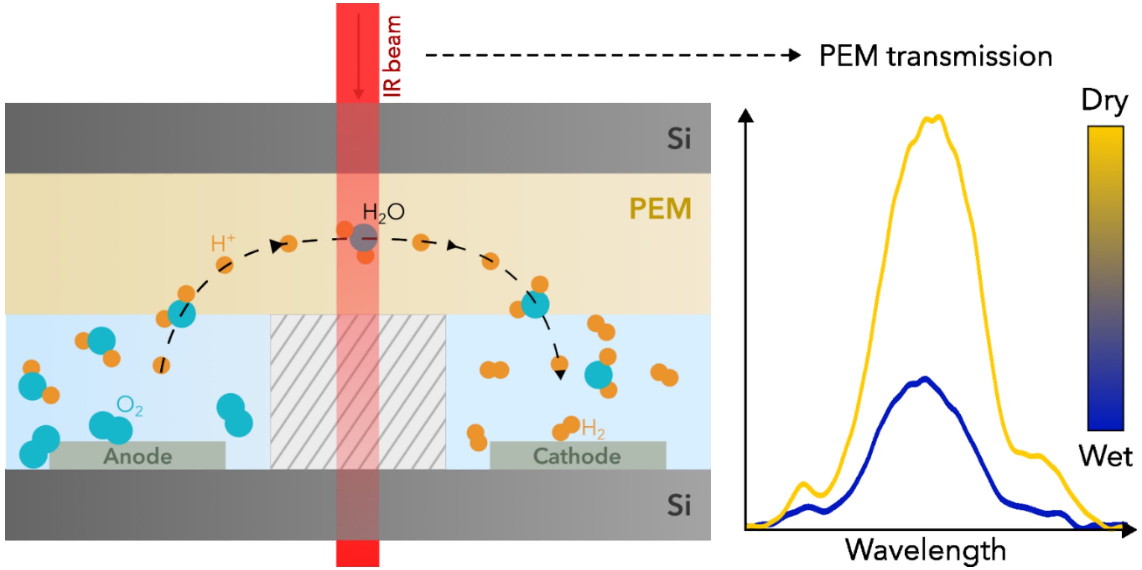
Characterizing membrane hydration in a microfluidic polymer electrolyte membrane water electrolyzer via operando synchrotron Fourier-transform infrared spectroscopy

Kevin Krause, Marine Garcia, Dominique Michau, Brant Billinghurst, Gérald Clisson, Jean-Luc Battaglia, Stéphane Chevalier

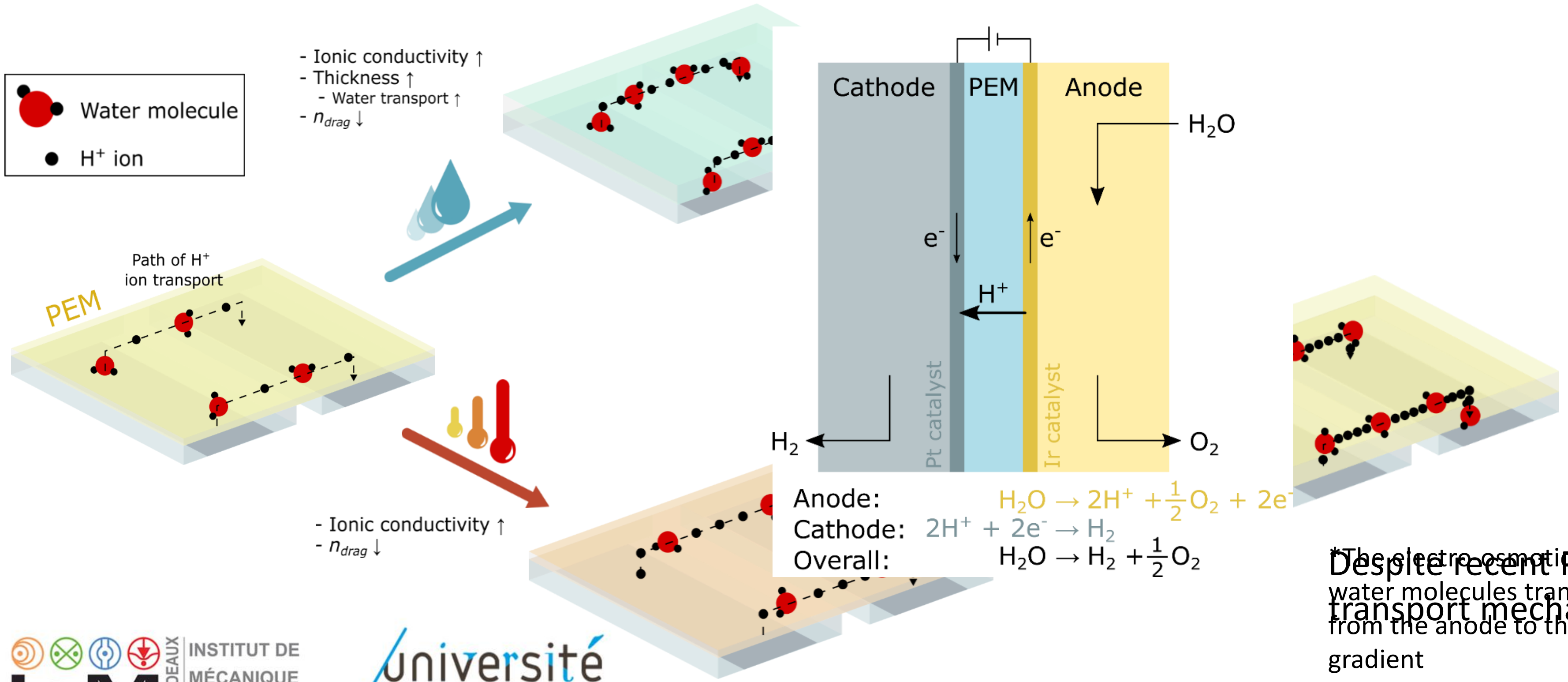
Canadian Light Source
Centre canadien de rayonnement synchrotron
Bordeaux INP
Arts et Métiers Sciences et Technologies
CNRS
Solvay
I2M Bordeaux Institut de Mécanique et d'Ingénierie
Université de Bordeaux



kevin.krause@u-bordeaux.fr

Context

- Compared to other water electrolyzers, polymer electrolyte membrane (PEM) electrolyzers have:[1]
  - Benefits: (1) higher current density operation (2) high energy efficiency (3) high product gas purity (4) a high dynamic range (ideal for intermittent energy)
  - Drawbacks: (1) high capital costs (2) ideal performance at 50 °C - 80 °C
- Optimizing proton transport within the PEM would reduce costs



Anode: $H_2O \rightarrow 2H^+ + \frac{1}{2}O_2 + 2e^-$

Cathode: $2H^+ + 2e^- \rightarrow H_2$

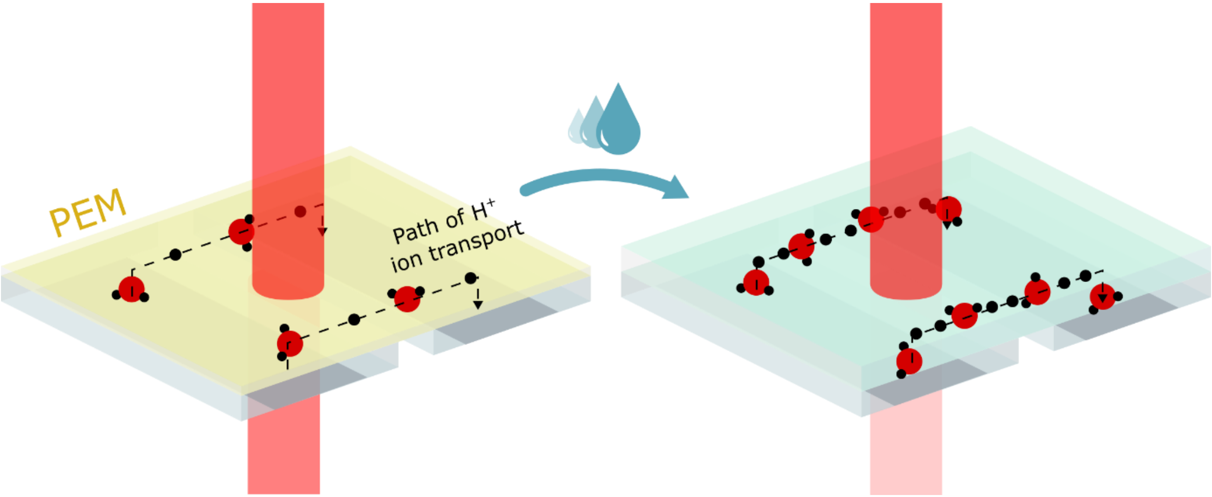
Overall: $H_2O \rightarrow H_2 + \frac{1}{2}O_2$

Despite recent PEM advancements, internal transport mechanisms remain poorly understood

*The electro-osmotic drag coefficient (n_{drag}) is the number of water molecules transported per proton when protons move from the anode to the cathode in the absence of a concentration gradient

Context

- X-ray and neutron imaging techniques are often used to characterize operando PEM characteristics, but also damage it in the process[1,2]
- Infrared characterization is safe due to the low beam energy levels, but suffer from short penetrative path lengths
  - IR is highly sensitive to water attenuation
- Microfluidics are a potential solution
  - Conforms to short IR path lengths
  - Precise control of operating parameters
- Objectives
  - Develop a microfluidic PEM electrolyzer that is semi-transparent in IR
  - Characterize losses attributed to the PEM in an electrolyzer
  - Observe the operando membrane water content via synchrotron FTIR spectroscopy



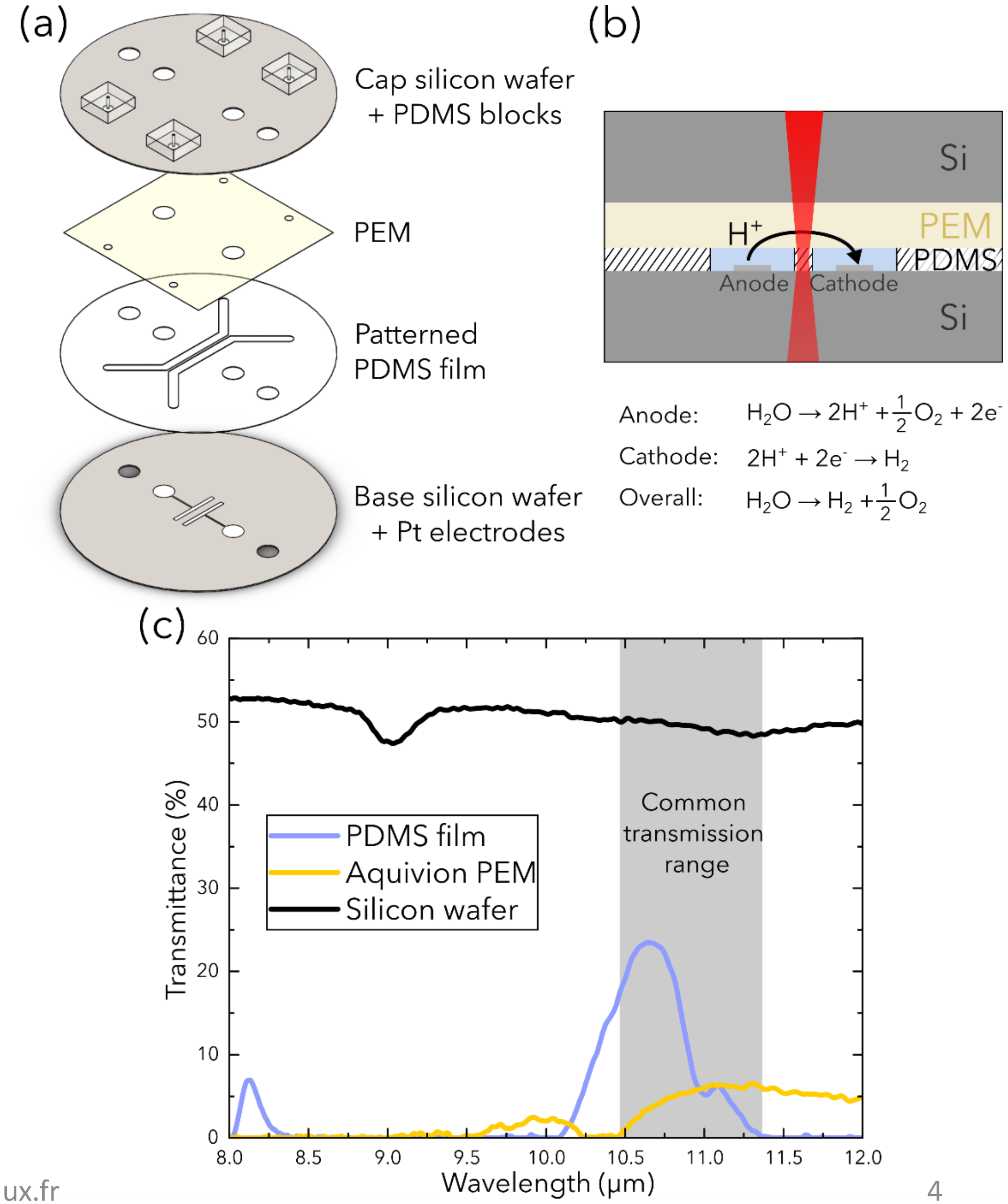
---

[1] J. Roth, J. Eller and F. N. Büchi, *J. Electrochem. Soc.*, 2012, **159**, F449–F455.
[2] J. Eller and F. N. Büchi, *J. Synchrotron Radiat.*, 2014, **21**, 82–88.

kevin.krause@u-bordeaux.fr

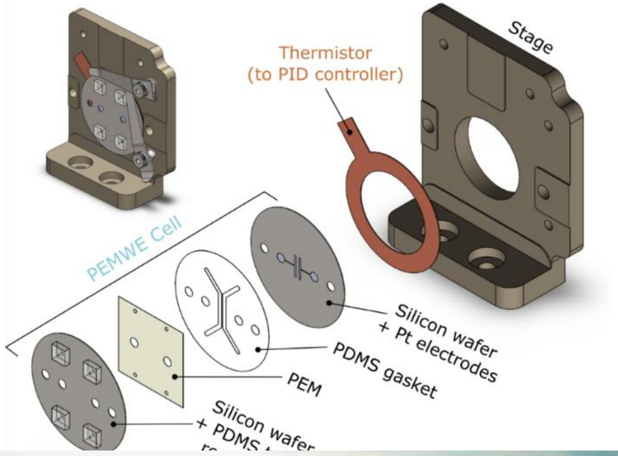
Fabrication – material selection

- Components that are semi-transparent in far-IR, allowing us to isolate PEM's transmission
- We use a stack of 4 layers:
  - Cap double-side polished silicon wafer (279 µm thick)
  - Aquivion PEM (E87-05S)
  - PDMS film (38 µm thick)
    - Channel dimensions of 1.8 mm width, 15 mm length, 38 µm height, with channels spaced 500 µm apart
  - Base double-side polish silicon wafer
    - Sputtered with ~60 nm thick titanium adhesion layer, and then ~300 nm thick platinum electrodes, with electrodes 1.2 mm apart



Experimental setup

- Synchrotron facilities have extremely sensitive equipment, allowing us to capture water attenuation through the PEM
  - We traveled to the Canadian Light Source (Saskatoon, Canada) for the partnership between CNRS and the University of Toronto



rotron
ctrometer

kevin.krause@u-bordeaux.fr

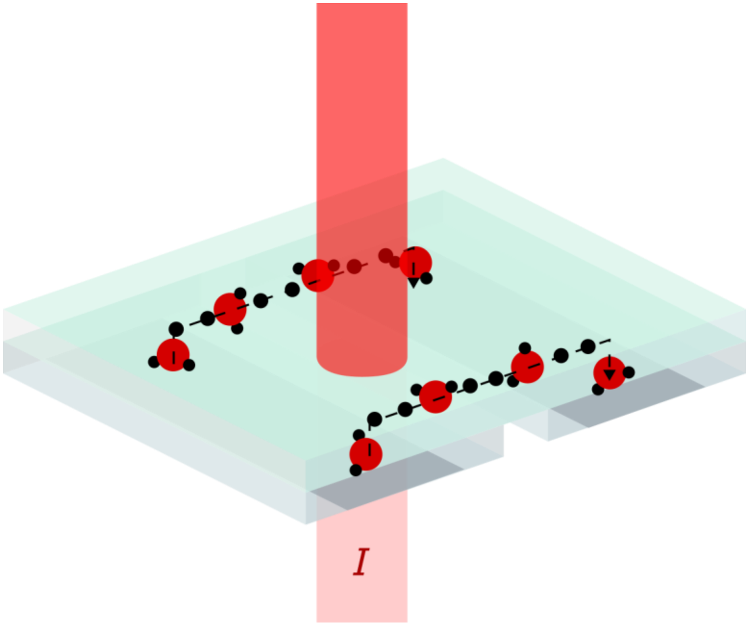
Water quantification

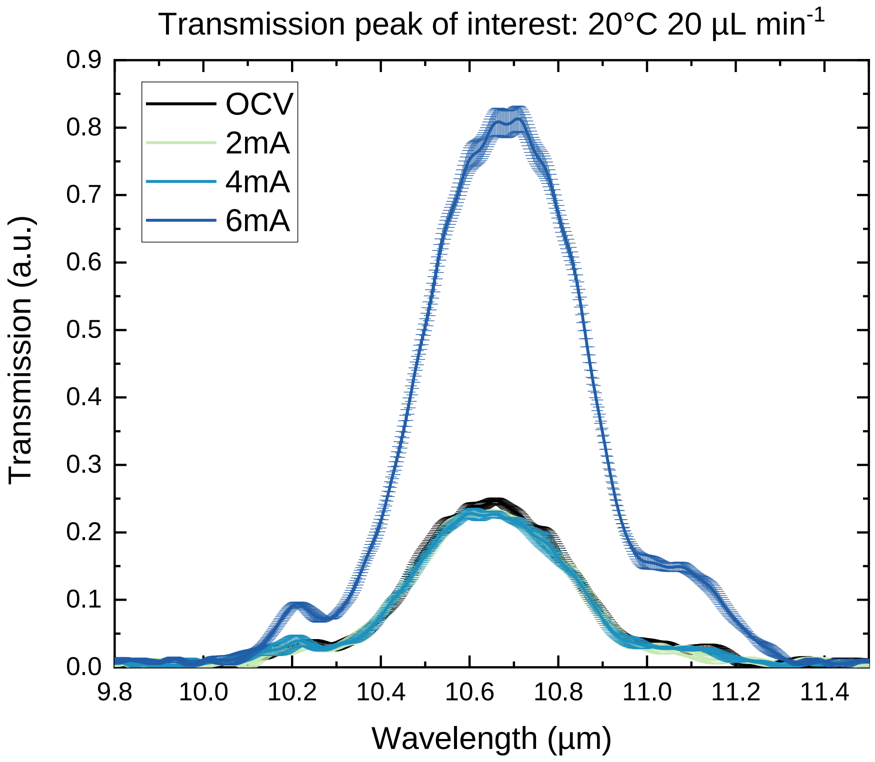
- The acquired IR spectra are processed via the Beer Lambert Law to quantify the change in water thickness

$$l_w(\lambda) = -\frac{1}{\mu_w(\lambda)}\ln\left(\frac{I(\lambda)}{I_{OCV}(\lambda)}\right)$$

- This is then converted to percent change in water saturation

$$\Delta S = \frac{\overline{l_w}}{t_{PEM+PDMS}}$$





kevin.krause@u-bordeaux.fr

Experimental conditions

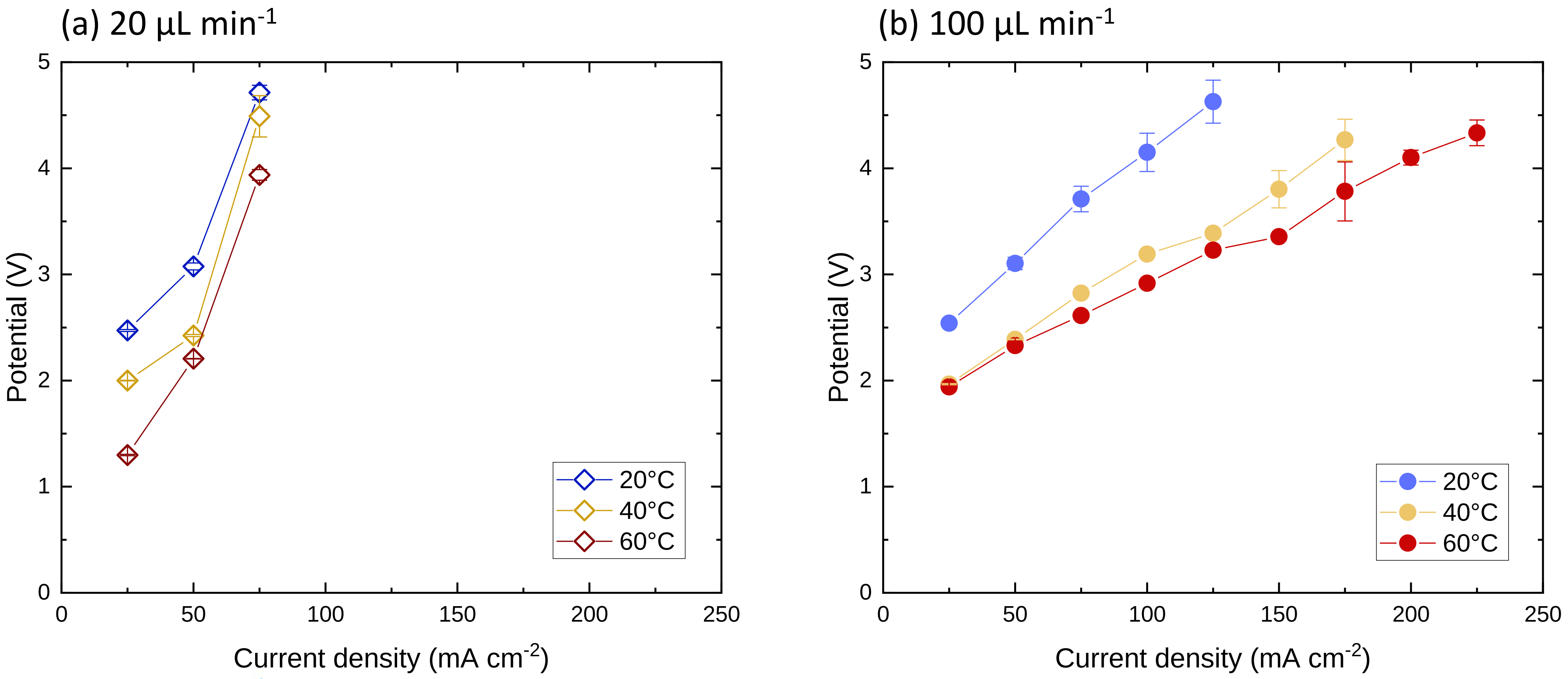
- Remaining objectives
  - Characterize losses (specifically ohmic and mass transport) attributed to the PEM in an electrolyzer
  - Observe the operando membrane water content via synchrotron FTIR spectroscopy

- Controlled parameters:
  - Current density
    - Increasing from OCV in steps of 25 mA cm^{-2} until potential response exceeds 5 V
    - Staircase Galvano Electrochemical Impedance Spectroscopy (SGEIS) is performed between each applied current to estimate ohmic losses
  - Two flow rates (20 and 100 µL min^{-1}) for 0.5 mol L^{-1} H_2SO_4 reactant
    - Low flow rate is chosen to induce reactant-starving mass transport dominated overpotentials
    - High flow rate is chosen to drive ohmic-dominated overpotential
  - Three temperatures (20, 40, and 60 °C)
    - Higher temperatures are associated with improved performance
    - Varied to observe membrane behavior at each condition

kevin.krause@u-bordeaux.fr

Results - electrochemical performance

- Polarization curves of results:



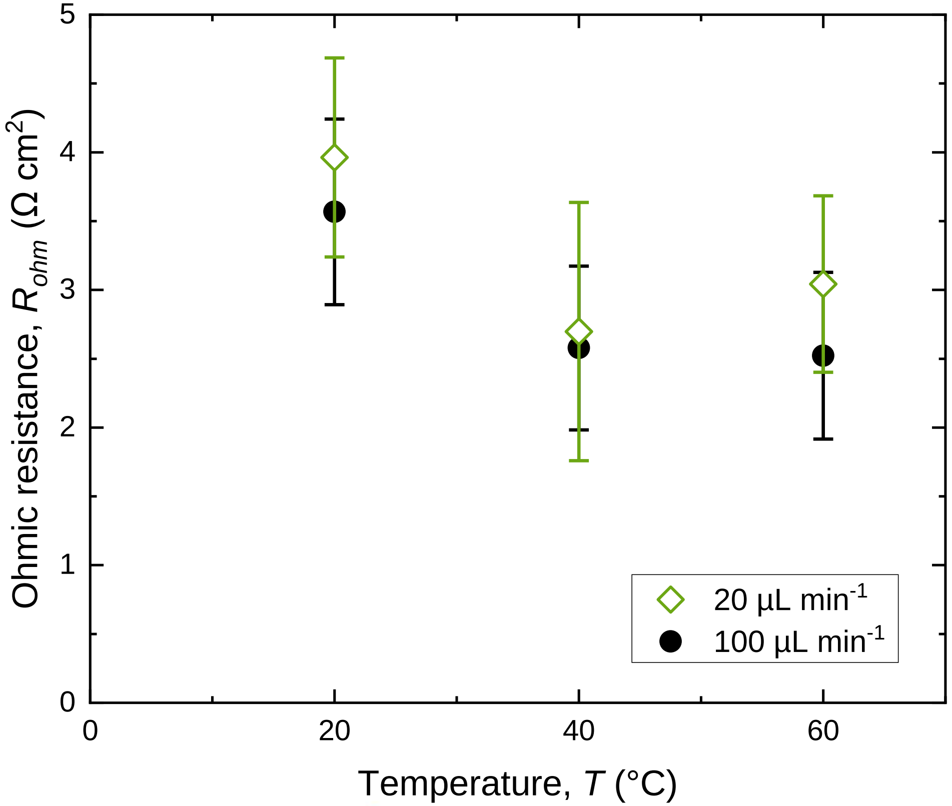
(a) 20 µL min^{-1}

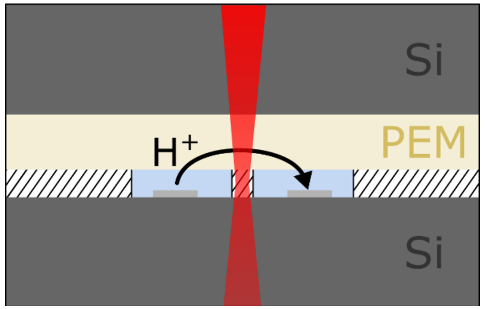
(b) 100 µL min^{-1}

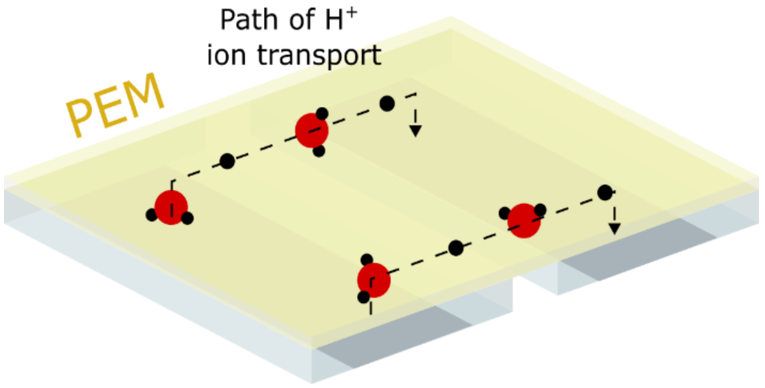
kevin.krause@u-bordeaux.fr

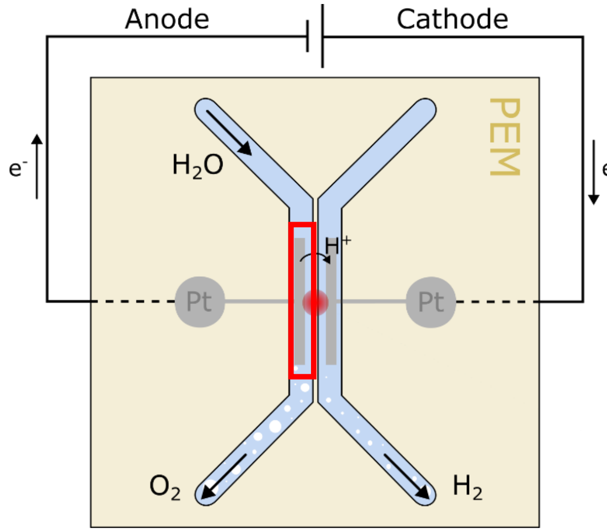
Results – ohmic resistance

- Ohmic resistance is one order of magnitude higher than commercially relevant electrolyzers (e.g. <300 mΩ cm^2)
- Large uncertainty in measurements is due to small active area





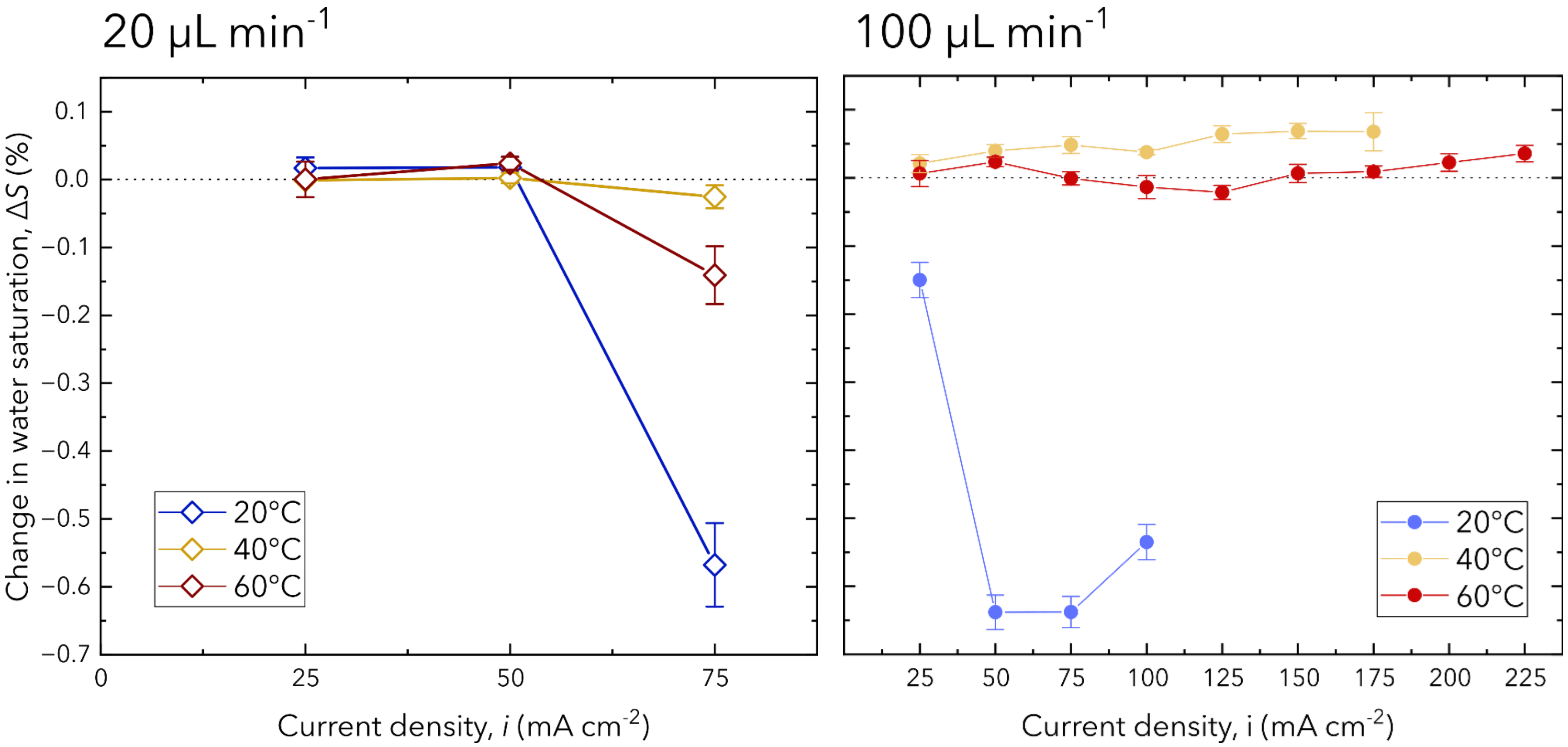




Active area = 0.08 cm^2

Results – change in water saturation

- For 20 µL min^{-1}
    - Gas saturation increases significantly immediately before cell failure at 75 mA cm^{-2}
        - Membrane drying occurs in parallel with cell failure
    - Most membrane drying at 20 °C, least membrane drying at 40 °C
- For 100 µL min^{-1}
    - Membrane drying only occurs at 20 °C
- Spectroscopic results may be limited to local information

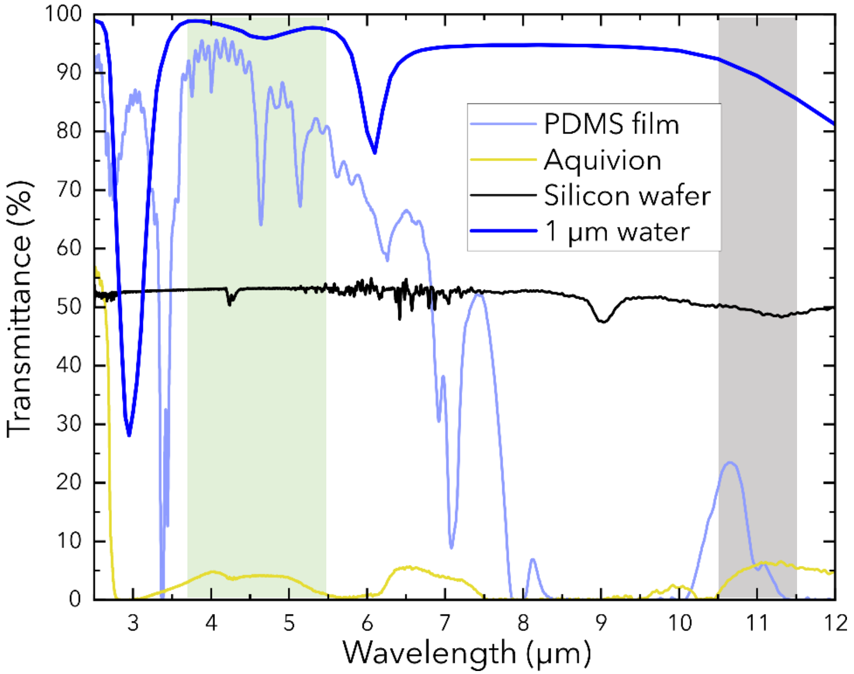


kevin.krause@u-bordeaux.fr

Summary

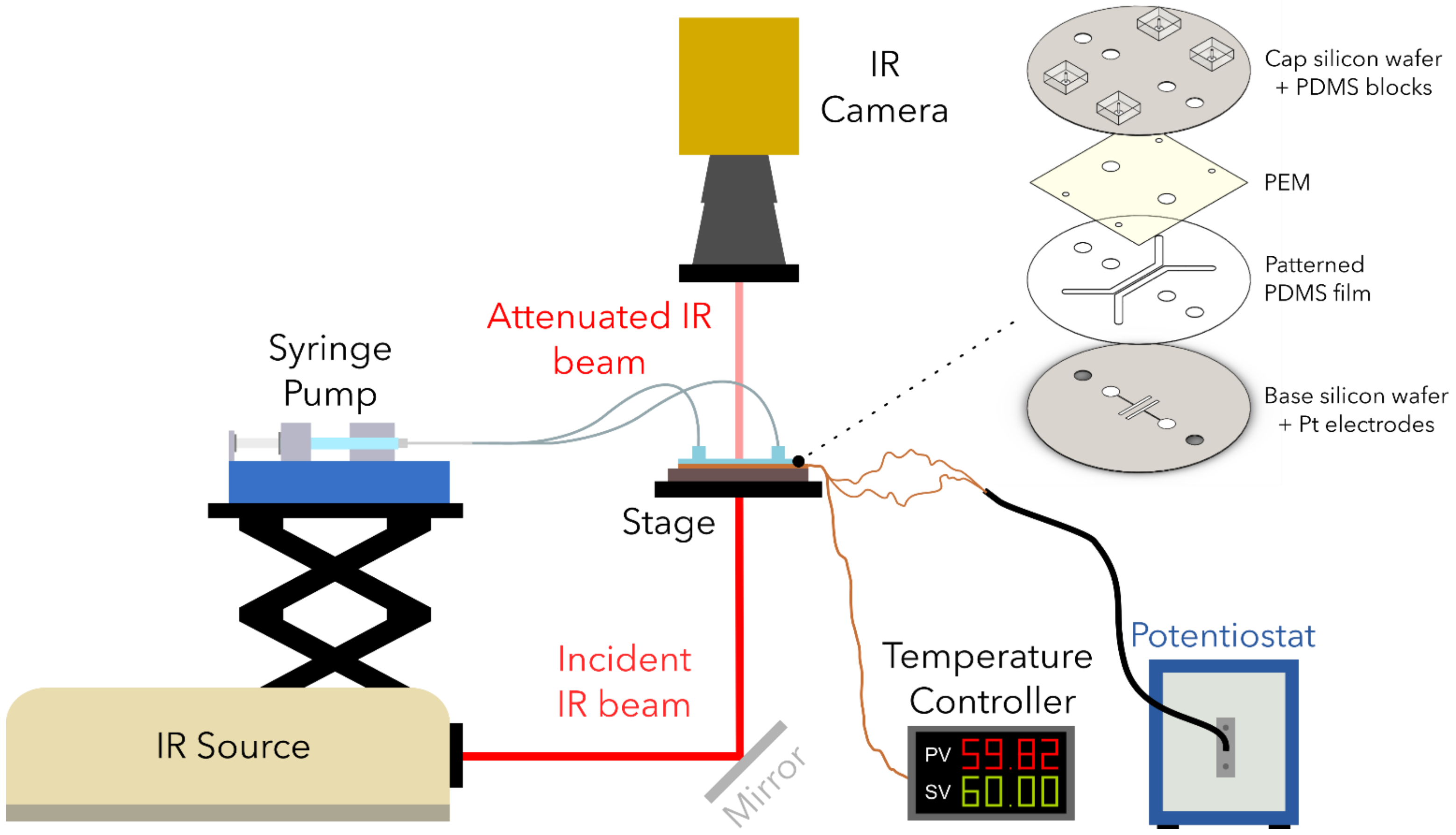
- Developed a microfluidic PEM electrolyzer that is semi-transparent in IR
- Characterized losses in the electrolyzer
  - Higher temperatures achieve higher current densities
- Quantified membrane water content using synchrotron FTIR spectroscopy
  - Mass transport driven membrane drying occurs with cell failure at low reactant flow rates

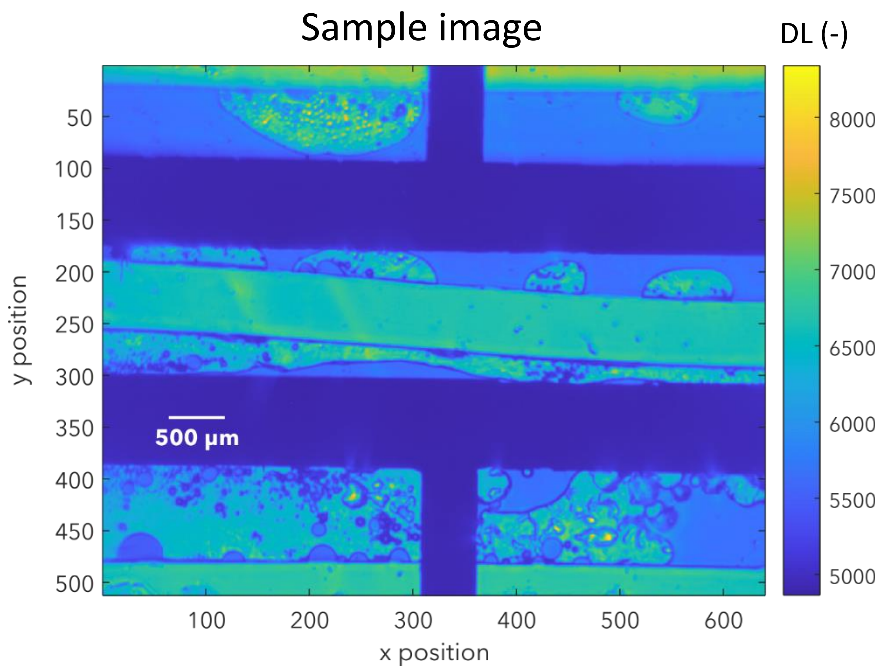
- Transitioning to IR imaging
  - Implement our setup in Mid-IR for improved transmittance



kevin.krause@u-bordeaux.fr

IR imaging





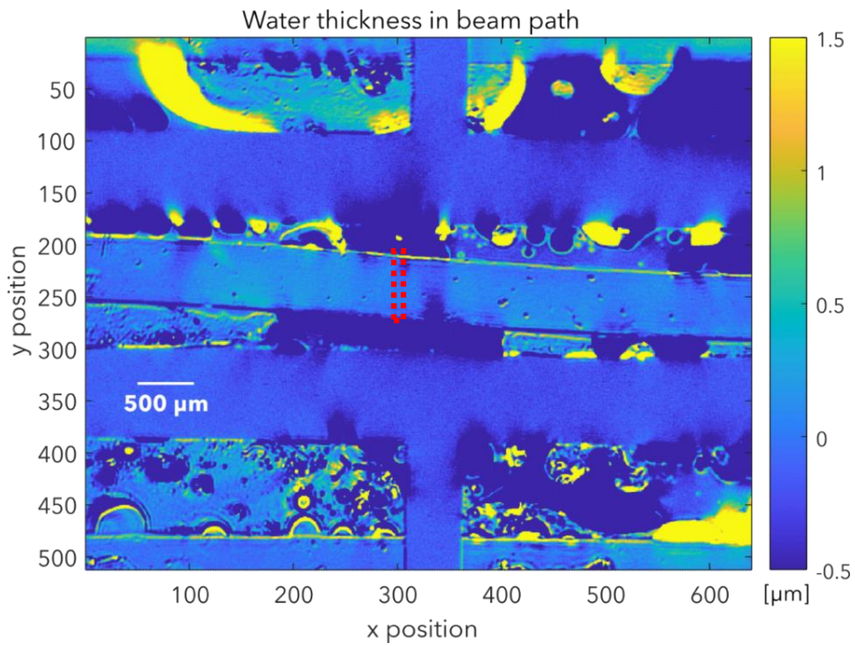
λ = 4 µm

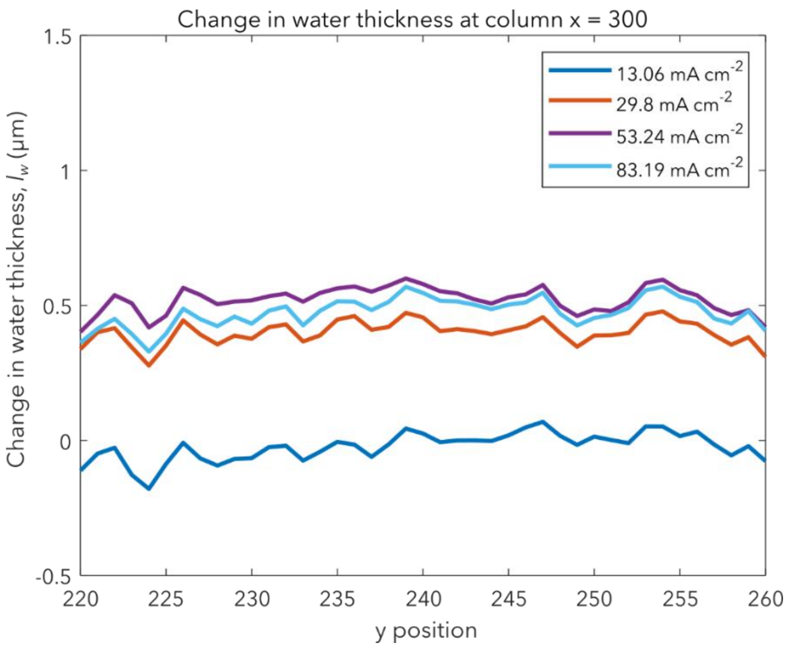
kevin.krause@u-bordeaux.fr

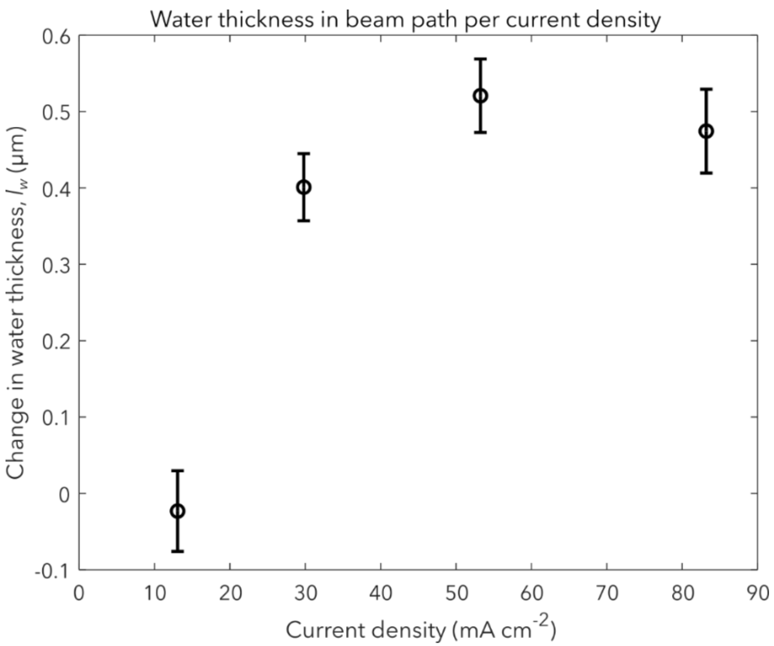
IR imaging

- Preliminary IR imaging shows no gradient in PEM absorbance between channels, but a change in the water thickness with the operating current density

$$l_w = -\frac{1}{\mu_w}\ln\left(\frac{I(\lambda)}{I_{OCV}(\lambda)}\right)$$


Water thickness in beam path


Change in water thickness at column x = 300


Water thickness in beam path per current density

INSTITUT DE MÉCANIQUE ET D'INGÉNIERIE I2M BORDEAUX

université de BORDEAUX

kevin.krause@u-bordeaux.fr

Acknowledgements

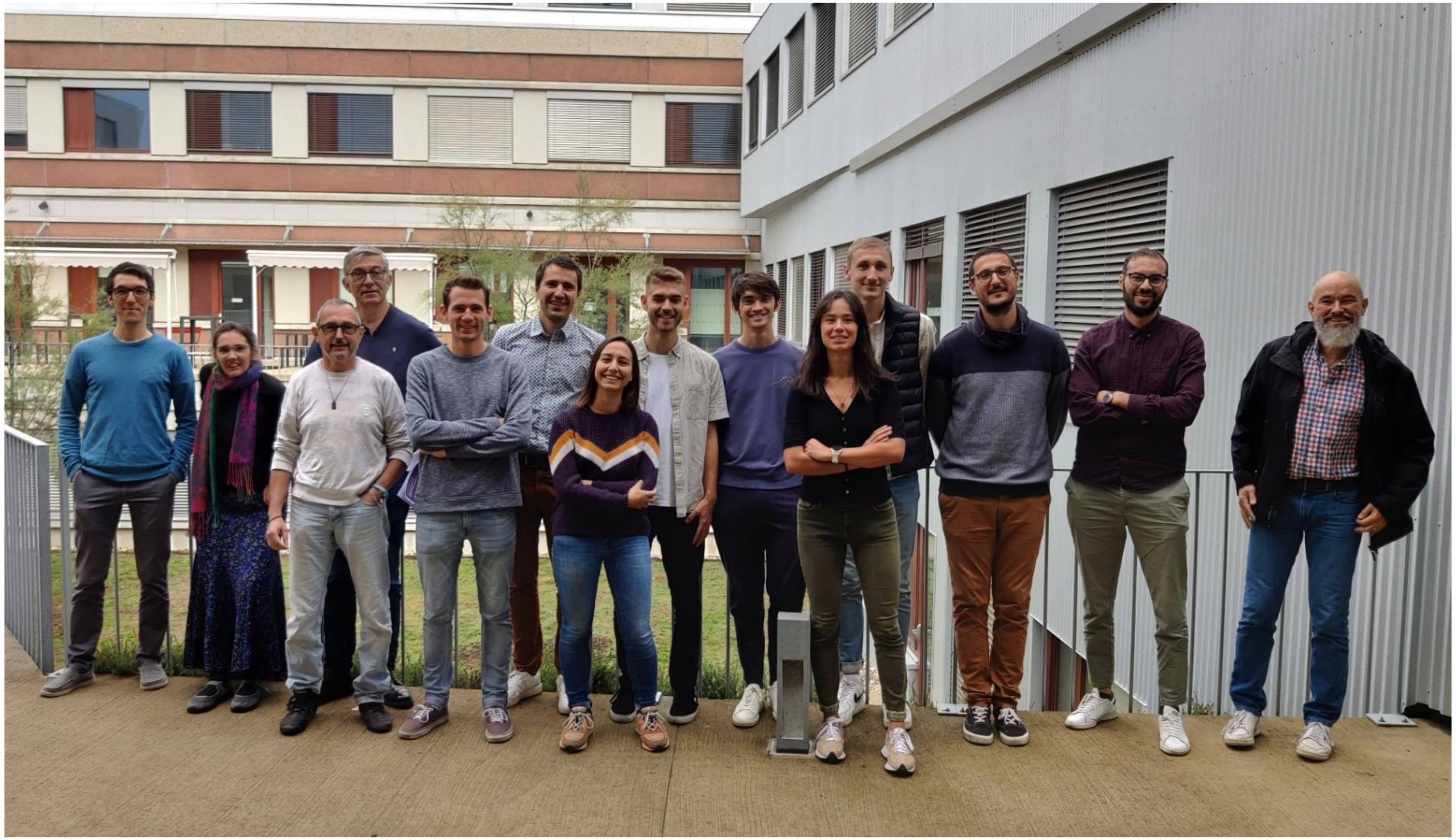
Arts Sciences et Technologies et Métiers

SOLVAY

Canadian Light Source
Centre canadien de rayonnement synchrotron

BORDEAUX INP

cnrs



I2M BORDEAUX INSTITUT DE MÉCANIQUE ET D'INGÉNIERIE

université de BORDEAUX

kevin.krause@u-bordeaux.fr