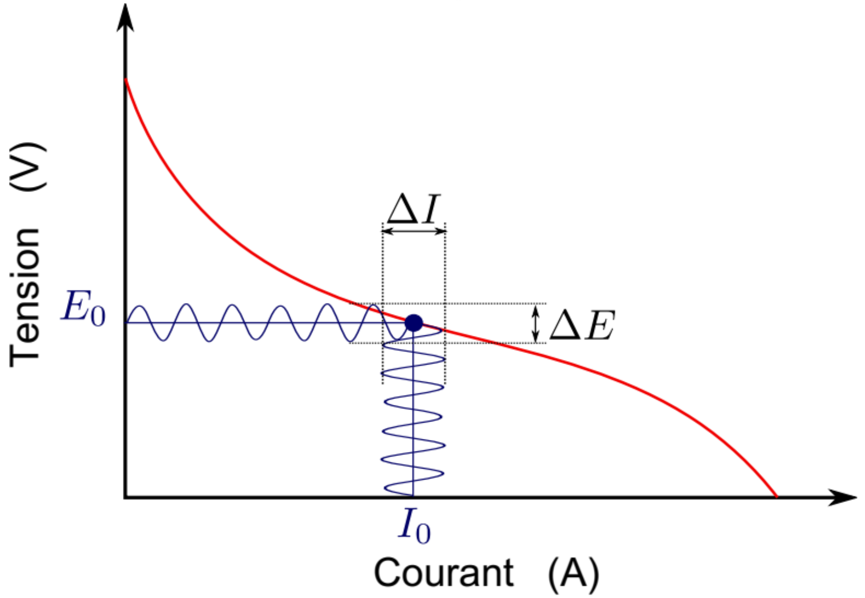


→ Controlling the current is the same as controlling a thermal source ➔ we can use it to increase our SNR !

A new combination of electrochemical spectroscopy and visible spectroscopy





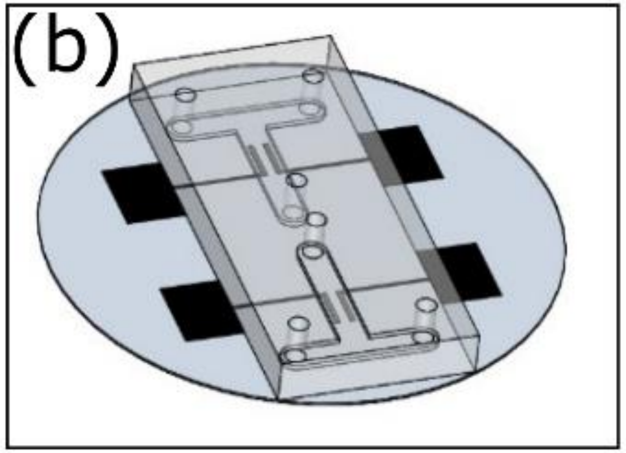


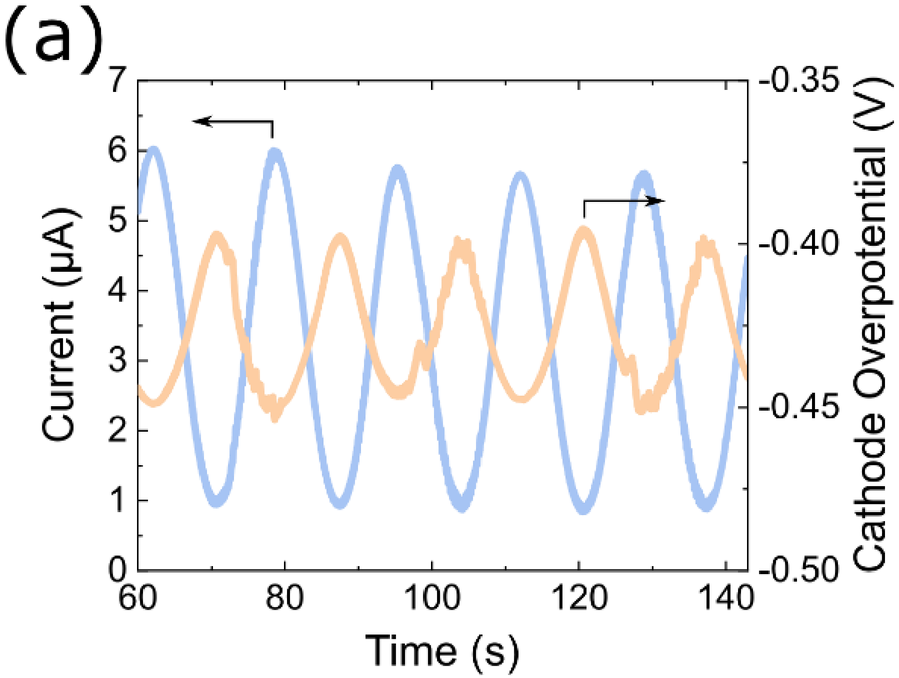
(1) Chevalier, S et al. *Int. J. Hydrogen Energy* **2013**, *38* (26), 11609–11618.

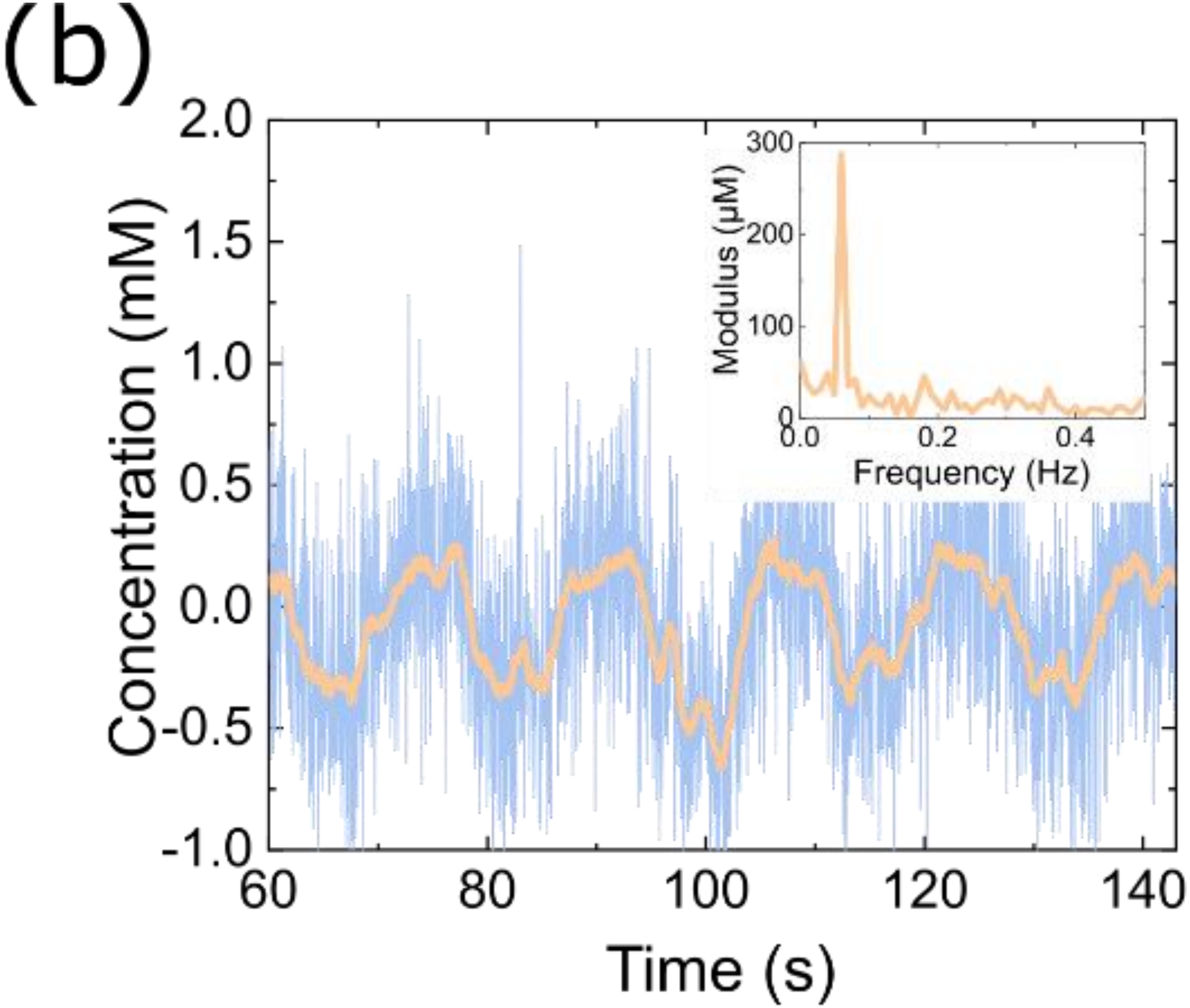
(2) Chevalier, S. et al. *Fuel Cells* **2014**, *14* (3), 416–429.

Garcia, M. et al. *Electrochim. Acta* **2023**, *460*, 142489.

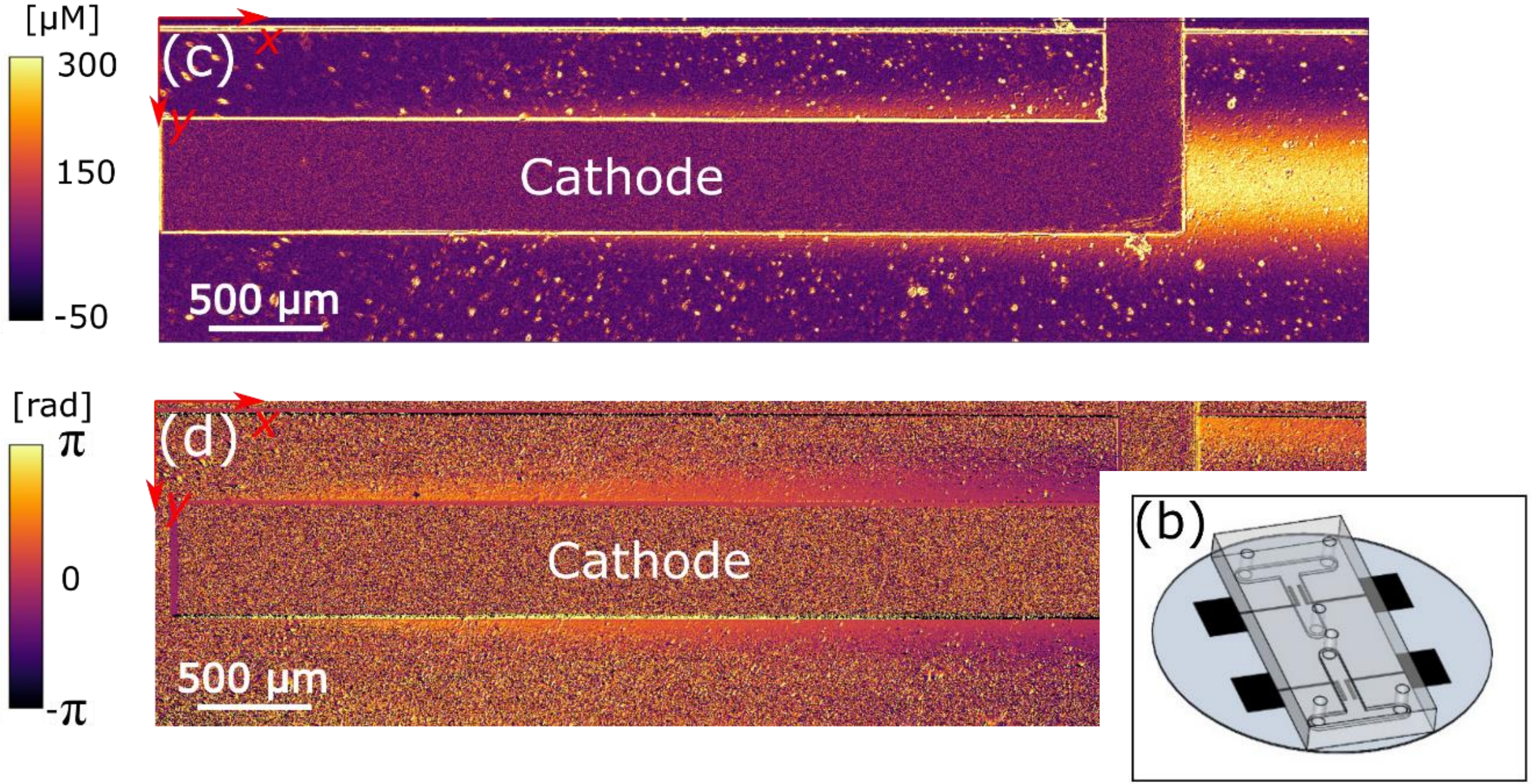
EXPERIMENTAL RESULTS







EXPERIMENTAL RESULTS



New data for inverse methods !

$$\underline{\delta c} = \int_{-\infty}^{+\infty} c(t)e^{-i\omega t}d\omega$$

Mass transport model in Fourier space :

$$i\omega\underline{\delta c} + v\vec{\nabla}\underline{\delta c} = D\nabla^2\underline{\delta c} \pm \underline{R}$$

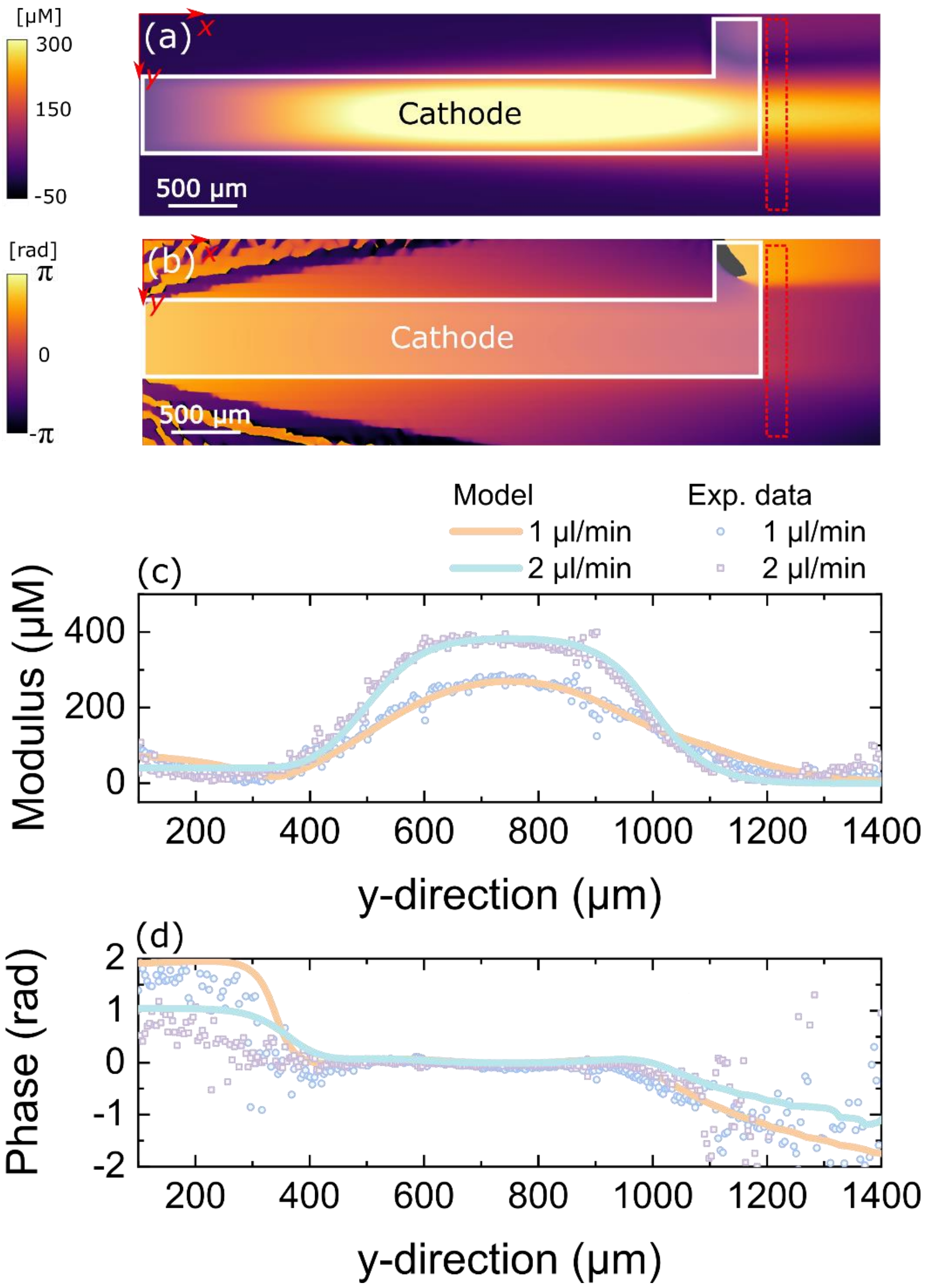
Non linearities from electrochemistry solved:

$$\underline{R} = \frac{i_0}{zFhc^{ref}} e^{-\eta_c^0/b}\left(\frac{c^0}{b}\underline{\delta\eta_c} + \underline{\delta c}\right)$$

Identification of operando electrochemical kinetics !

$$i_0 = (6.8 \pm 1.9) \times 10^{-3}\ \mu\text{A/mm}^2$$

$$b = 30 \pm 4\ \text{mV}$$



In conclusion

Developments of lock-in imaging method for both heat and mass transfers

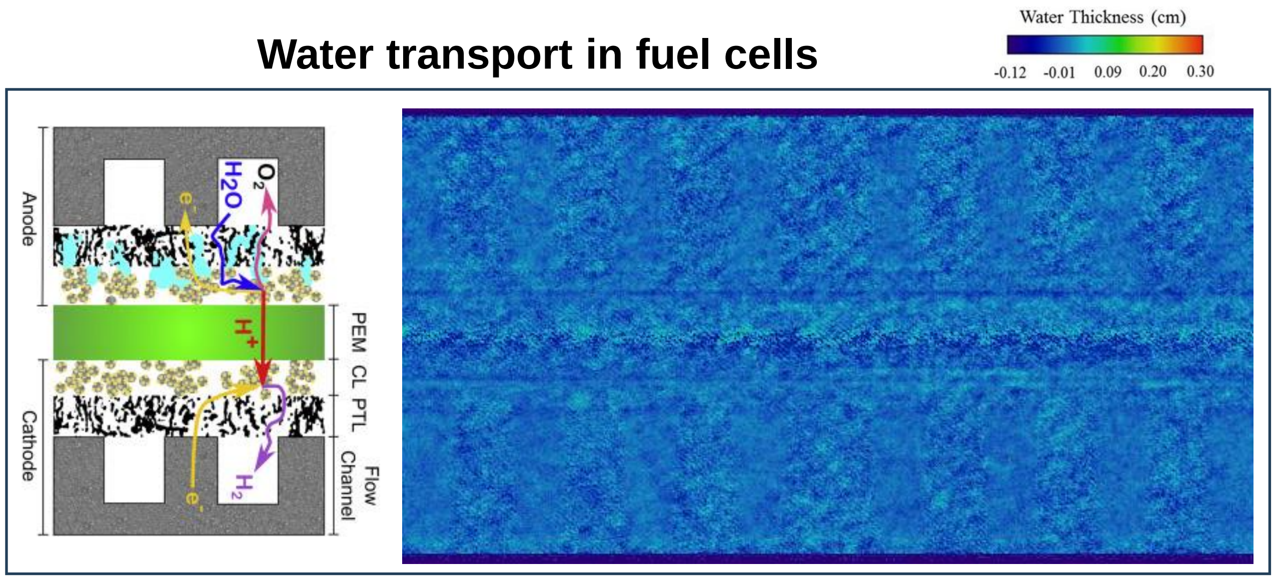
Experimental setup + numerical/ analytical modeling

➔ parameters estimation/inverses methods

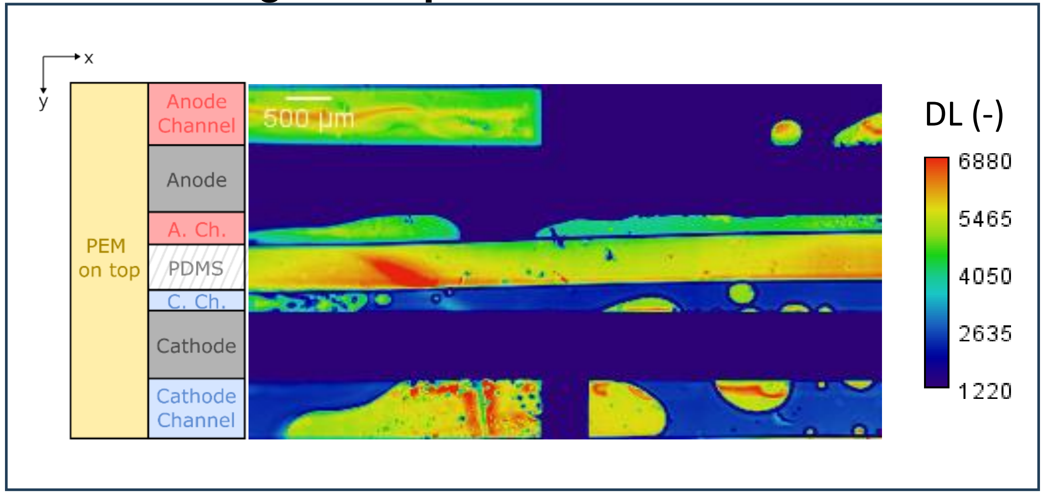
Extension of TIFC skills toward thermal tomography and electrochemical systems

Few others main results (X rays, microfluidic electrolyzers…)

Water transport in fuel cells



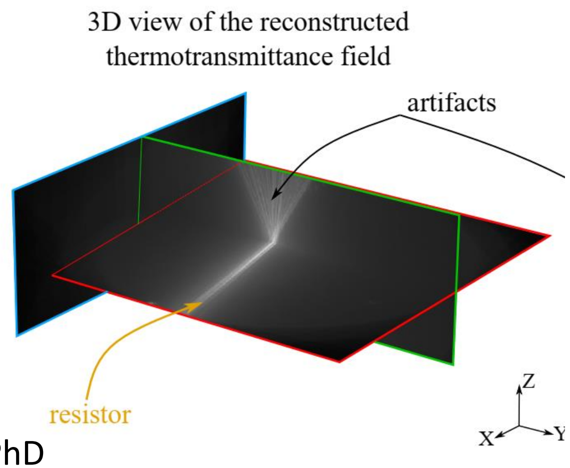
Charge transport in PEM Membrane



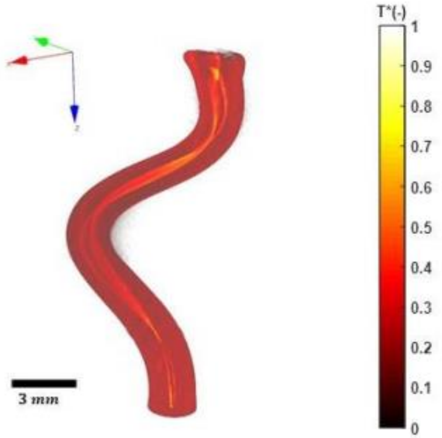
Research Project

How to measure heat and mass transfers in MECD at microscale?

1. Switching from 2D to 3D



C. Bourges PhD



A. Aouali PhD

2. Current optical limits of IR imaging

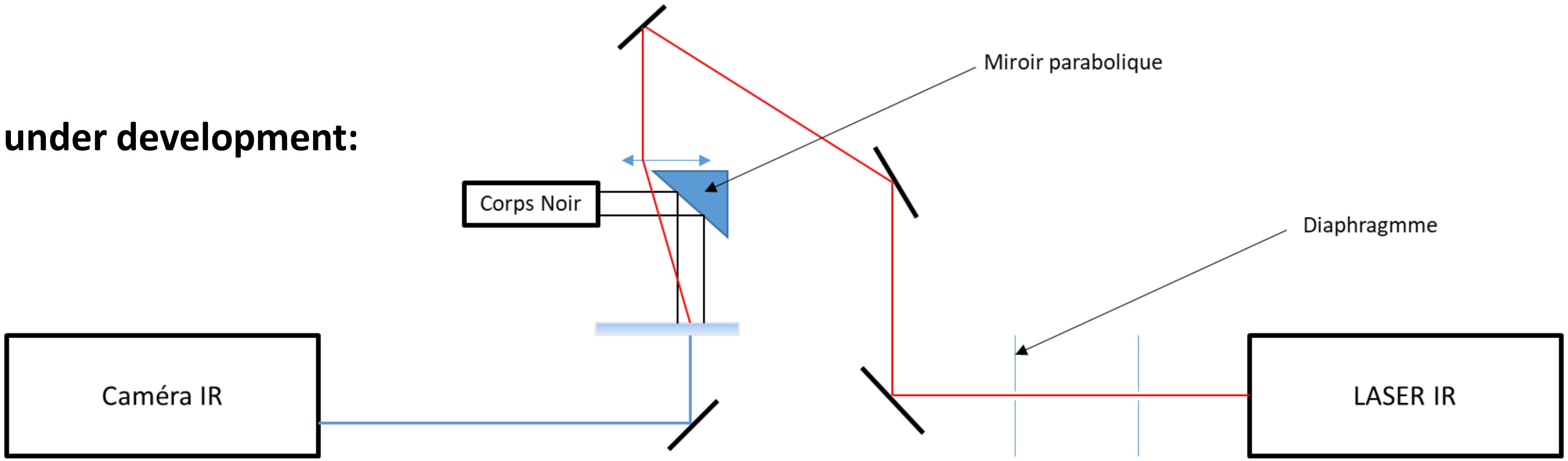
Next steps: improving our setup
Collab: J. Maire

Roadmap and locks
- ✓Chopper to be removed
- ✓Electrical resistance to be removed
- ✓Volumic heating!
- ✓100 mK thermal resolution
- ✓Measurement time lower than 10 s

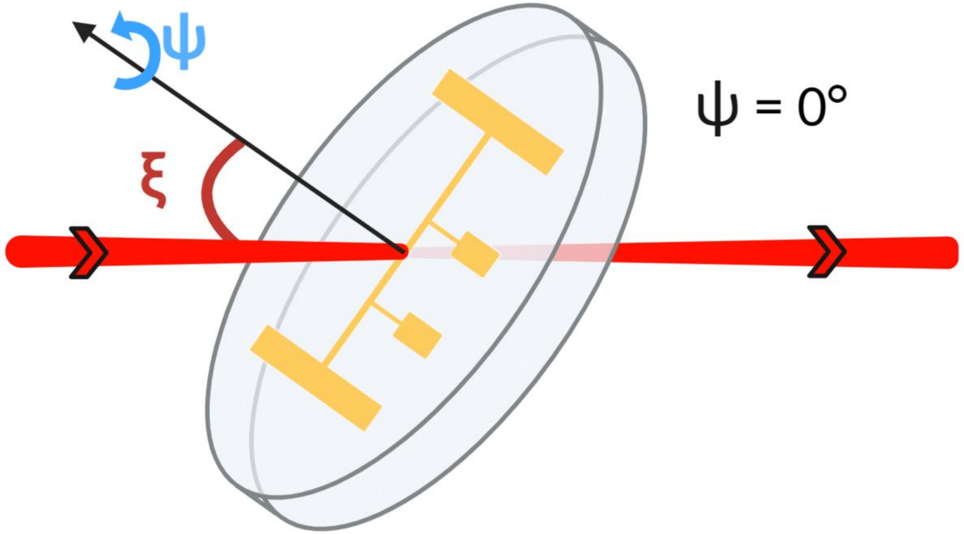
High-Power IR Emitters:

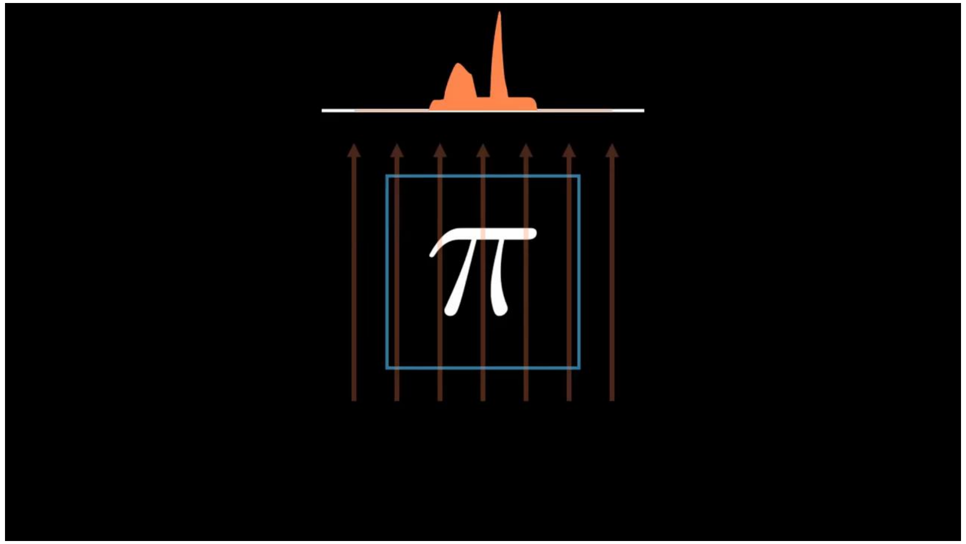
Quantum Cascade Lasers:

New setup under development:



Next steps: working on the algorithm -> SIRT (*Simultaneous Iterative Reconstruction Technique)*
J. Letessier (Postdoc)

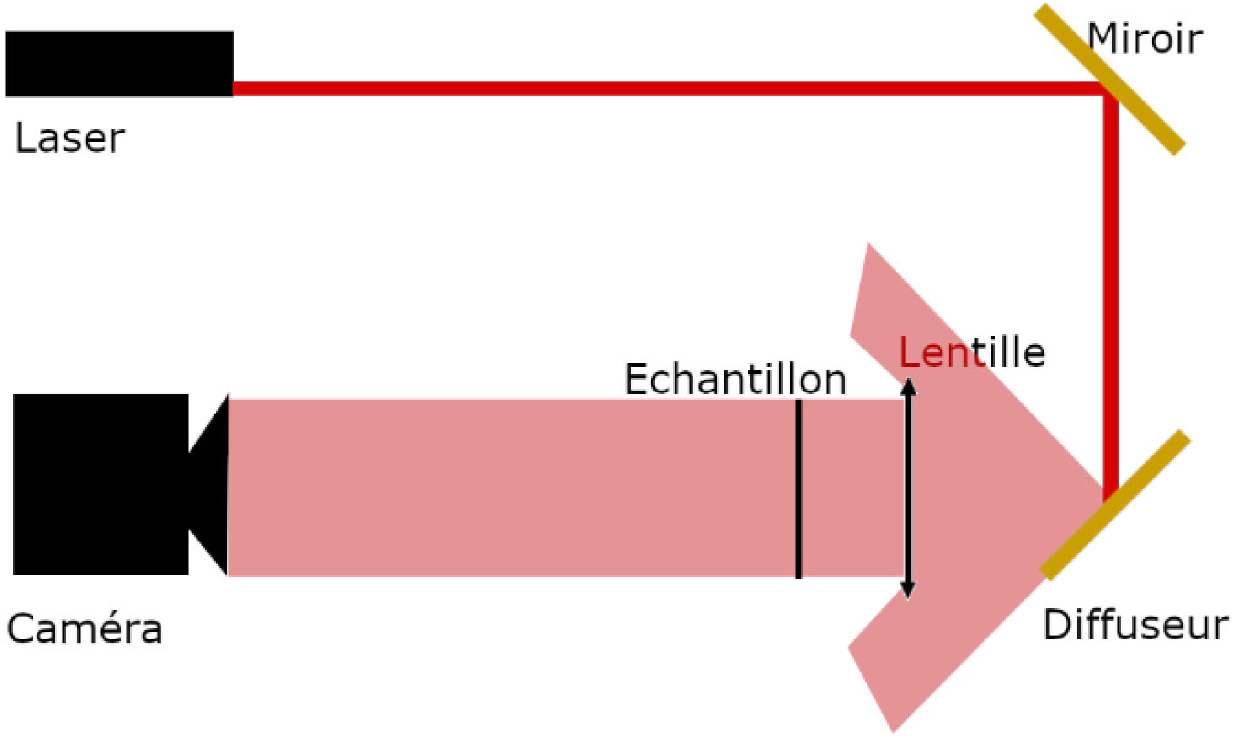


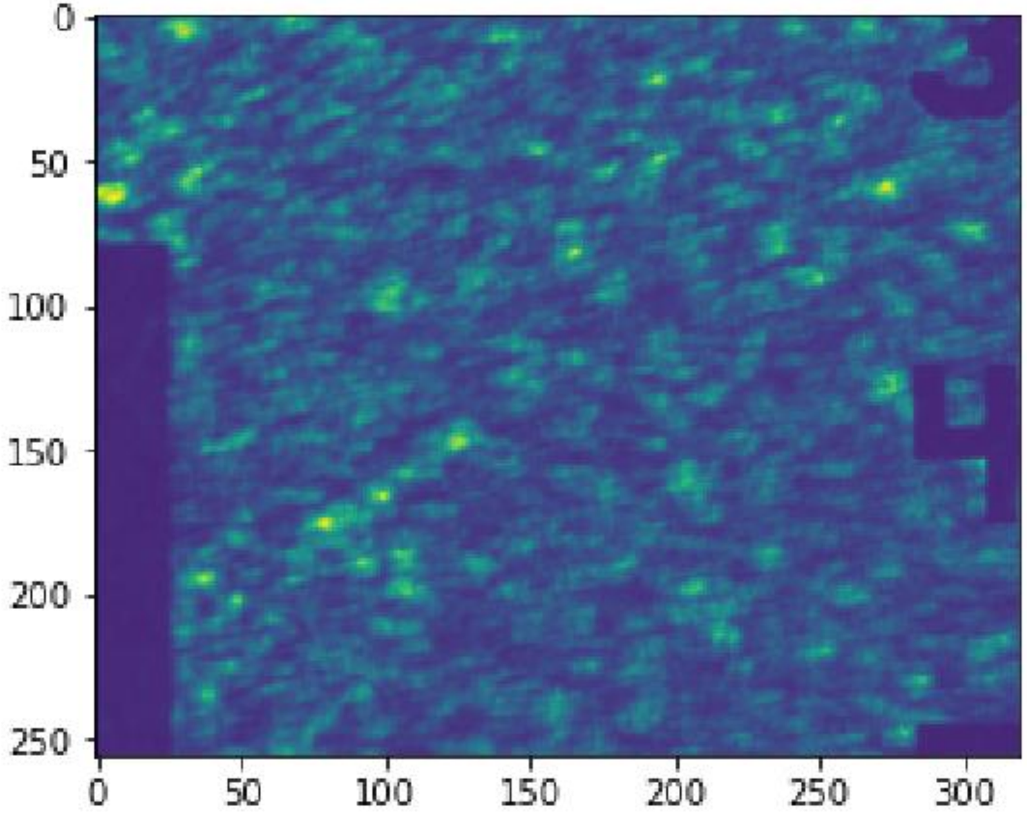


→ Challenge : Thermal fields are low frequency, so filters needs to be adapted !

https://en.wikipedia.org/wiki/Tomographic_reconstruction

Central topic in the research group: Groz, M. et al. *Quant. Infrared Thermogr. J.* **2024**, *0* (0), 1–24.
Still using lasers!





→ Generating sub-pixel pattern !

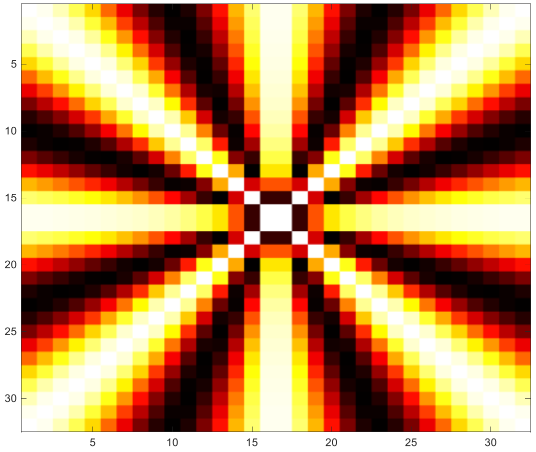
Still using Inverse Methods!

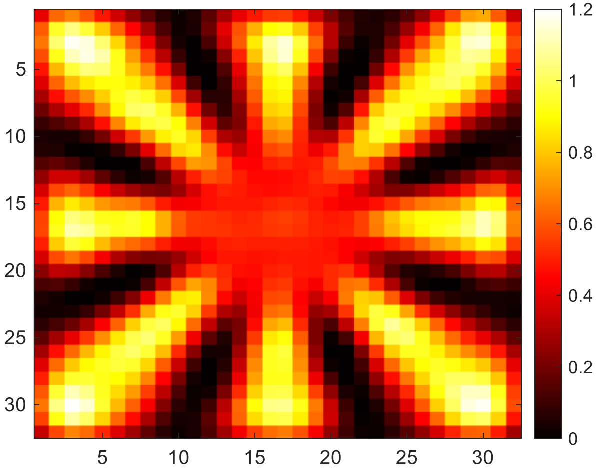
$$I_m = h \otimes (\rho \phi_m) + \epsilon$$

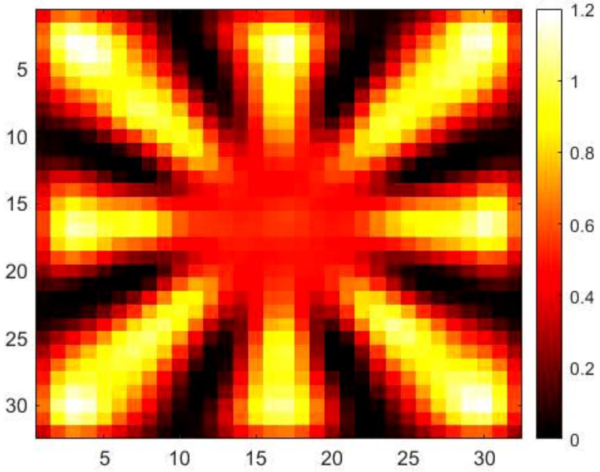
h : Point Spread Function → low pass filter

Minimisation problems

$$F(\rho) = \sum_{m=1}^{M} \| I_m - \boldsymbol{H}(\rho \phi_m) \|^2$$





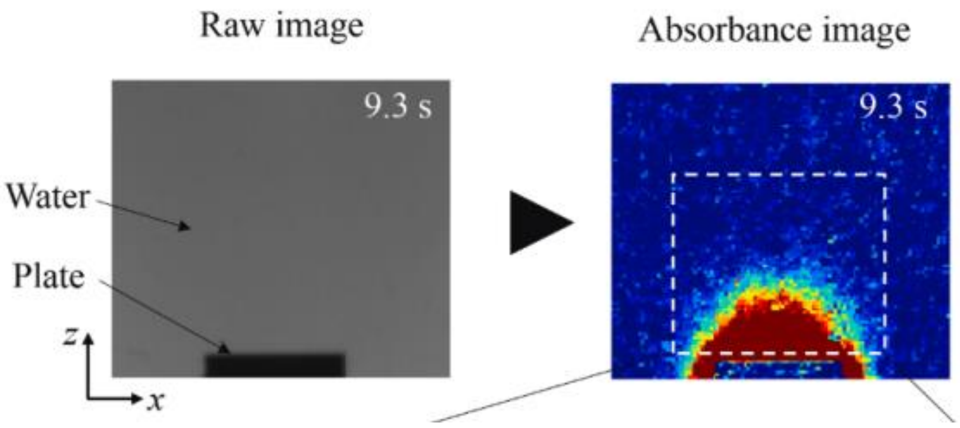


→ Challenges: Transient regime, diffusive problem.
→ Low frequency for diffusion, high frequency for structure !

First results obtained in F. Crouau PhD

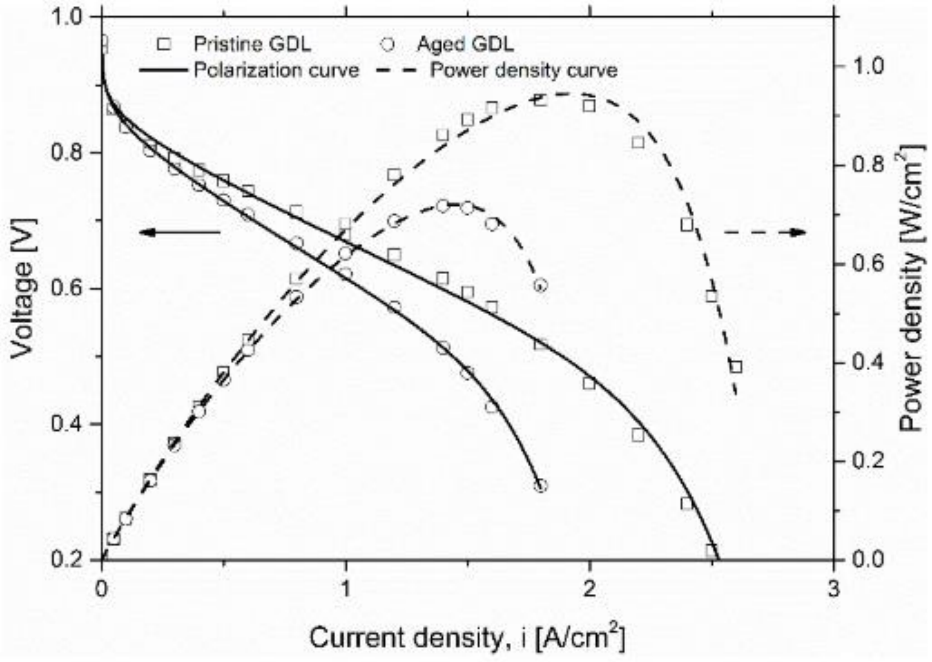
What are the operando heat and mass transfer properties in MEDC?

➔ Combining spectroelectrochemistry and thermottransmittance in fluid



Nguyen, T.-A.; *Exp. Therm. Fluid Sci.* **2023**, *142*

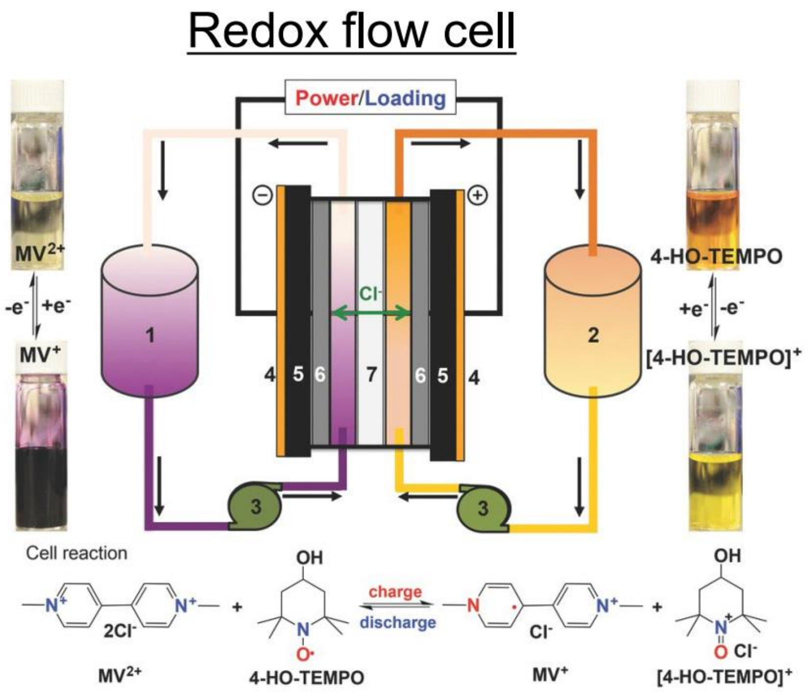
➔ Another great asset of microfluidic : ageing studies

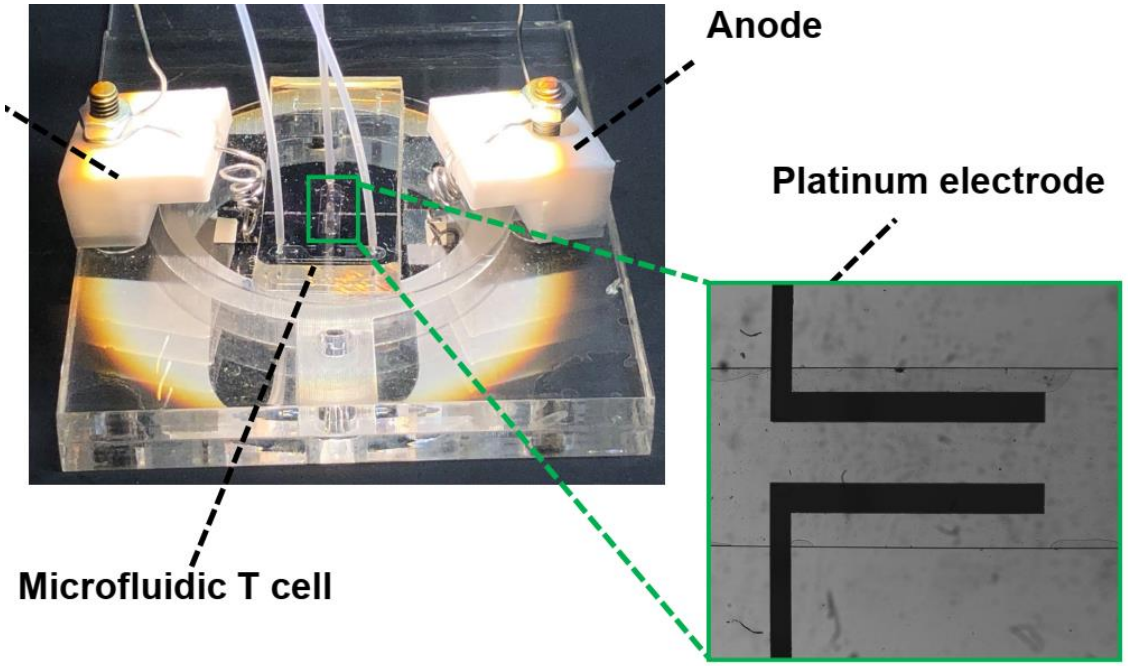


Ageing a 1 kW PEMFC stack over 1,000 h will cost 60 bottles of hydrogen and between 1,500 and 2,500€.

Two main applications

SmartBat project: collaboration I2M/Tokyo University



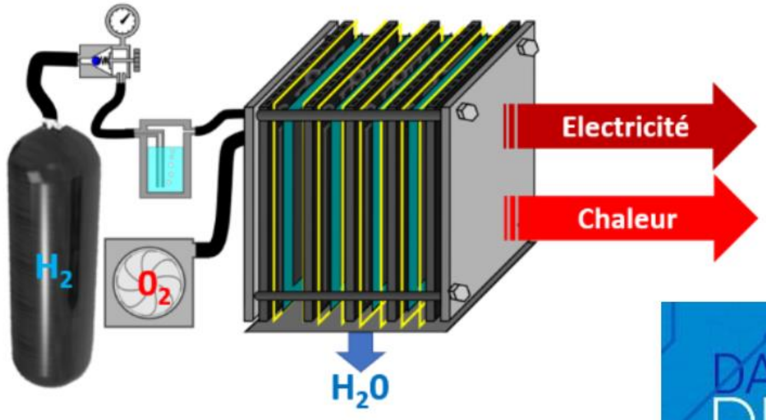


The key idea is to combine:

1. modulated electrochemical methods (like electrochemical impedance spectroscopy)
2. Concentration and thermal imaging methods (like IR or Vis spectroscopy)

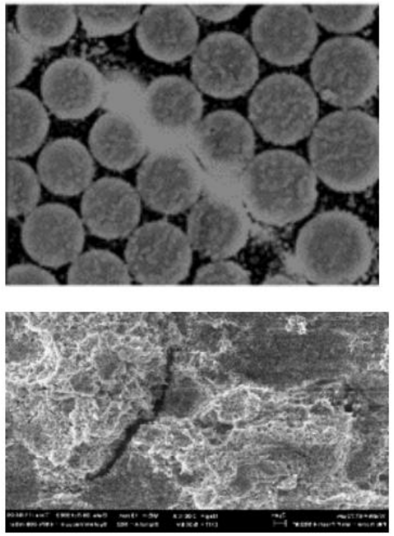
Purpose: imaging very low concentration fields (few mM) in microfluidic electrochemical devices (sensors, energy converters, ...) → A. Svirina PhD

OptUseH2 and the Hydrogen platform

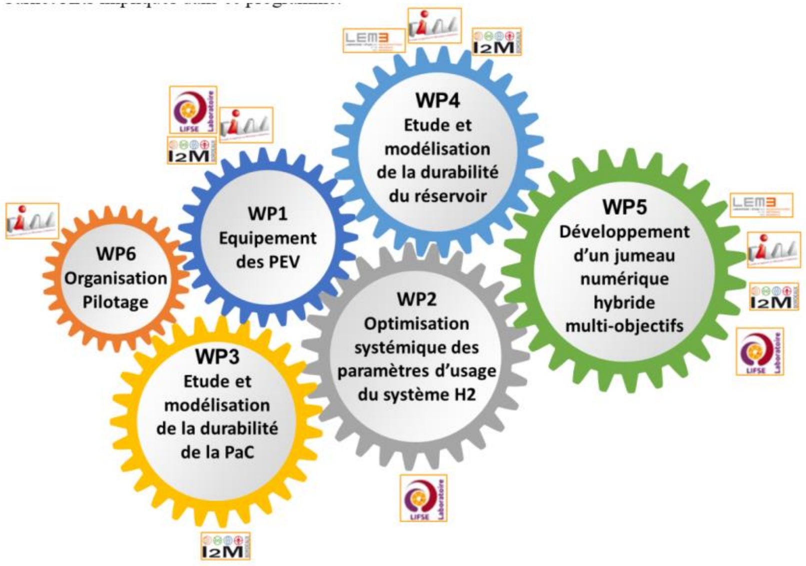


Système hydrogène

Optimisation systémique



Durabilité



The key idea is to combine:

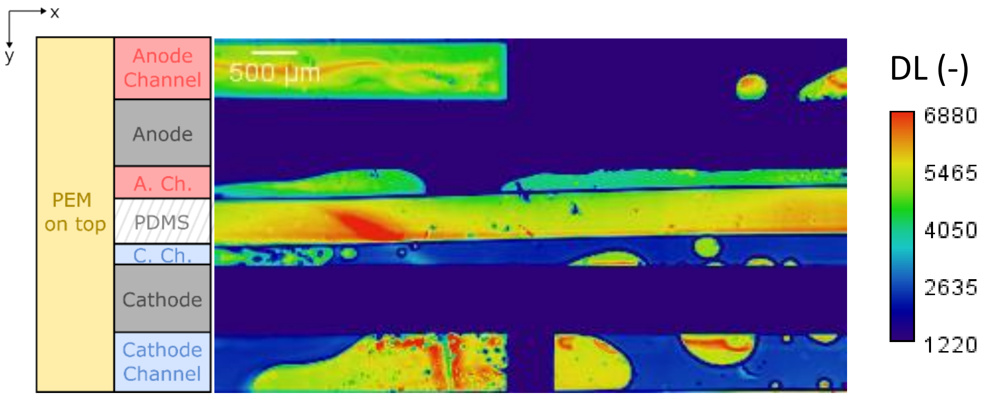
1. Systemic modelling of heat and mass transfer
2. Microfluidic fuel cells and electrolyzers

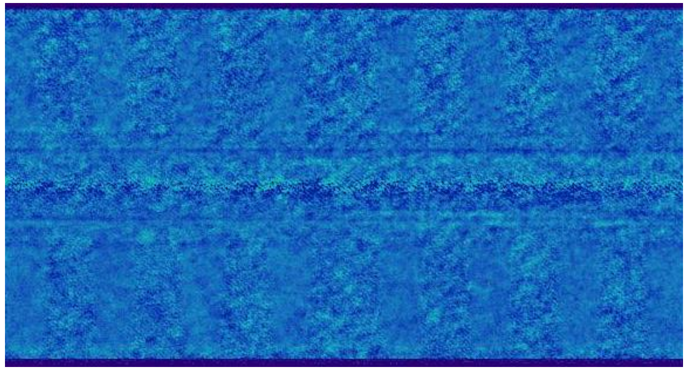
Purpose: building an Hydrogen platform to study fuel cell chain durabilities

➔ Strong side effect of this project concerning educational aspect

CONCLUSIONS & PERSPECTIVES

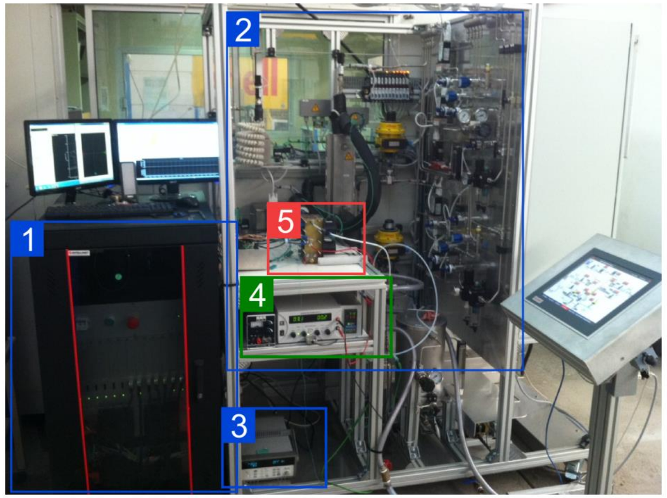
Development of new characterization methods for MECD

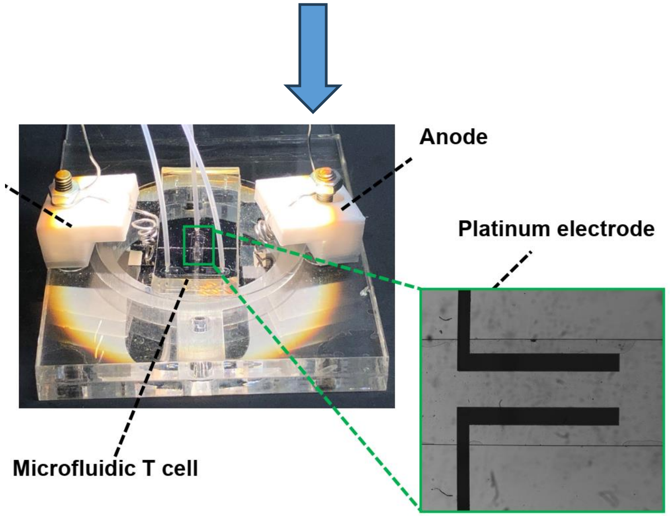




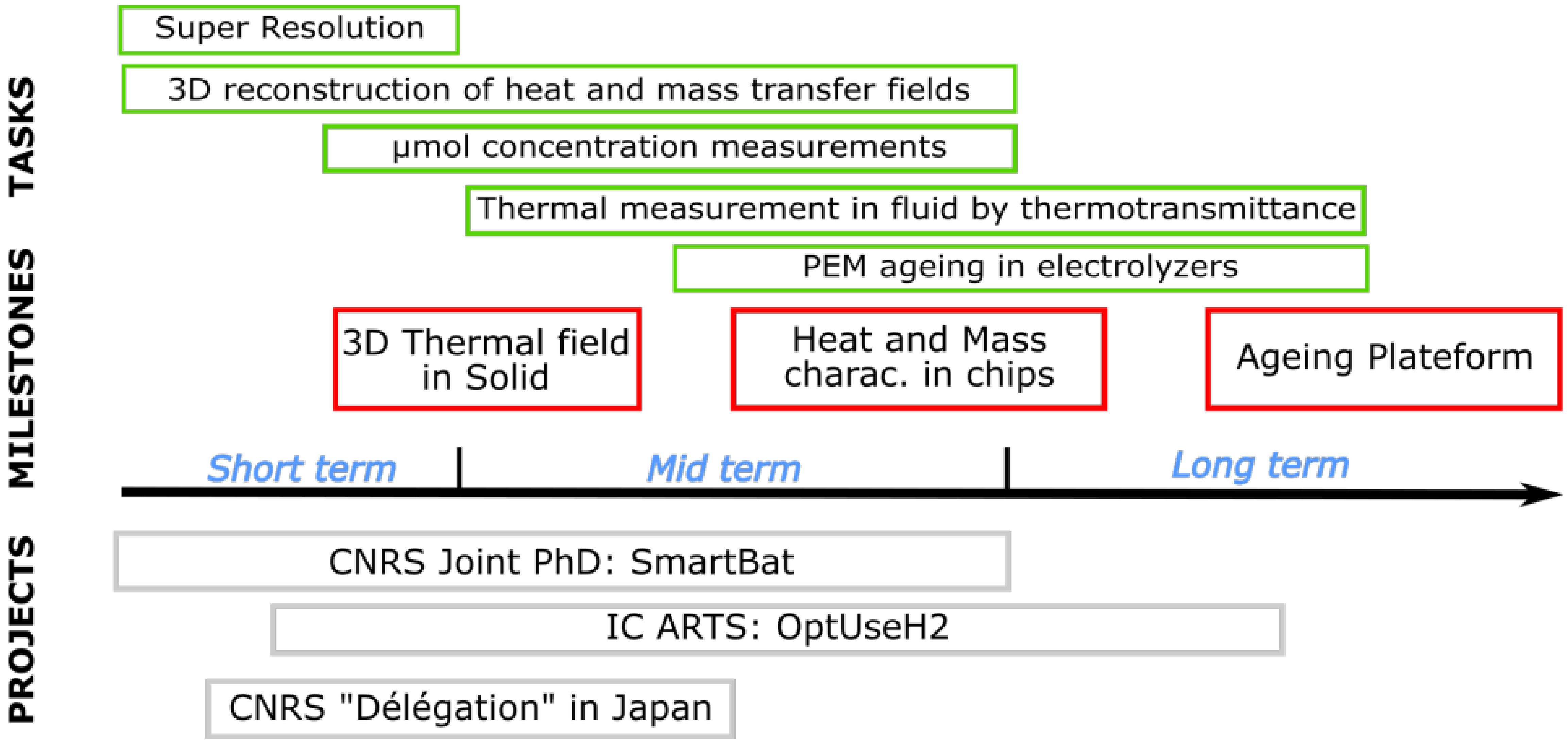
- ✓ Operando parameters estimations
- ✓ Better understanting of heat and mass transfers in these systems

Keep decreasing time and space scales in 3D





Perspectives



ACKNOWLEGMENTS