Characterization of the mass transport in microfluidic fuel cells

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Arts et Métiers Sciences et Technologies

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Introduction

What are the challenges for tomorrow's energy ?

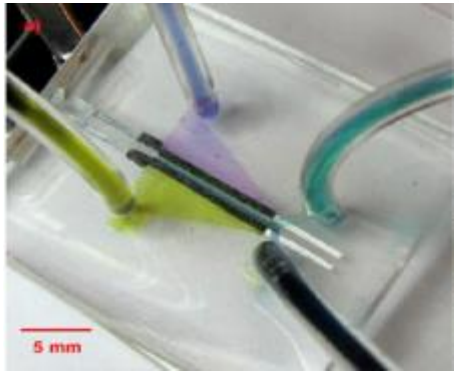
- Alternatives to fossil energy
- Portable energy
- Energy storage
- Meet the needs

Electrochemical reactions to produce electricity

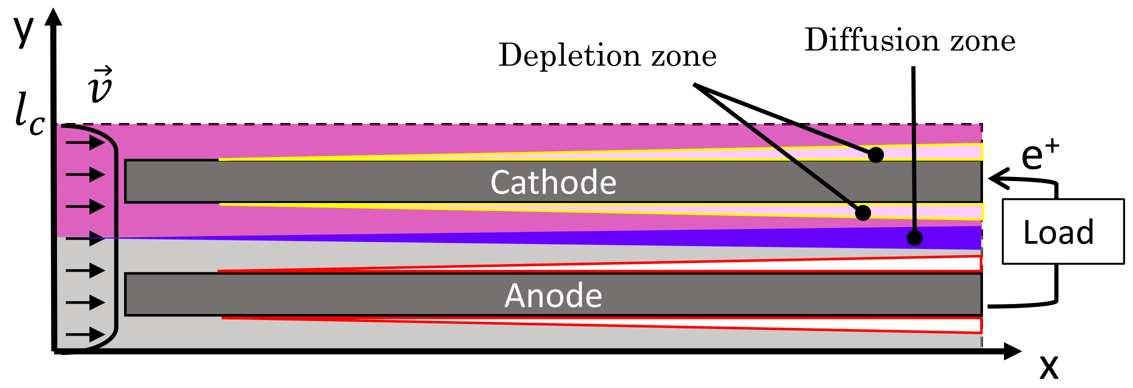
- Proton exchange membrane fuel cell (PEM)
  - One of the most advanced technologies
  - Membrane hydratation and gas transport issues

Other emerging technology

- Microfluidic membraneless fuel cell (MFC)



Presentation of a MFC



Channel height: 20-200 µm

At the anode

R1 ⟶ R1' + H^+ + e^-

At the cathode

R2 + e^- + H^+ ⟶ R2'

Liquid reactants are used to convert chemical energy into electricity at the microscale

Multiphysical system

Fluid mechanics	→	Velocity profile
Diffusion	→	Mass transport, charges transport
Electrochemistry	→	Reaction kinetics

Performance depends on

Species concentrations / Diffusion

Flow rate

Ionic conductivity of the solutions

Understand and quantify transfer phenomena when the cell is operating

Objectives : Understand and quantify transfer phenomena when the cell is operating

Which technique for each transfer ?

Charge → **Electrochemical techniques**
- Polarization curves, 3 electrode techniques, EIS…

Mass → **Imaging method**
- PEM : X-rays or neutron radiography
- Microfluidic systems : Raman, florescence, Spectroscopie…

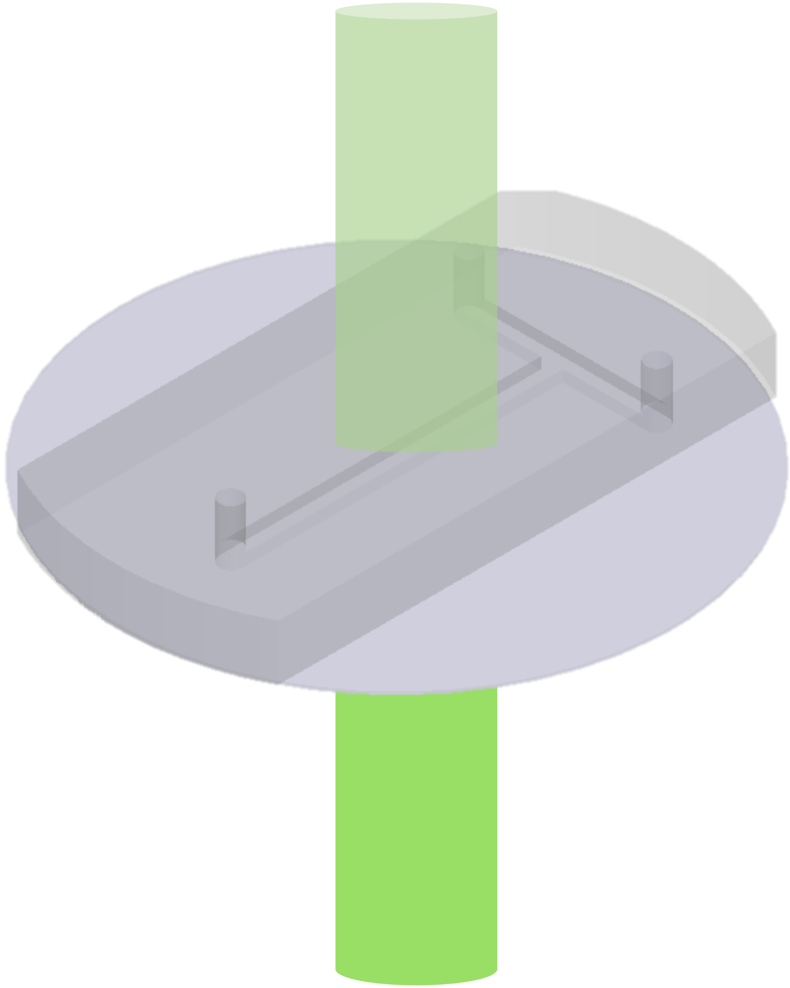
Numeric → **Modeling**
- Inverse method, COMSOL

Challenges

- Develop an imaging technique
- Develop a MFC compatible with an imaging setup
- Evaluate mass and charge transports
- Develop a MFC model to implement inverse method
- Determine in-situ parameters (diffusivity D, reaction rate k_0)

Spectroscopy and fabrication

- Beer Lambert law : Relates variation of light intensity to the concentration of the species

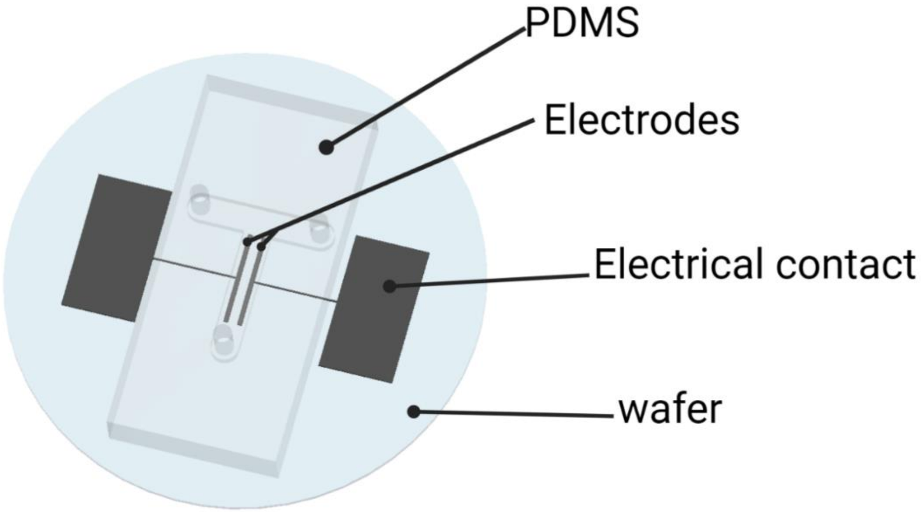


Compatibility criteria of the MFC

- Transparency of the cell
- Microscale dimensions for hydrodynamics and model
- Good pressure resistance
- Metal electrodes
- Access to the electrodes for electrical contacts

Spectroscopy and fabrication

Constraint…	…ions
Geometry to simplify the model	
Microscale dimensions channel h…	
Transparency	
Sealing and good pressure resistance	Plasma treatment to seal PDMS on the wafer
Metal electrodes	IGMCB equipement (sputtering)
Access to the electrodes for electrical contacts	Integration of electr… tact points



Channel height = 20 µm

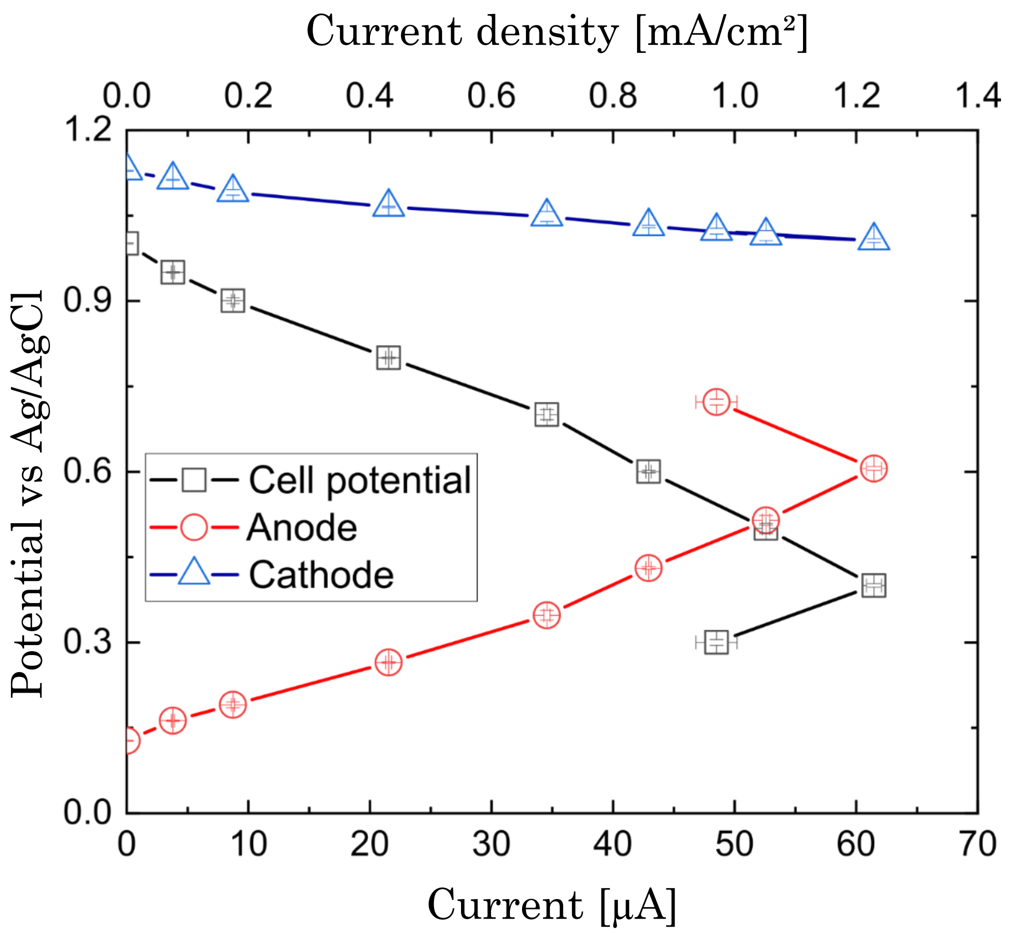
Distance between electrodes = 1 mm

Catalyst : Platinum

Cathode solution = $KMnO_4 + H_2SO_4$

Anode solution = $HCOOH + H_2SO_4$

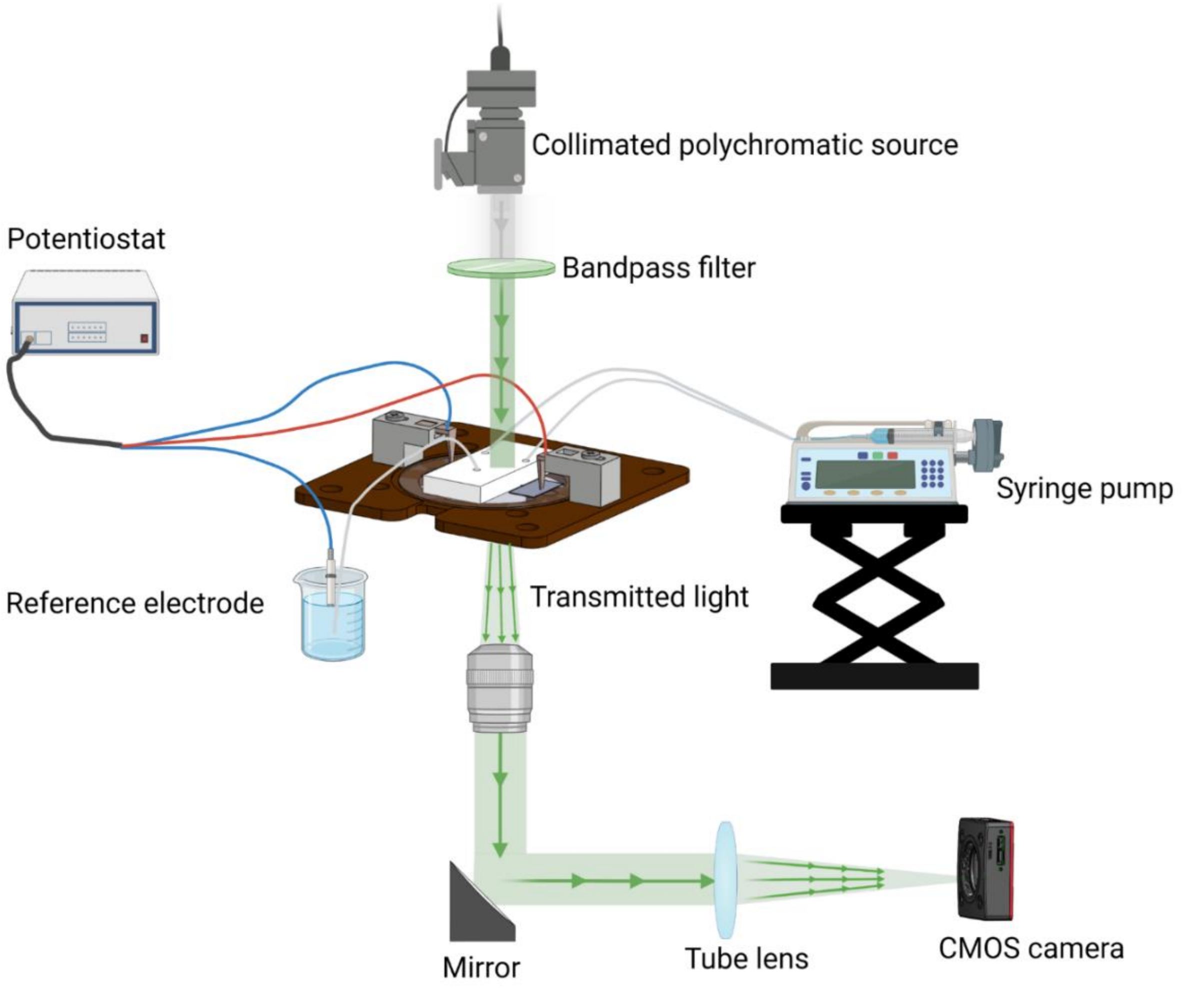
Polarization curve



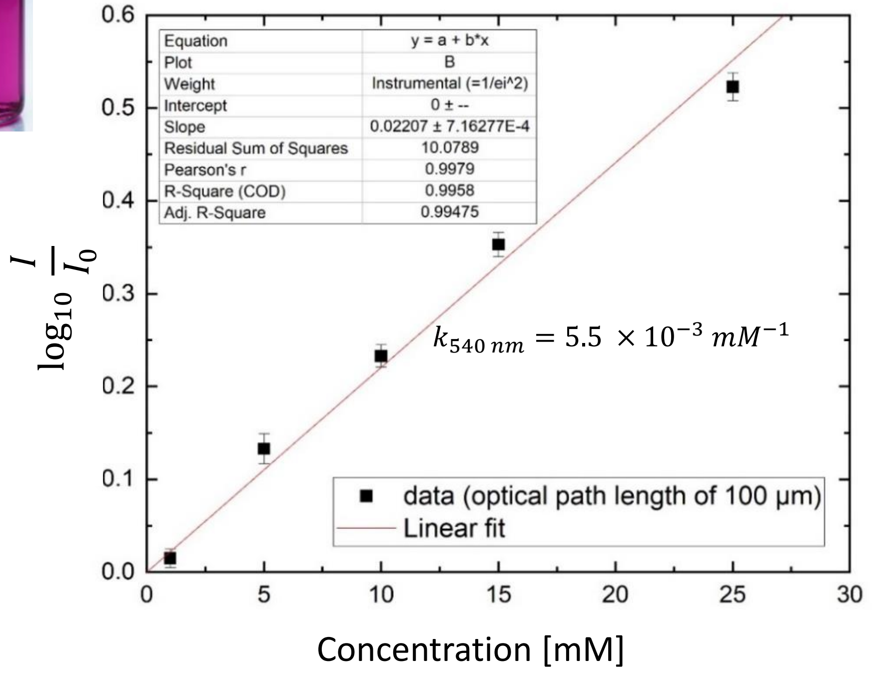
- Better performance can be found in literature
  - Reasons: geometry, catalysts, operating conditions…
- 3 electrode measurements
  - Information about cathode and anode potentials
- Anode limits the performance
  - HCOOH + platinum causes CO poisoning
- Tafel parameters could be estimated from cathode potentials

How to observe concentration variations when the cell is operating ?

Experimental setup

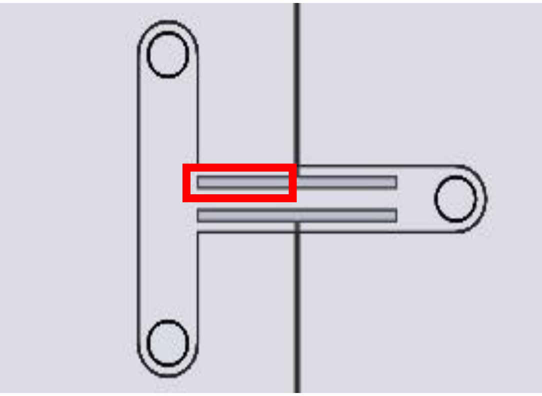


Absorption coefficient at 540 nm



Measurement of electrochemical performance + concentration fields using visible spectroscopy

Concentration fields measurements



A current of 20 µA is imposed

Total flow rate is 2 µl/min

↓

At the cathode:

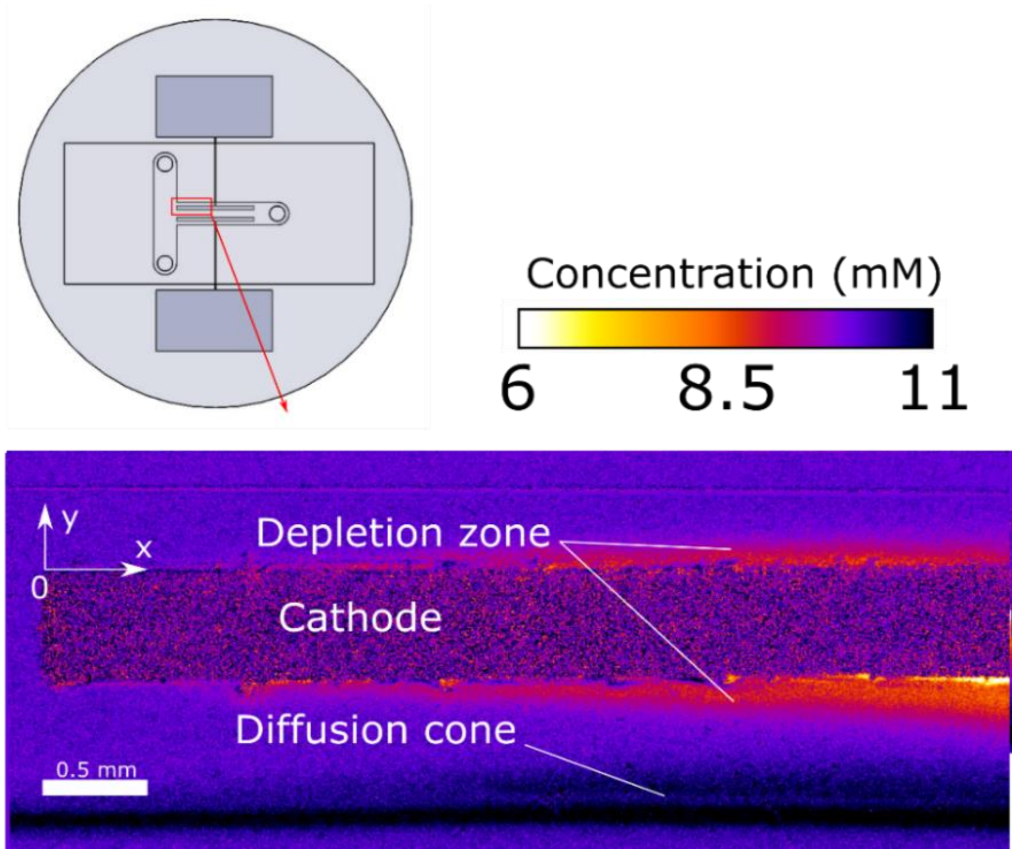
$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

↓

Concentration of $\mathbf{MnO_4^-}$ will decrease

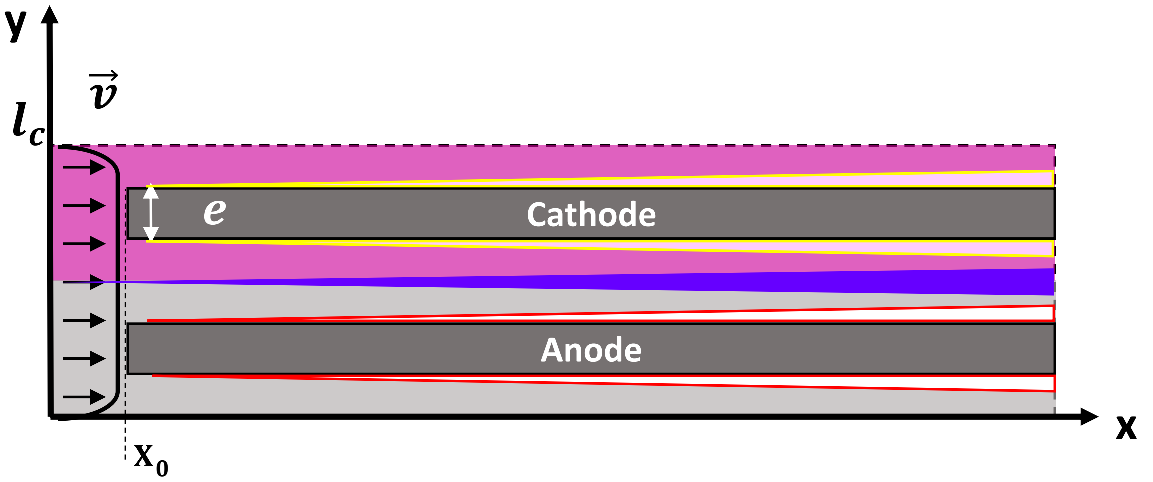
Beer Lambert law : $\Delta c(x,y) = -k_{540nm}^{-1} \ln(\frac{I_0+\Delta I}{I_0})$

Variation of the KMnO4 concentration as current is applied



Inverse method: Analytical equation

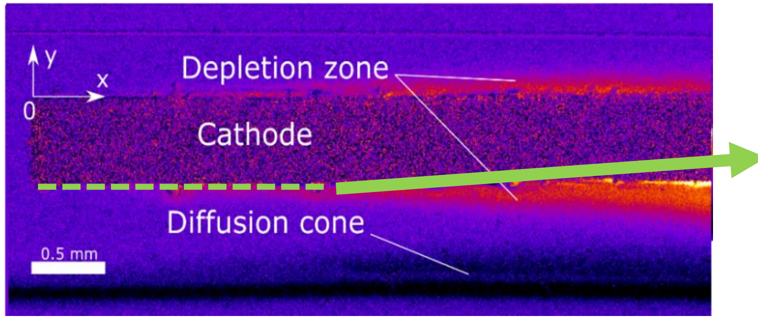
- Fast model to descibe phenomenon occuring at the cathode
  - Model can be simplified thanks to the geometry
- Hypothesis
  - High aspect ratio $\frac{l_c}{h} = 150$
    - No diffusion in the z-direction
  - Peclet number >>1 in the x-direction
    - No diffusion in the x-direction
  - Constant velocity
  - Semi-infinite in the y direction
  - Symetry of the reaction
    - We consider model one side of the electrode

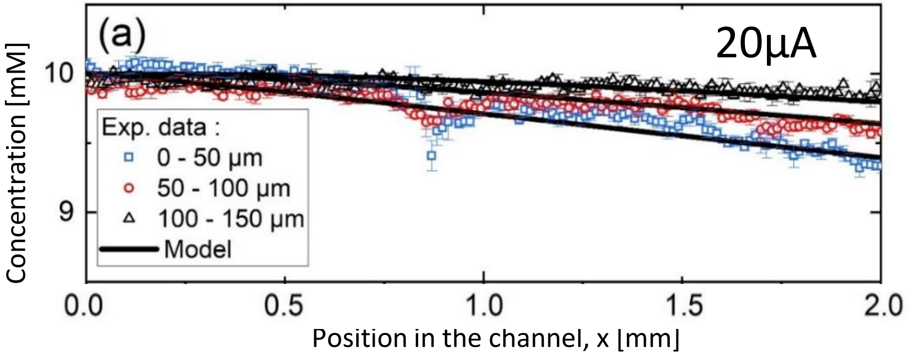


$$c(x,y) = \int_0^x c_e(x-x_0)\sqrt{\frac{\delta(y)}{\pi\, x_0^3}}\exp\left(-\frac{\delta(y)}{x_0}\right)\mathrm{d}x_0\,,\quad \forall y > \frac{e}{2}\quad \text{With}\quad c_e(x) = \mathcal{L}^{-1}\left\{\frac{-k_0}{p\, h\, D\, \alpha_2}\,\frac{e^{\alpha_1 \frac{e}{2}}\tanh(\alpha_2 \frac{e}{2})}{\alpha_1 + \alpha_2 \tanh(\alpha_2 \frac{e}{2})}\right\}\ \text{and}\ \delta(y) = \frac{v\, y^2}{4\, D}$$

Results

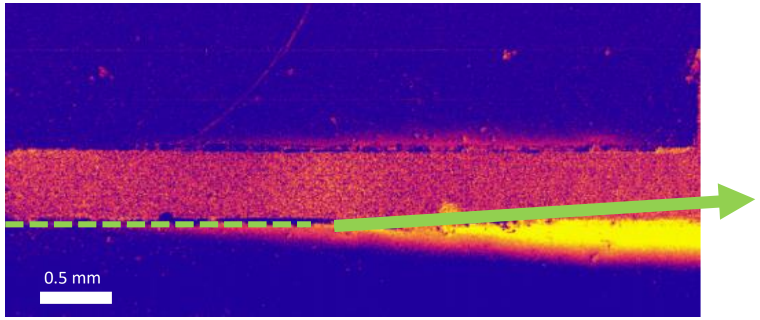
- Estimation of D and k_0
  - Minimization algorithm: Find the optimum D-k_0 to minimize the error between the model and the experimental data

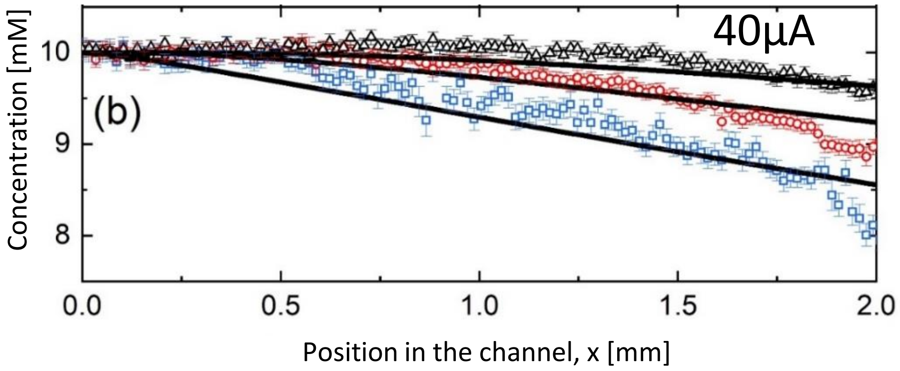




$D = (5.5 \pm 2.5) \times 10^{-3}$ mm²/s

$k_0 = (0.9 \pm 0.1) \times 10^{-3}$ mm/s





$D = (3.7 \pm 0.5) \times 10^{-3}$ mm²/s

$k_0 = (2.4 \pm 0.1) \times 10^{-3}$ mm/s

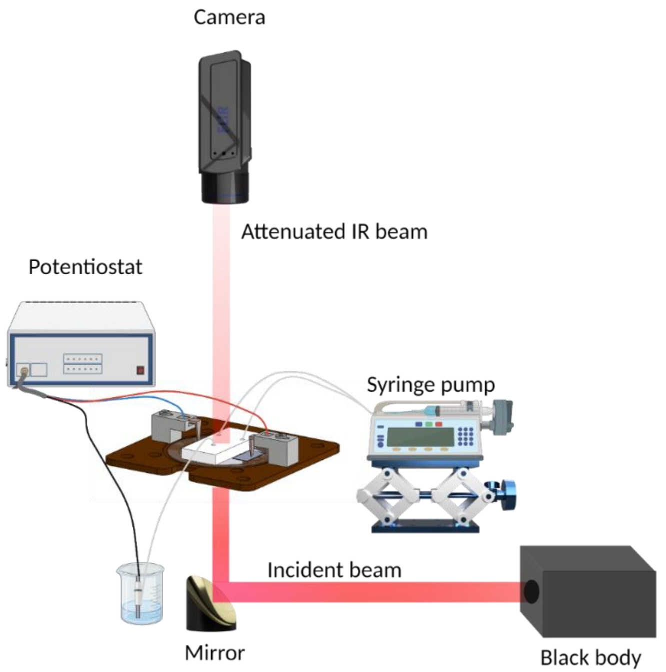
D is not in the range expected
Poor sensitivity on D

Still a convergence to a global minimum
k_0 increases with increasing current

Conclusion and perspectives

- First measurements of reactant concentration variation via operando imaging
  - Development of a MFC adapted for a visible light imaging platform
  - The MFC performance is good enough to measure concentration gradients along the electrode
- Platform to characterize mass and charge transfer
  - New perspective for the characterization of MFC
- Publication : https://doi.org/10.1016/j.electacta.2023.142489

- Improve the model validity
  - Determine D prior to k_0
- Change the anode catalyst
- Study other chemicals
- Use IR spectroscopy to study mass transfer at the anode



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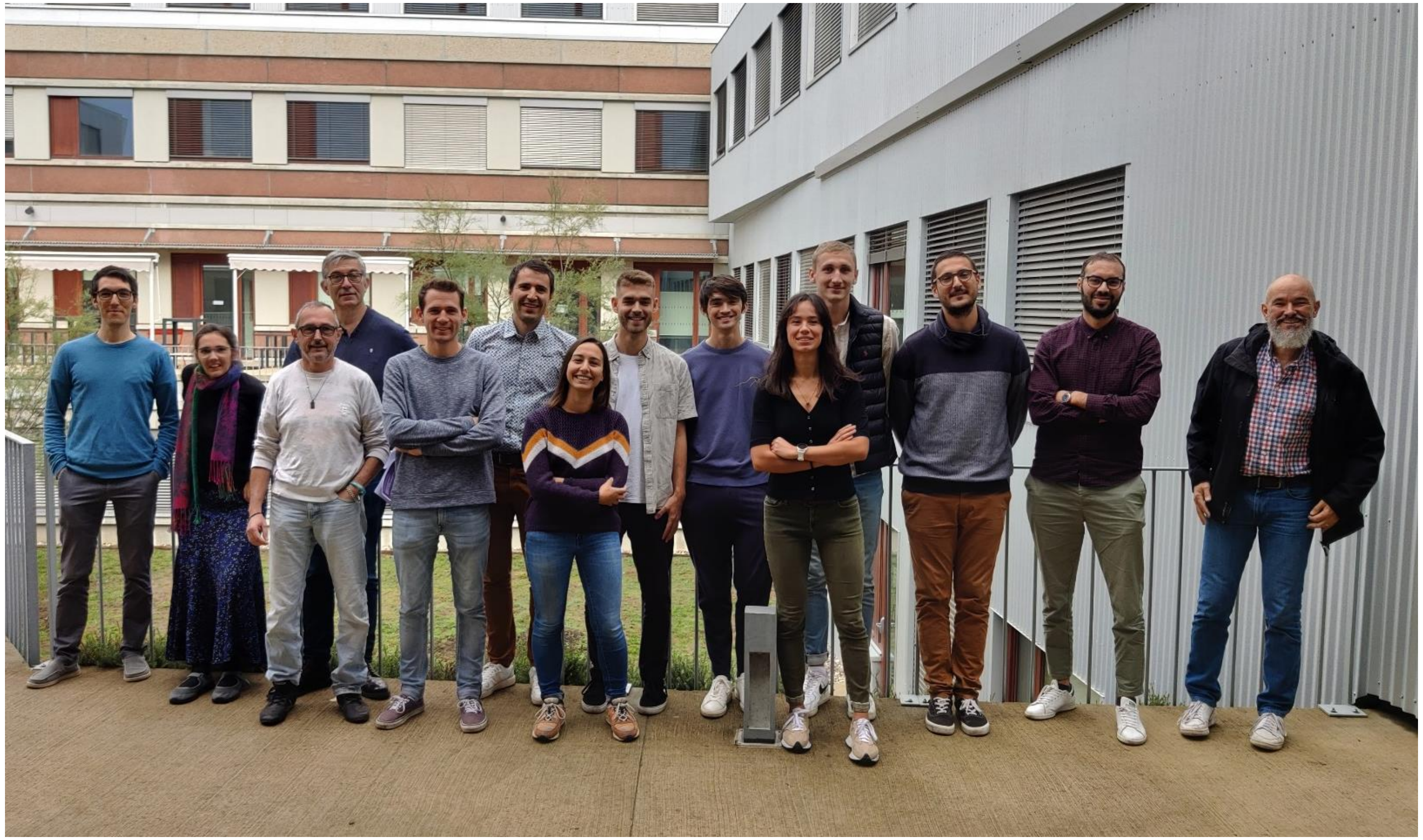

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Model

- Fast model to descibe phenomena occuring at the cathode
  - Solve the equation system in steady state
    - Fick's law for mass diffusion
    - Tafel equation for electrochemical reactions

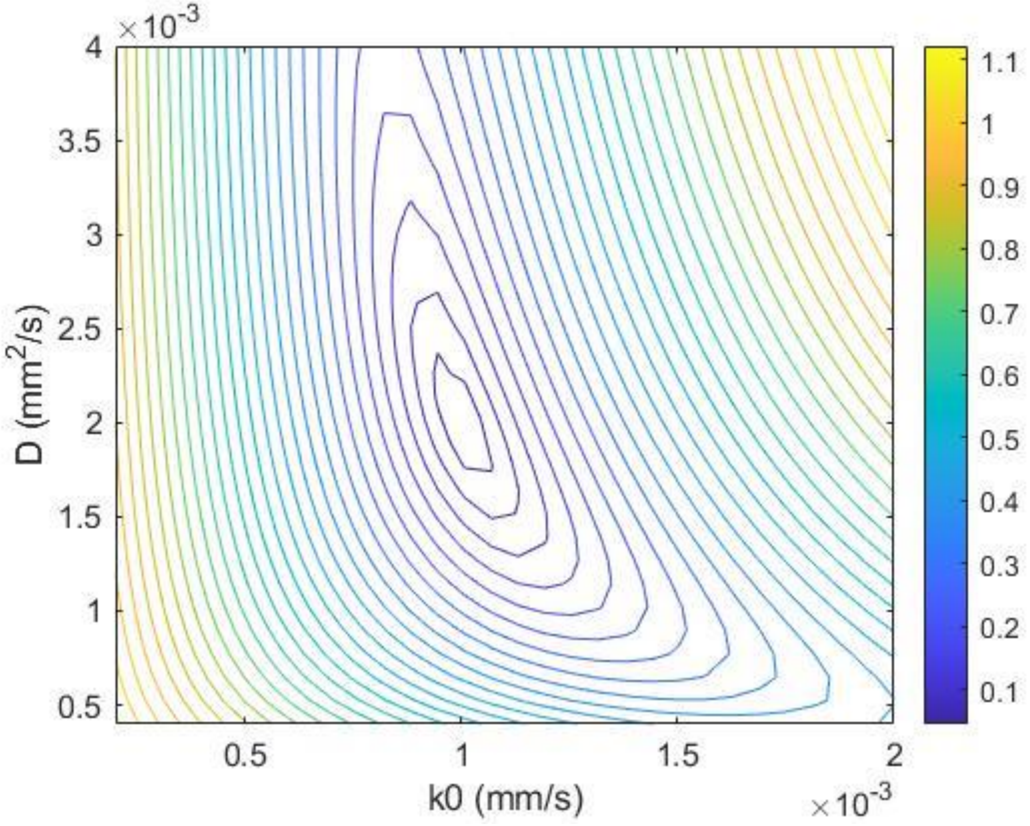
$$\nabla.(v_x\, c) = D\, \nabla^2 c$$

$$\left.\frac{\partial c}{\partial y}\right|_{y=0,l_c} = \left.\frac{\partial c}{\partial y}\right|_{z=h} = 0$$

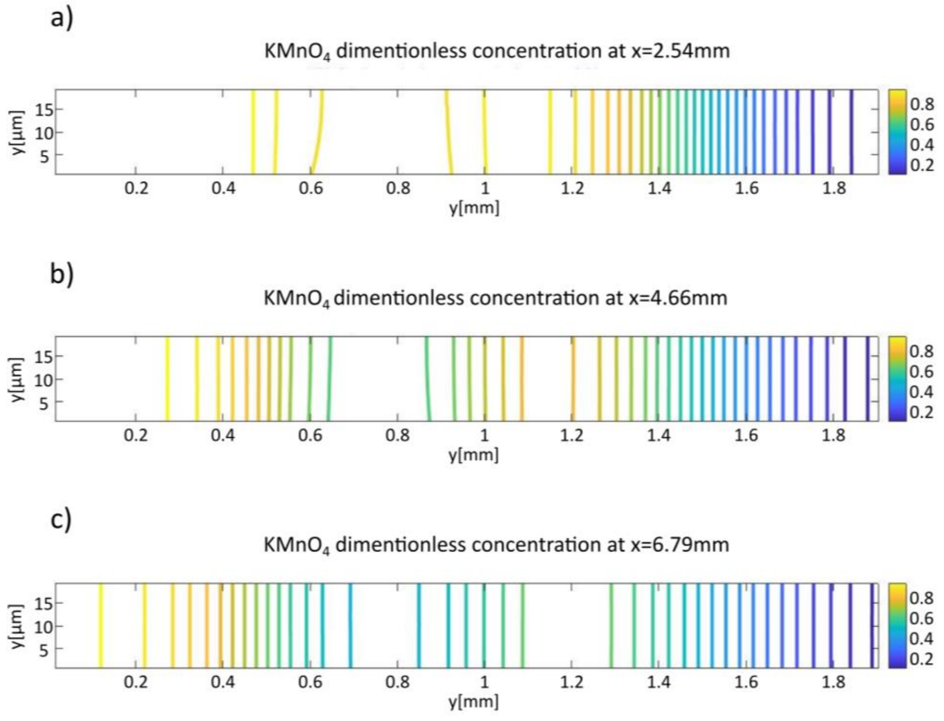
$$-D \left.\frac{\partial c}{z}\right|_{z=0} = -\frac{j(x,y)}{n_e\, F} = c(x,y,z=0)\,\frac{i_0\, \exp(\frac{\eta}{b})}{c_0\, n_e\, F}$$

$$c(x=0,y,z) = c_0(y)$$

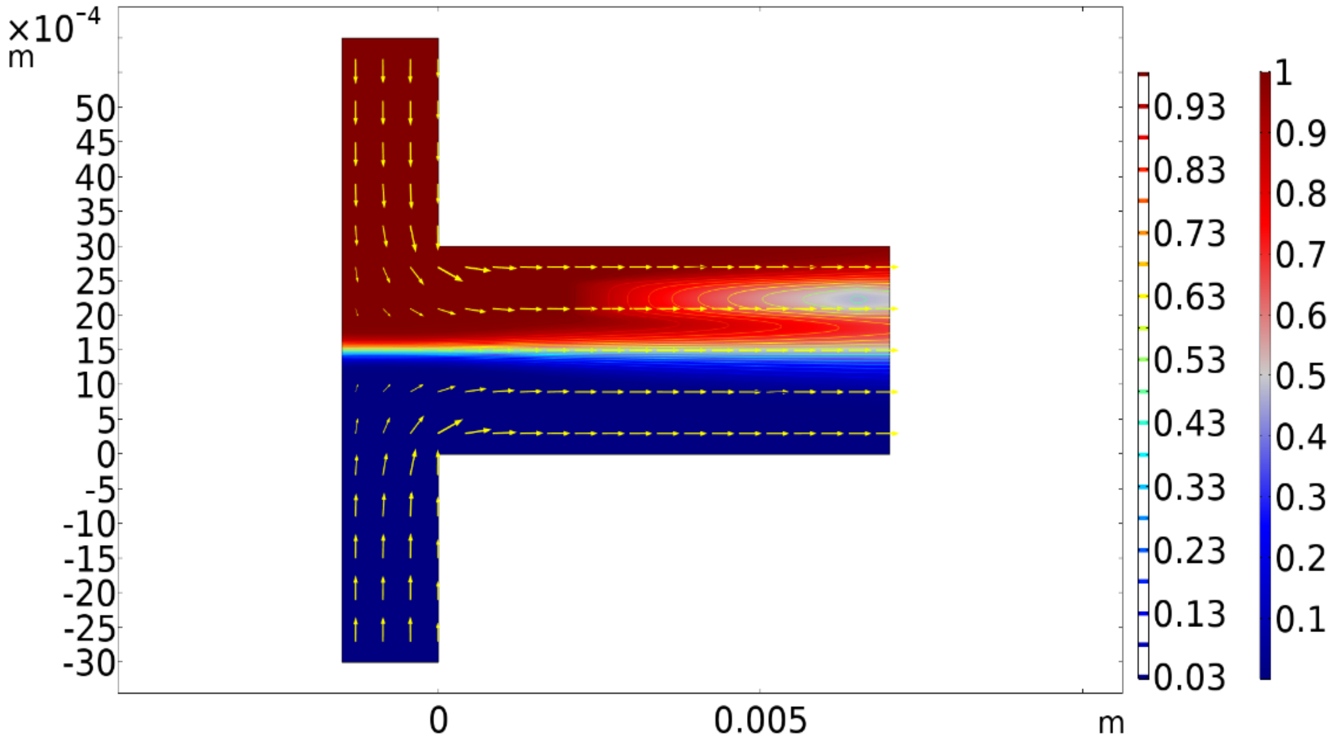
Parametric study



Model details



Concentration profiles in the z-direction



Concentration fields

Variation of MnO_4^- concentration as current is applied