A comprehensive COMSOL Modeling for the solar-driven CO_2 electroreduction to CO

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PON RICERCA E INNOVAZIONE 2014 - 2020

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Outline

Introduction

Circular economy and CO_2RR

Artificial Leaf

Introduction on the existing device and results

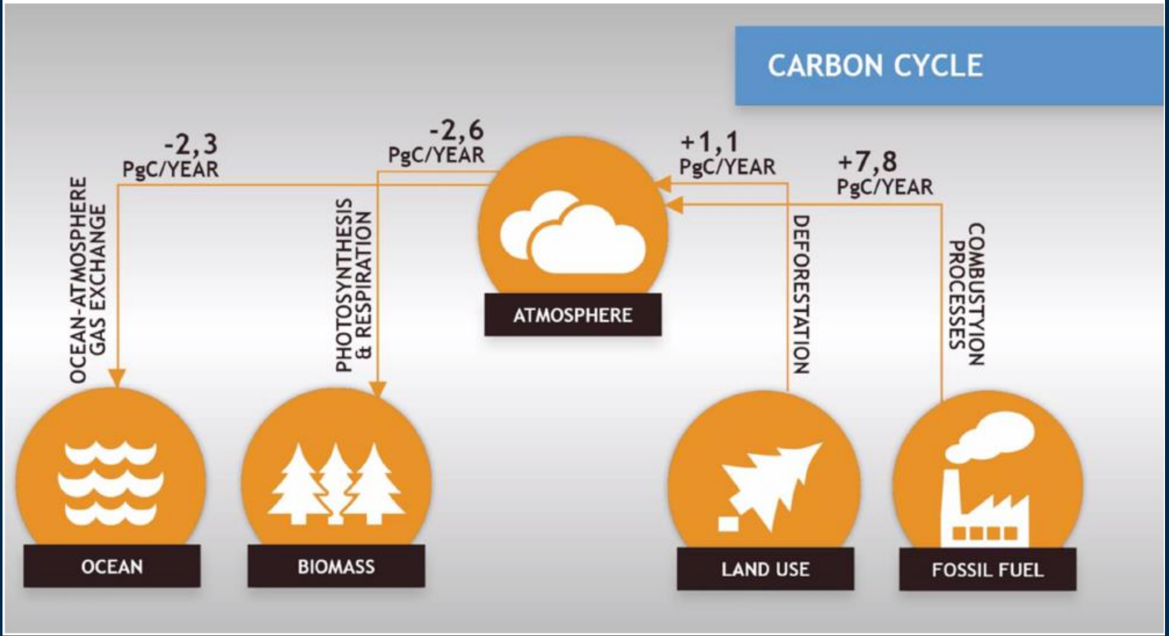
COMSOL Model

Mathematical model for the physical study of the electrochemical reactor.

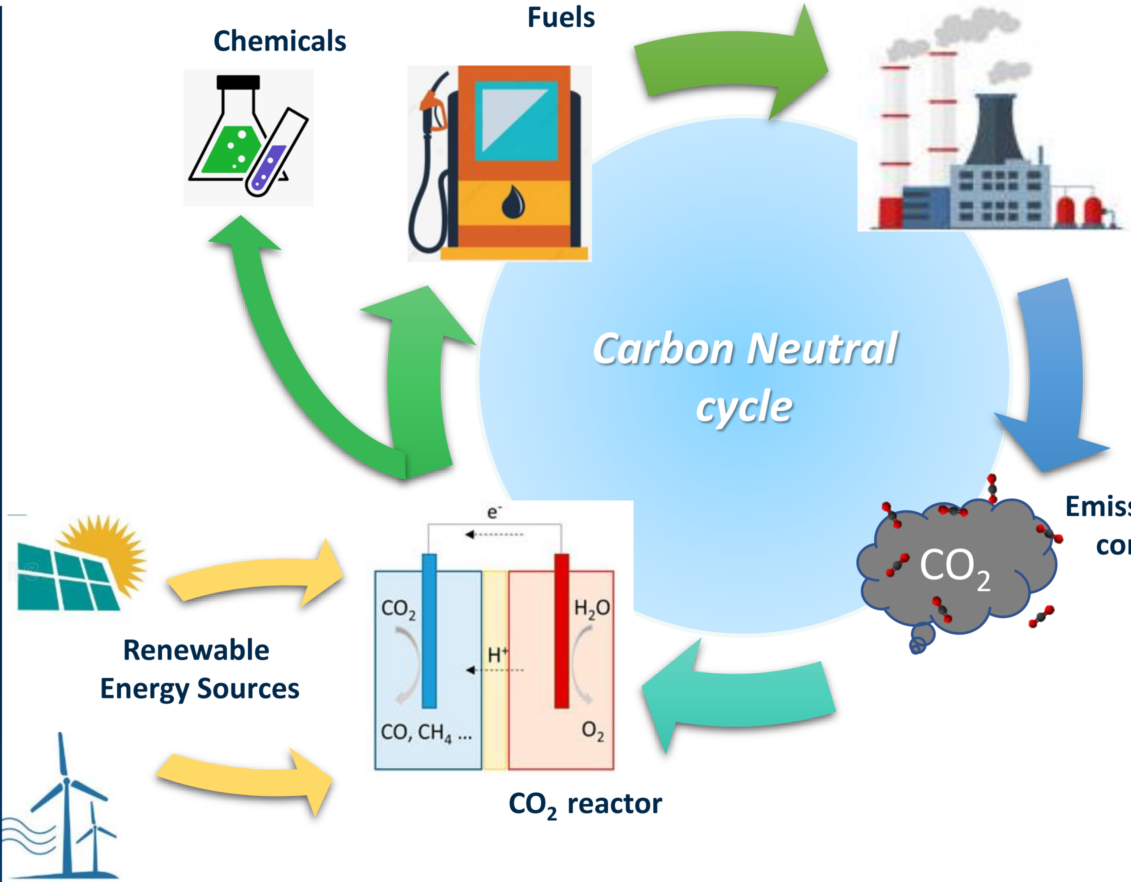
Conclusions

Conclusions and brief hint about the perspectives of the future works

Introduction

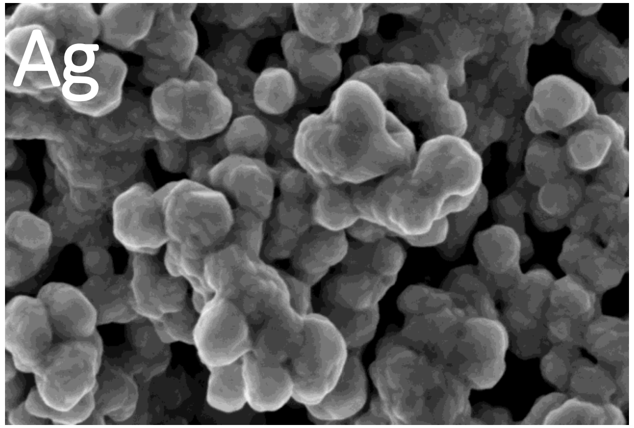


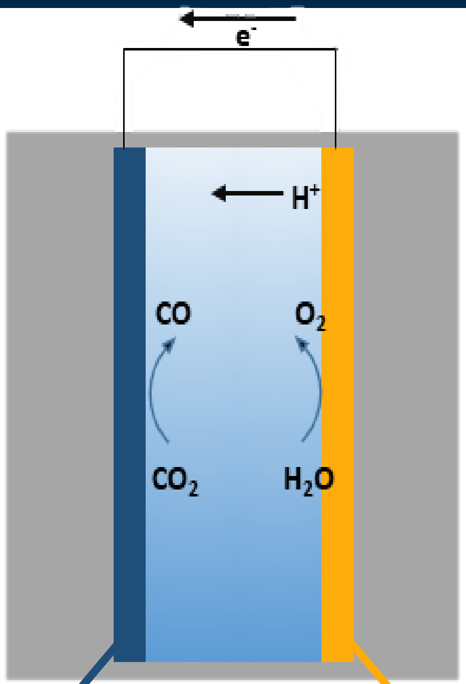
Positive net balance of carbon in atmosphere



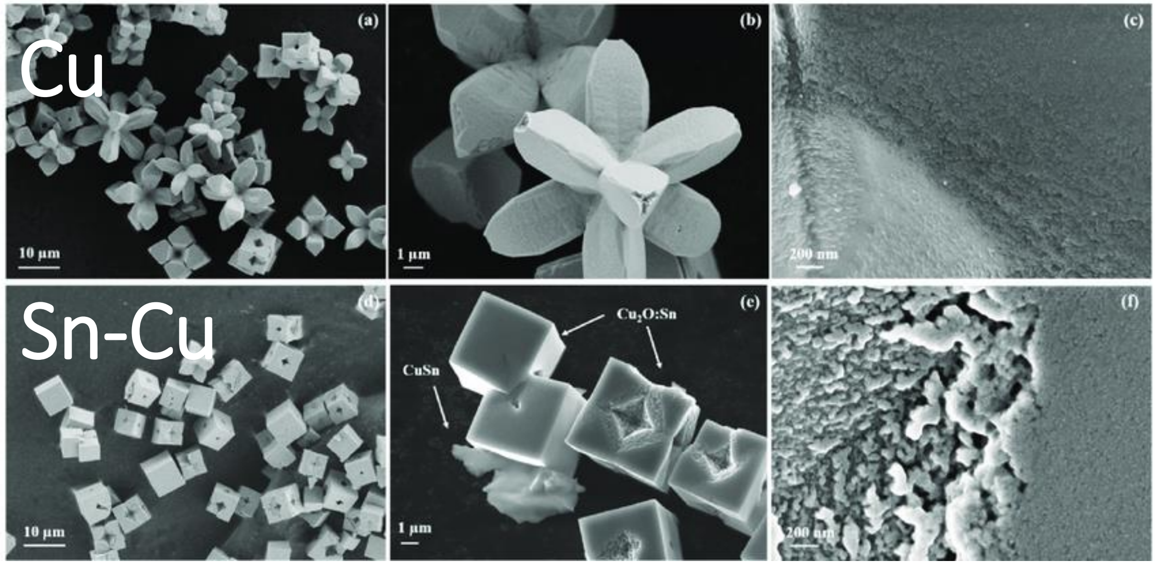
Carbon neutrality achieved by the transformation of CO_2 into valuable products, such as, Carbon monoxide (CO), Formic Acid ($HCOOH$). Methanol (CH_3OH), Methane (CH_4),Ethylene (C_2H_4) ...

Introduction





Zeng et al, Catalysts 2021



Cathode

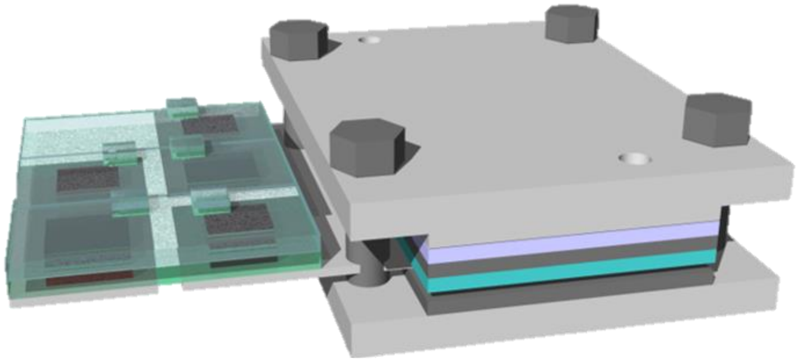
$$\left.\begin{array}{l} CO_2 + 2H^+ + 2e^- \rightarrow \boldsymbol{CO} + H_2O \\ CO_2 + 8H^+ + 8e^- \rightarrow \boldsymbol{CH_4} + 2H_2O \\ 2CO_2 + 12H^+ + 12e^- \rightarrow \boldsymbol{C_2H_4} + 4H_2O \\ [\ldots] \end{array}\right\} \text{CO}_2\text{RR}$$

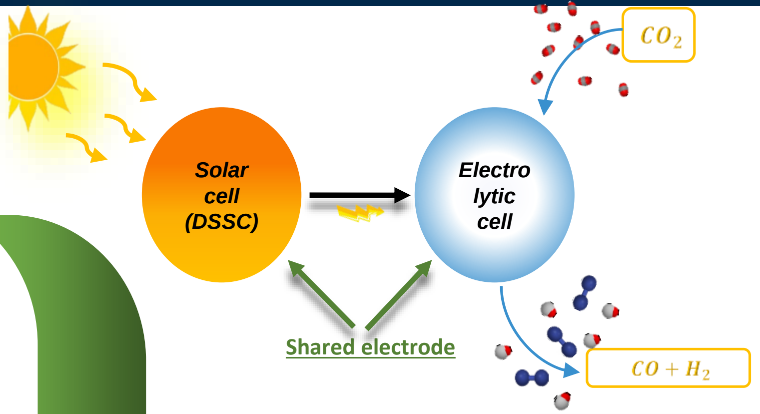
$$2H^+ + 2e^- \rightarrow H_2 \quad \} \text{ HER}$$

Anode

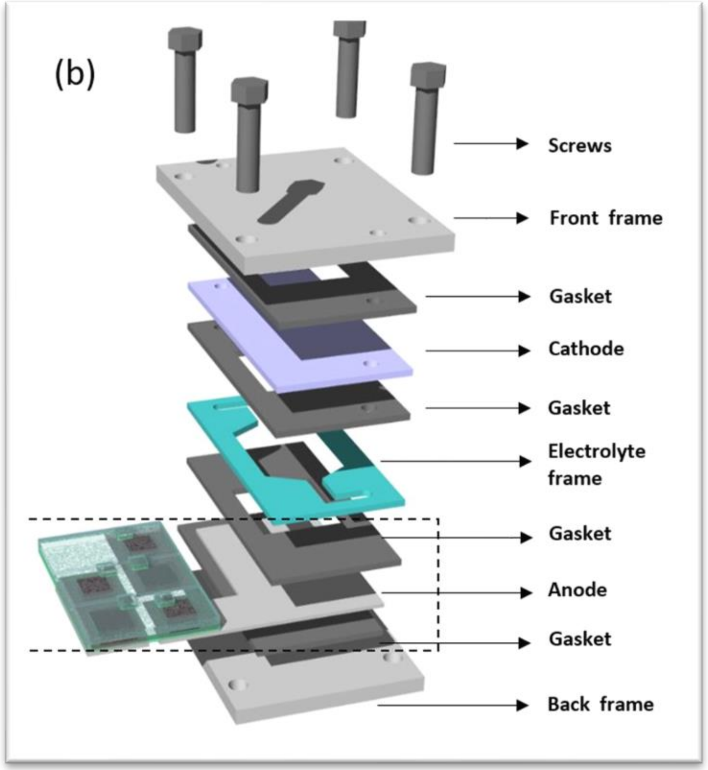
$$2H_2O \rightarrow 2H^+ + \tfrac{1}{2}O_2 + 2e^- \quad \} \text{ OER}$$

Artificial Leaf project





Sacco et al, Sust. Chem. Eng. 2020



- Dye-sensitized solar cells
- **Pt** cathode
- TiO_2 photo-anode

- Electrolytic batch cell
- Ag NPs cathode
- **Pt** anode

Overall Reactions

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

Cathode: $CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$

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

COMSOL Simulation: **WHY**?

Predict chemical conditions in:

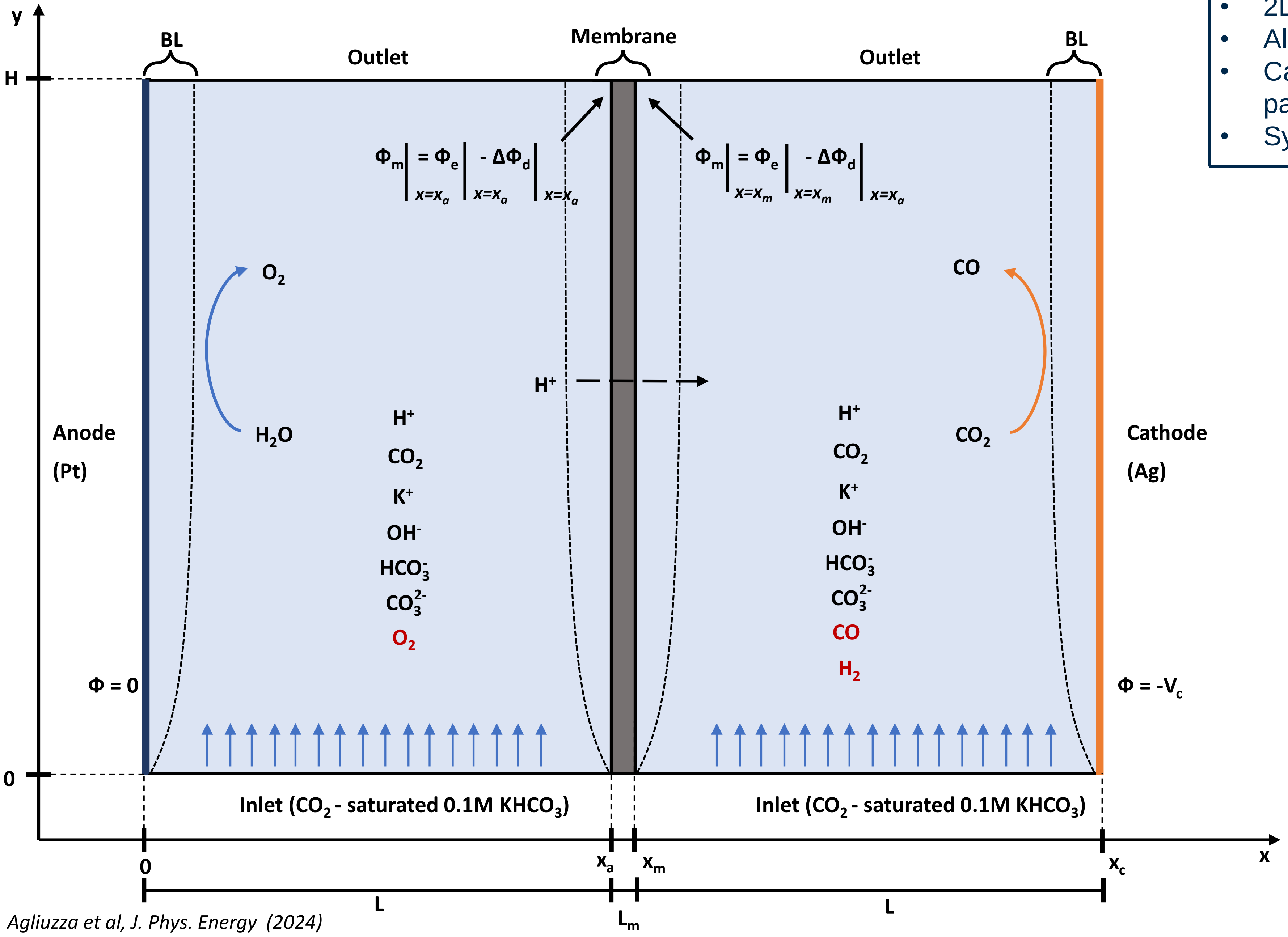
- boundary layers at interfaces
- bulk

Predict performance of the device

Lead the scaling-up process of the electrochemical reactor

<u>Before prediction, the model is validated through experimental results</u>

EC Model: highlights



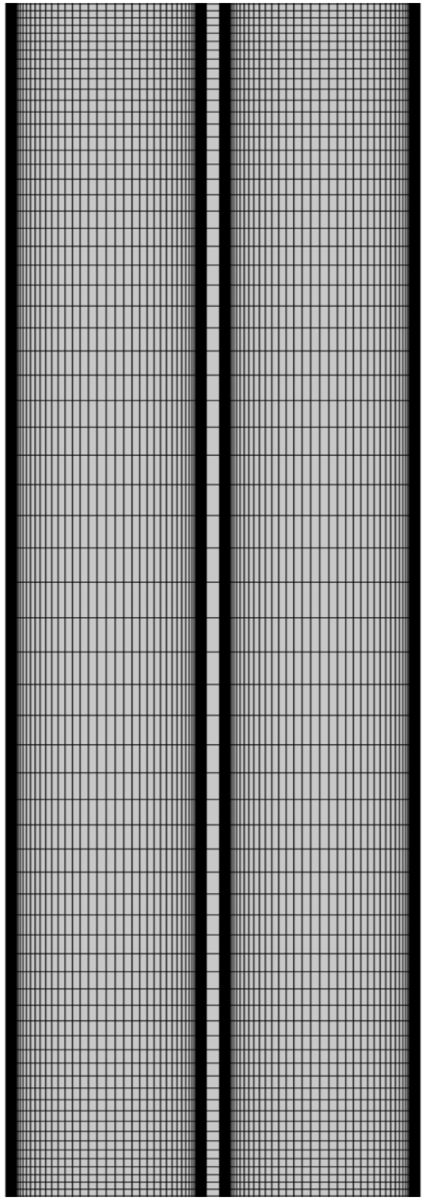
Assumptions

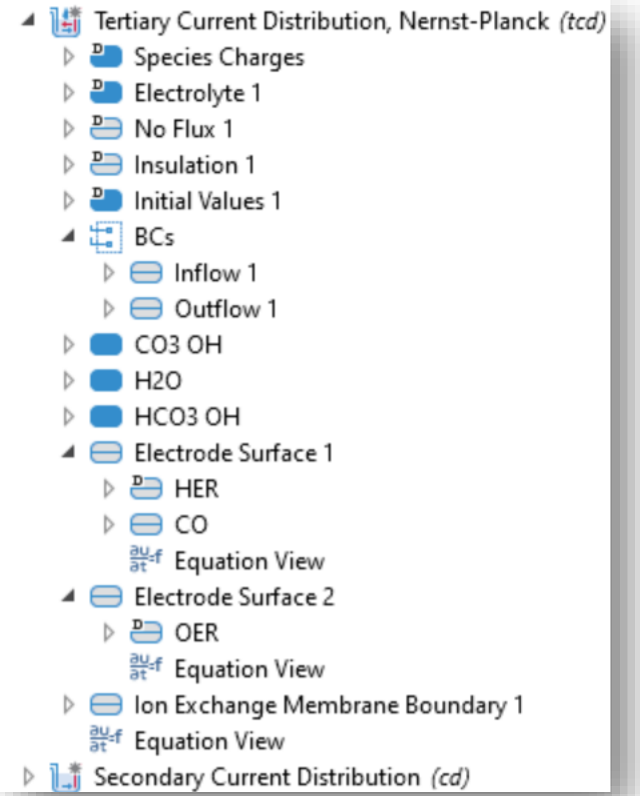
- 2D model
- All products and species remain in liquid phase
- Catalysts are simulated through their kinetic parameters
- System is isothermal @ ambient T°

- Recirculation through inlets/outlets
- Membrane is implemented as fixed space charge
- Stationary conditions are investigated

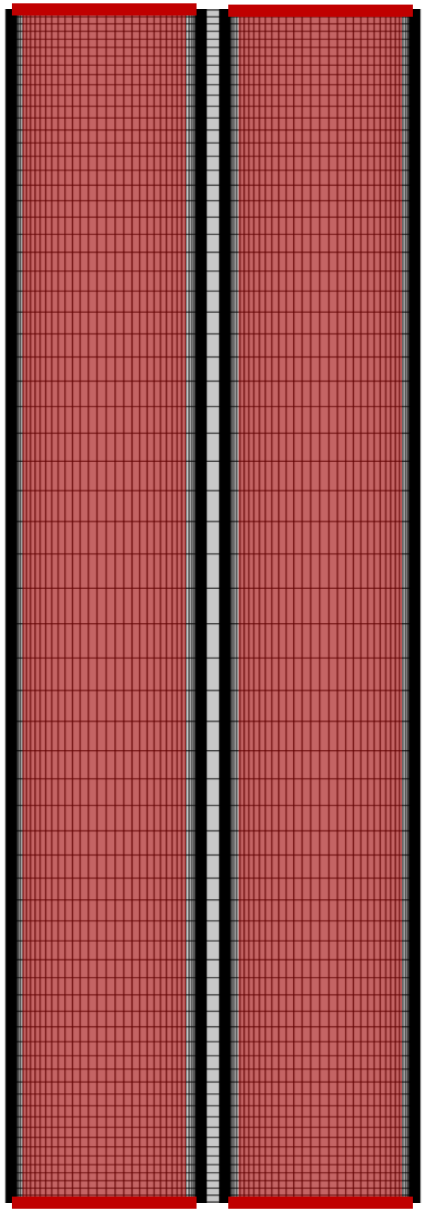
Agliuzza et al, J. Phys. Energy (2024)

Model: main equations





Anode – Cathode domains



Tertiary Current Distribution (TCD) – Electrochemistry module

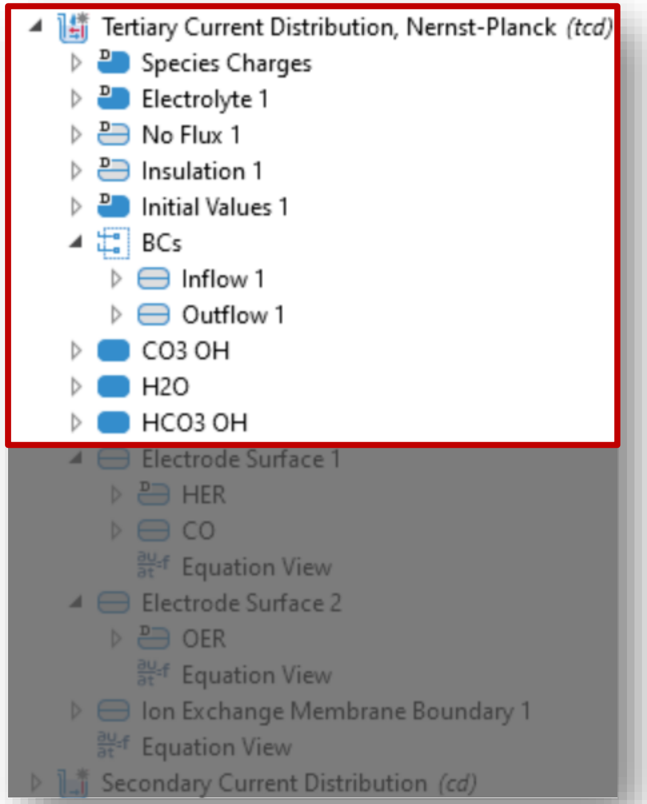
- ***Current distribution***

Nernst-Planck Equation: $N_i = \underbrace{-D_i \nabla c_i}_{\text{diffusion}} - \underbrace{z_i u_{m,i} F c_i \nabla \phi_l}_{\text{migration}} + \underbrace{c_i u}_{\text{convection}}$

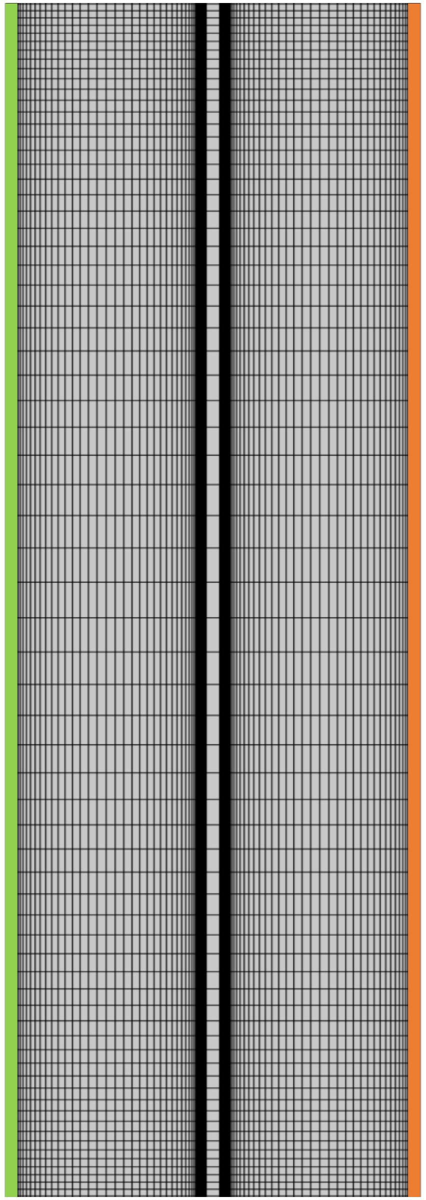
- ***Equilibrium reactions***

$$CO_2 + OH^- \leftrightarrow HCO_3^-$$
$$HCO_3^- + OH^- \leftrightarrow CO_3^{2-} + H_2O$$
$$H_2O \leftrightarrow OH^- + H^+$$

- ***Inflows/Outflows***



Anode – Cathode boundaries



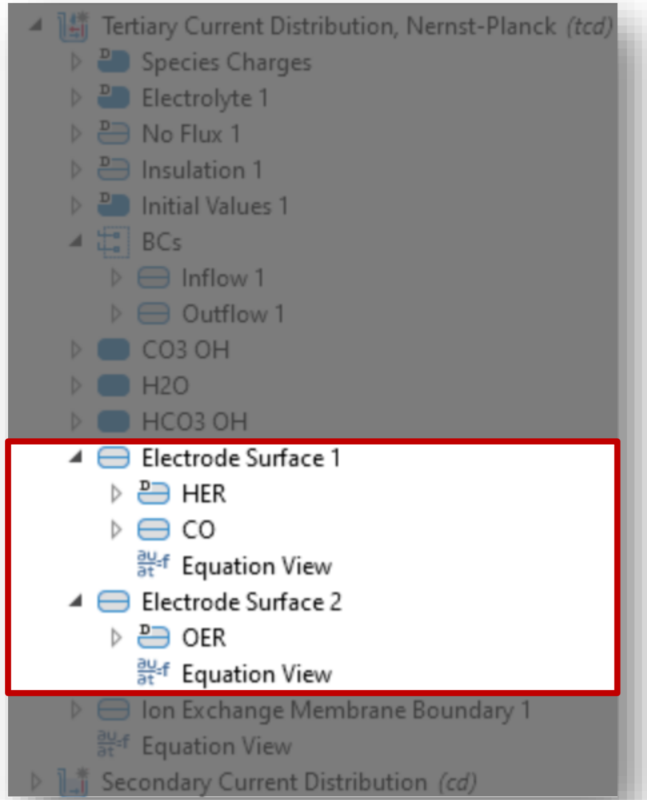
Tertiary Current Distribution (TCD) – Electrochemistry module

- ***Kinetics***

Butler-Volmer Equation: $$j_{partial} = j_0\left[C_R exp\left(\frac{\alpha_a F}{RT}\eta\right) - C_{Ox} exp\left(-\frac{\alpha_c F}{RT}\eta\right)\right]$$

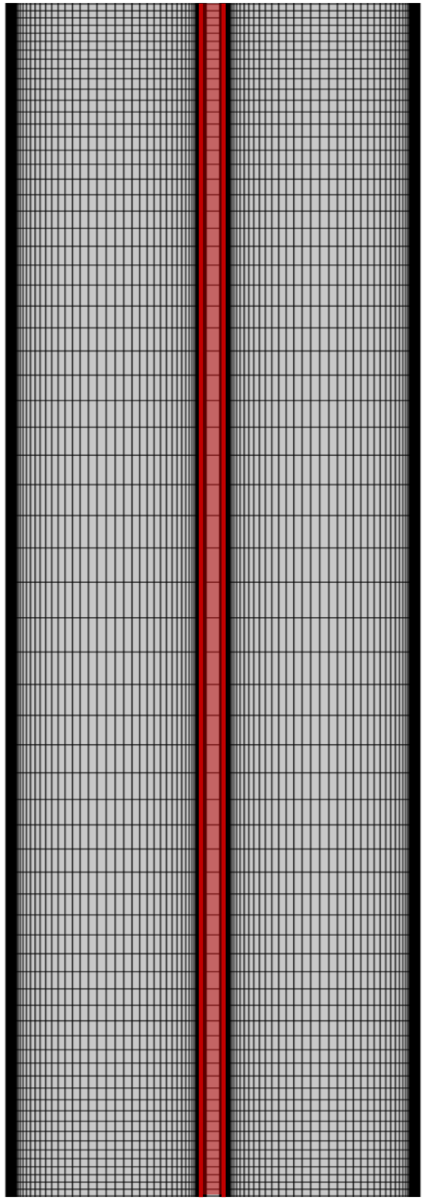
- ***Electrochemical reactions***

(■) $CO_2 + H_2O + 2e^- \rightarrow \mathbf{CO} + 2OH^-$	CO_2RR
(■) $2H^+ + 2e^- \rightarrow \mathbf{H_2}$	HER
(■) $4H_2O \rightarrow 4H^+ + \mathbf{O_2} + 4e^-$	OER



Membrane Domain

Secondary Current Distribution (CD) – Electrochemistry module



- ***Ohm's Law***

No significant concentration gradients are expected in the membrane

$$i_m = -\sigma_m \Delta\phi_m$$

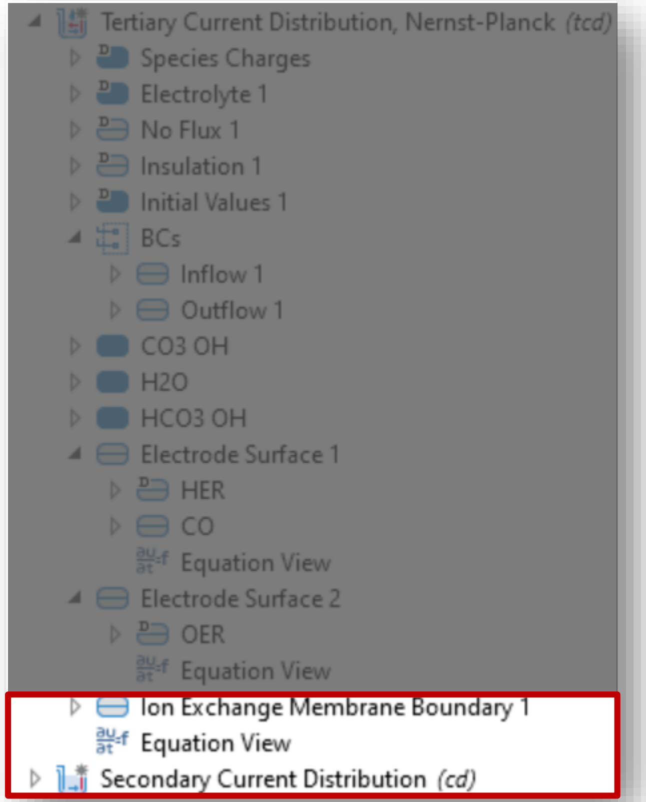
$$N_{H^+} = \frac{i_m}{F}$$

- ***Donnan potential***

Required to let TCD and CD interfaces interact

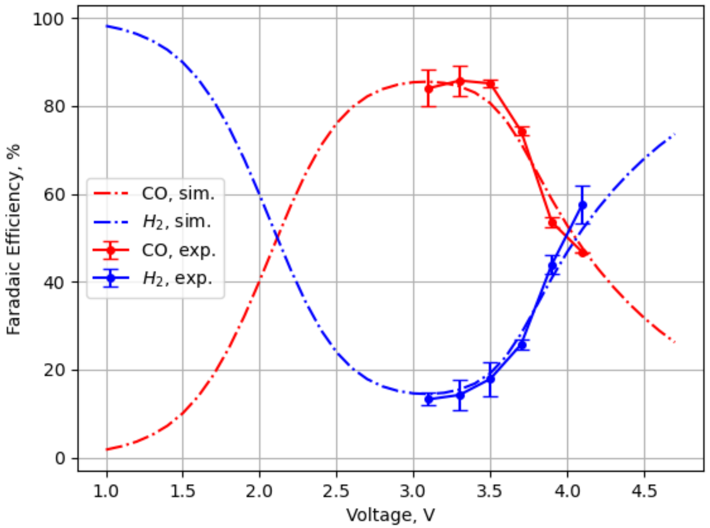
$$\phi_m = \phi_e - \phi_d$$

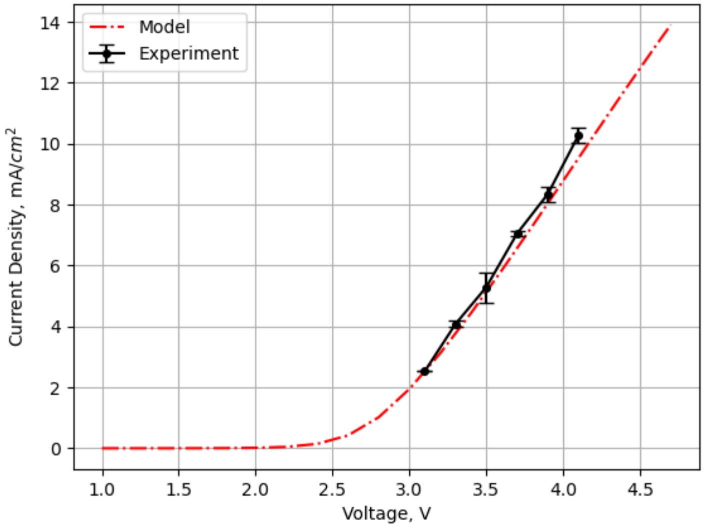
$$\Delta\phi_d = \frac{RT}{F} ln\left(\frac{[H^+]}{c_m}\right)$$



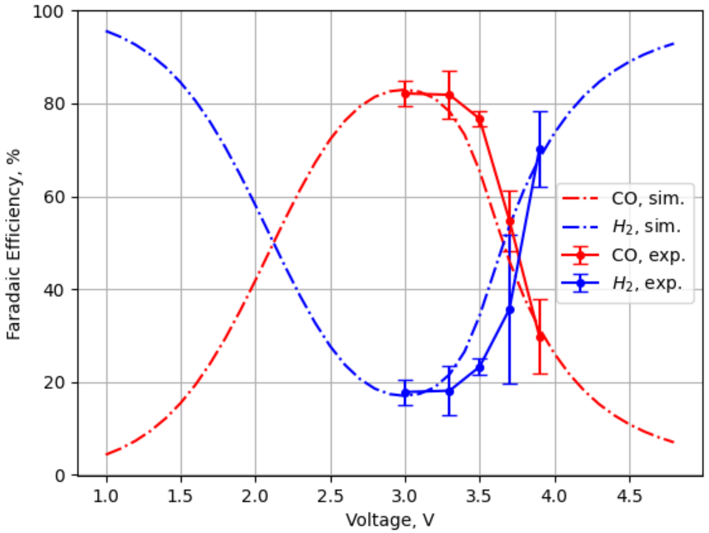
Results #1: Cell length L

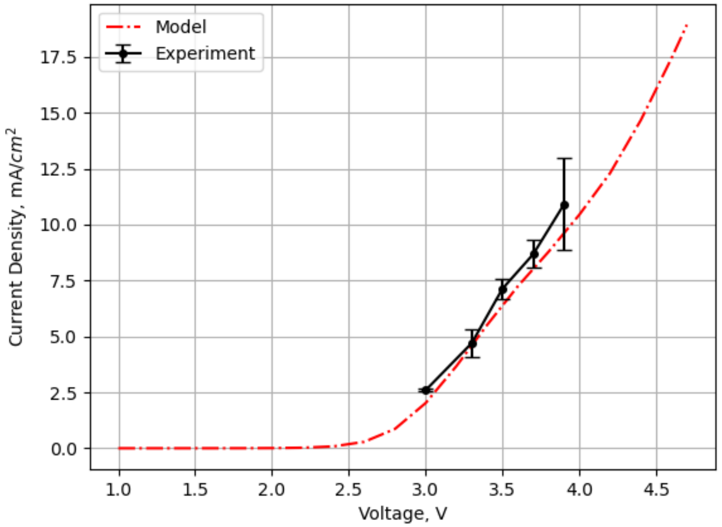
L=0.6 cm



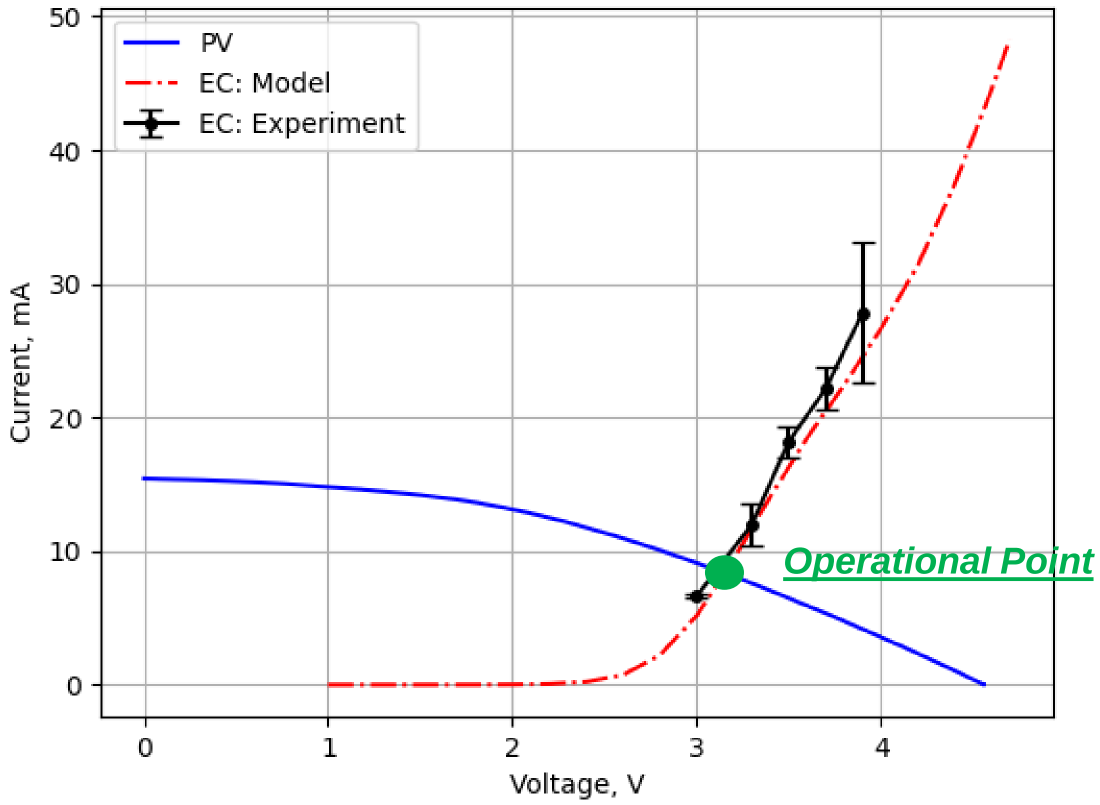


L=0.25 cm





Solar-driven CO_2 reduction: Experiment



Power matching requires a suitable match between the voltage-current points of both PV and EC modules.
The PV is made of a module of 6 Dye-Sensitized Solar Cells

- I_{op}=8.6 mA (approx. 3.4 mA/cm2)
- V_{op}=3.1 V
- FE_{co} = 82% , FE_{H2} = 18%

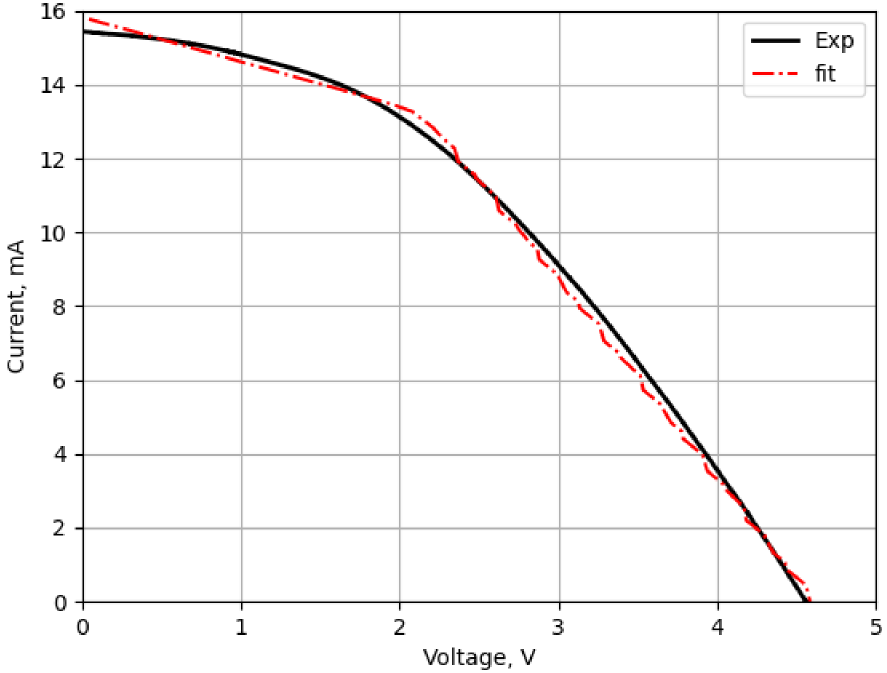
$|_{op}$ $|_{op}$

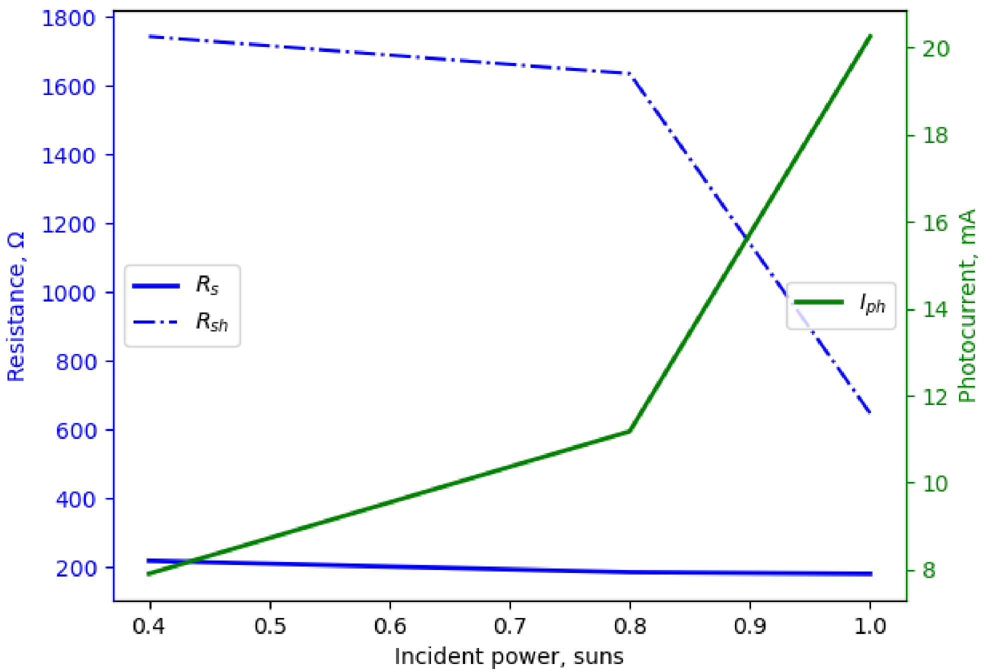
Solar-driven CO_2 reduction: Model

Step 1: Define the mathematical model for the solar cell

$$I = I_{ph} - I_0 \left[exp\left(\frac{V + IR_s}{nV_t} \right) - 1 \right] - \frac{V + IR_s}{R_{sh}}$$

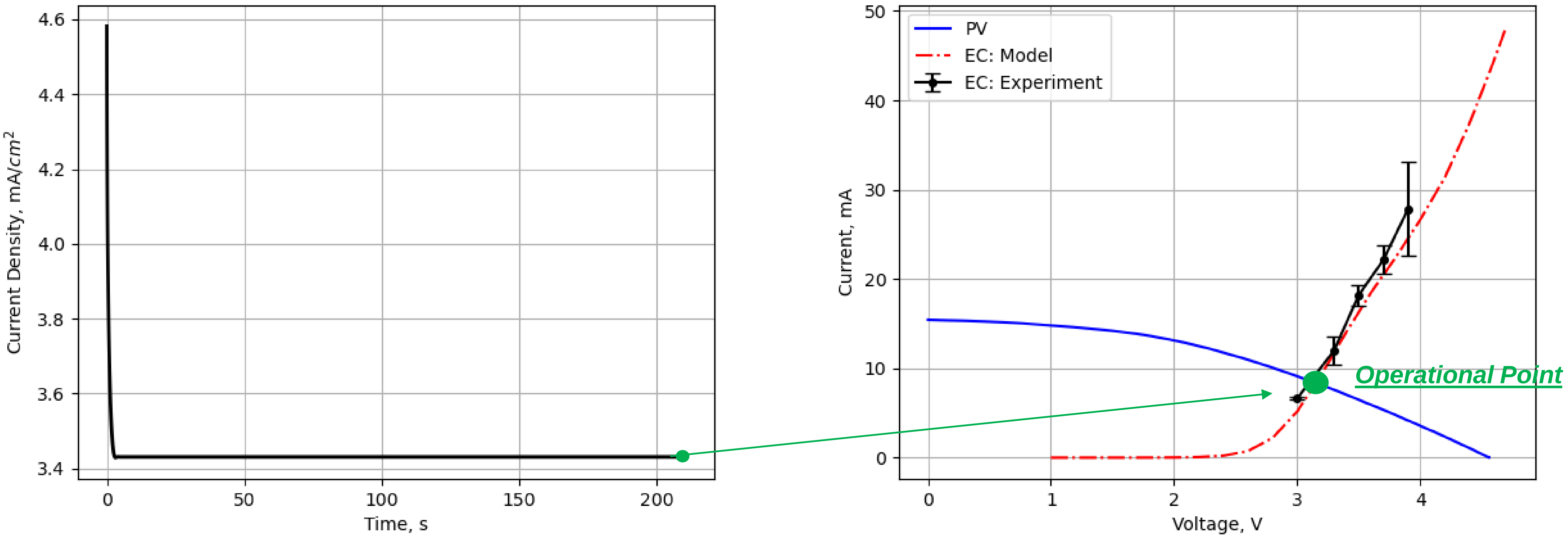
Step 2: Fit the experimental data and retrieve the parameters



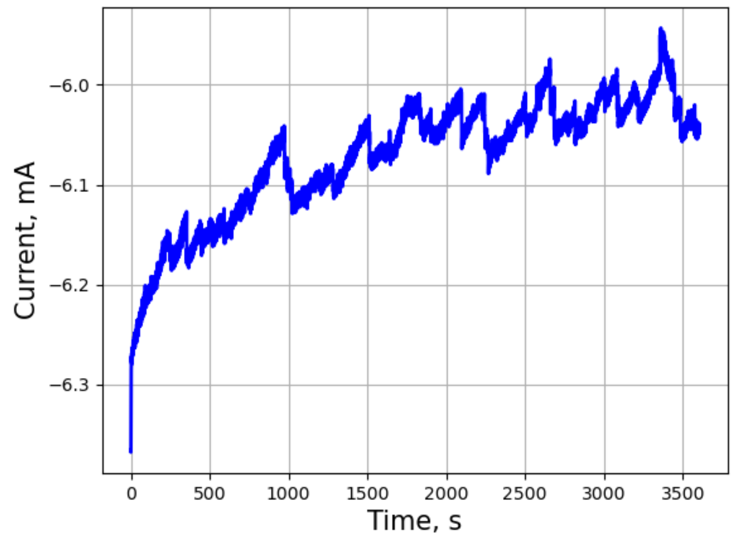


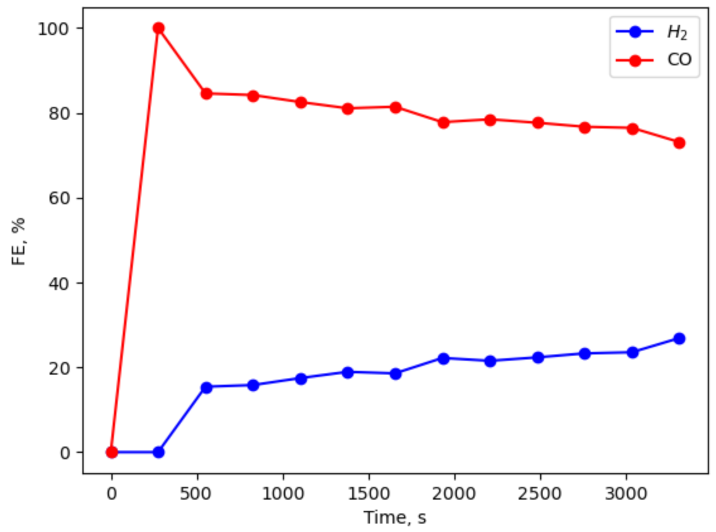
Solar-driven CO_2 reduction: Model

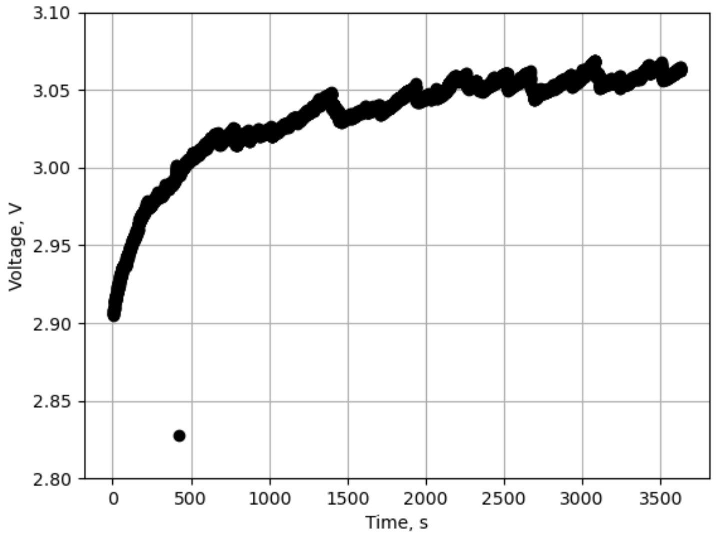
Step 3: implement the mathematical equation in COMSOL and perform the time-dependent simulation

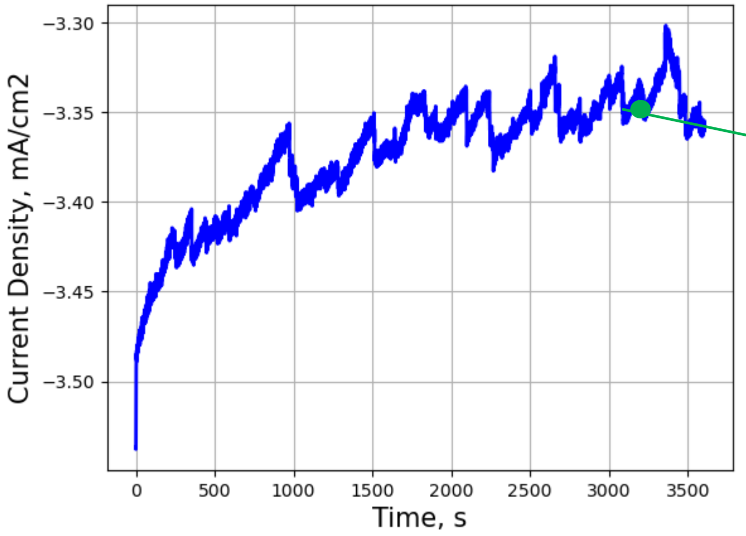


Solar-driven CO_2 reduction: first results









Approx. J=3.35 mA/cm2

(J_{model}=3.4 mA/cm2)

Conclusions and Future Perspectives

- A comprehensive model for the CO_2 electro-reduction is proposed, validated through experimental results
- The photovoltaics module is implemented through its governing equation
- More complex electrochemical cells will be implemented (e.g. Flow Cells)
- Optimize the model to be predictive for PV-EC performance under different incident light conditions (*e.g.* cloudy weather)

Thank you for your attention!

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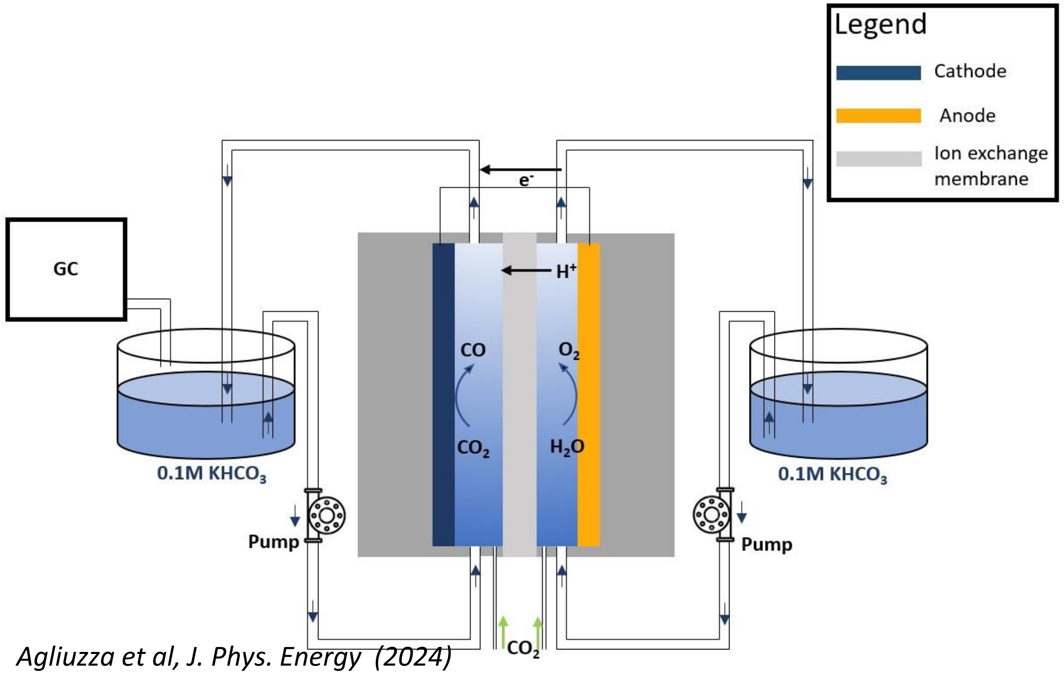
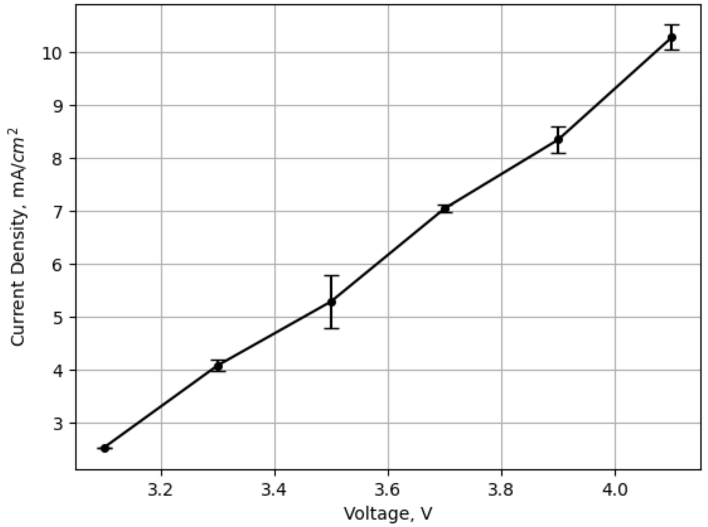
Experimental set-up

- Batch cell + electrolyte recirculation
- Catalyst: Ag NPs
- Electrolyte: 0.1M $KHCO_3$
- L_1= 1.2 cm ; L_2=0.5 cm
- Nafion membrane

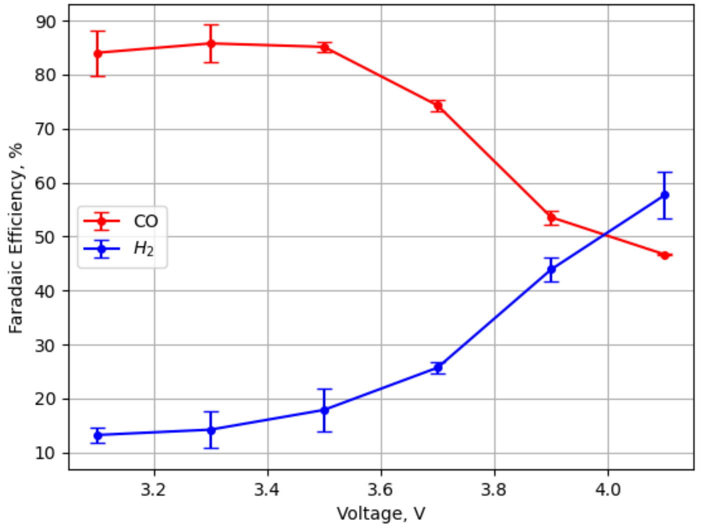


Agliuzza et al, J. Phys. Energy (2024)

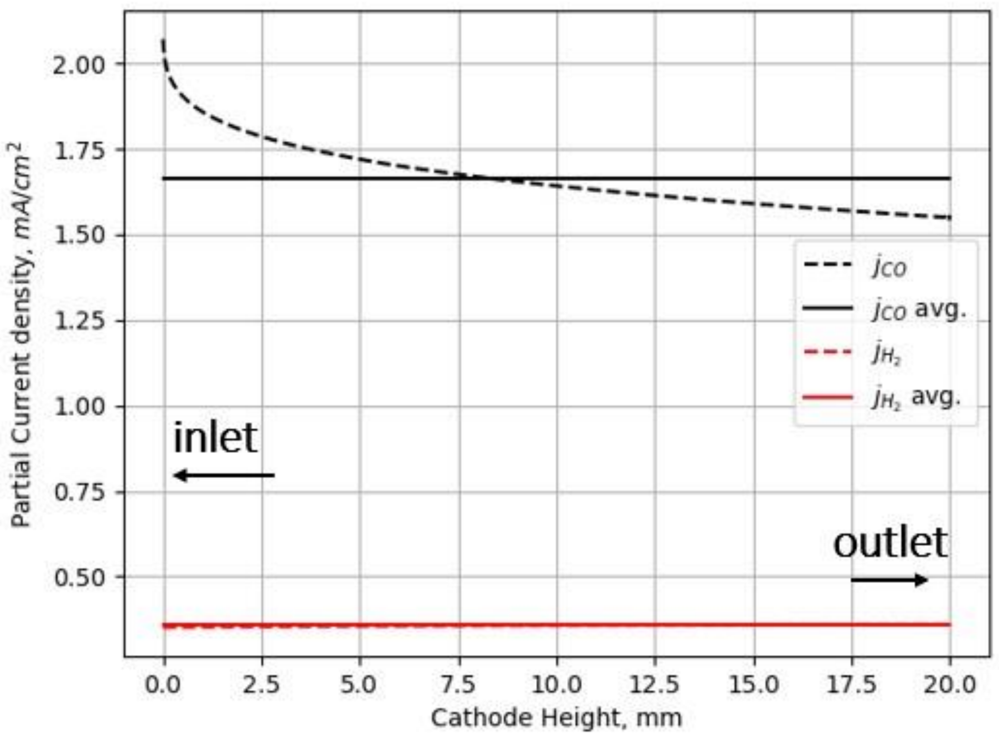
J: Current recorded for each Voltage applied and normalized on the catalyst surface area



FE: Figure of merit to determine the selectivity towards the production of the product of interest



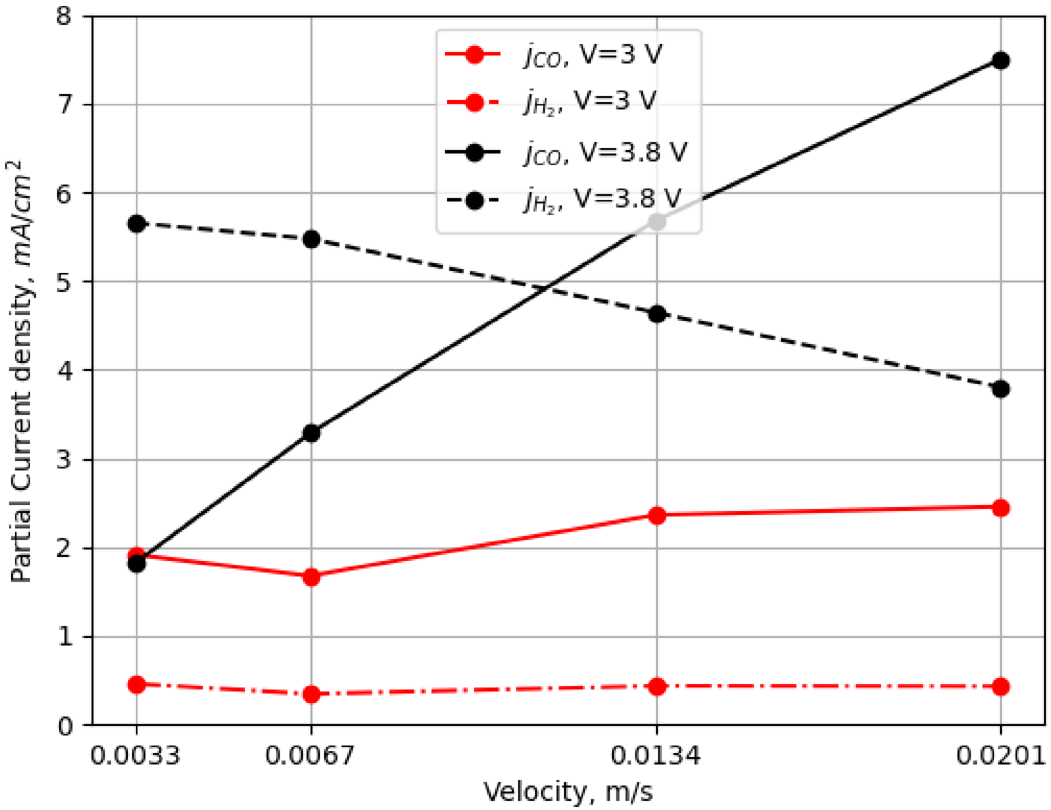
Results #0: Cathode-Height dependancy



The y-dependancy can be safely ignored.

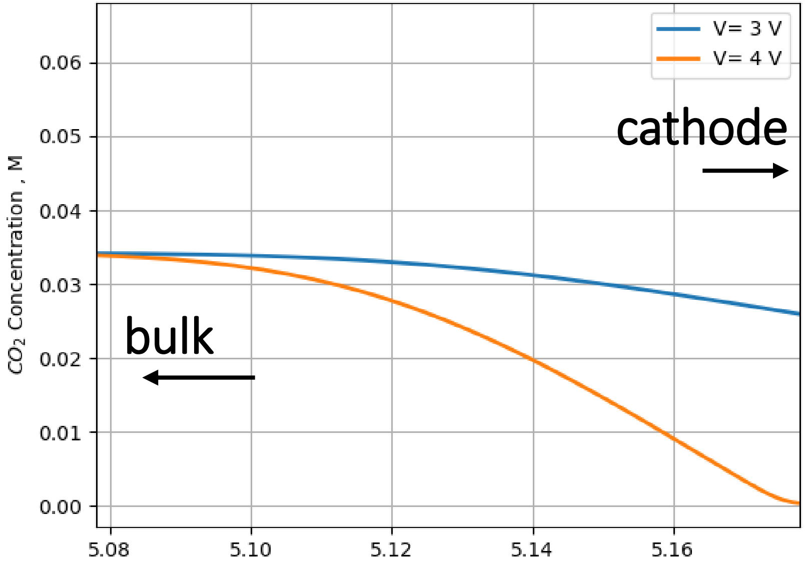
All the data are reported as the average across the cathode height.

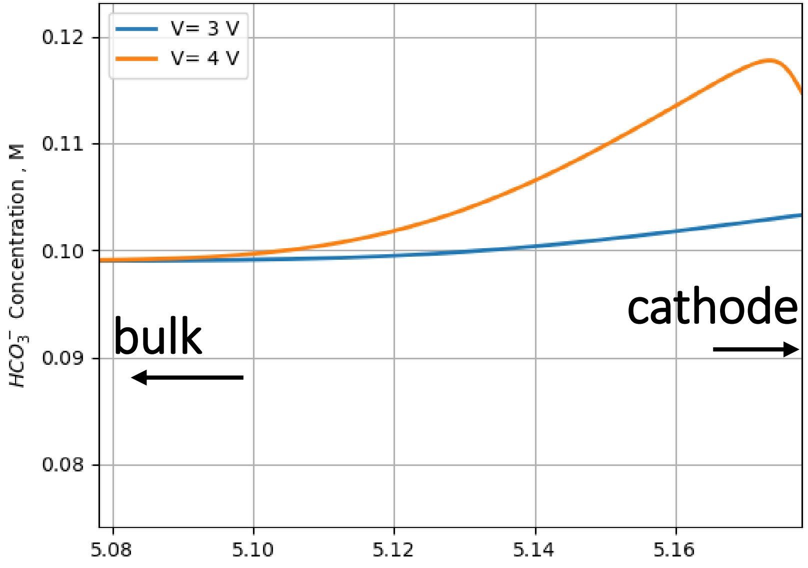
Results #2: inflow velocity u_0 @ L=0.25 cm

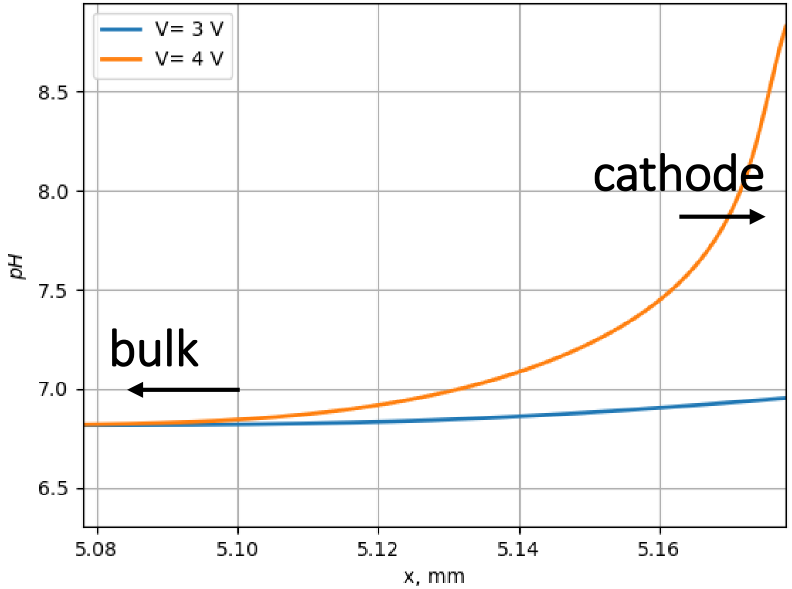


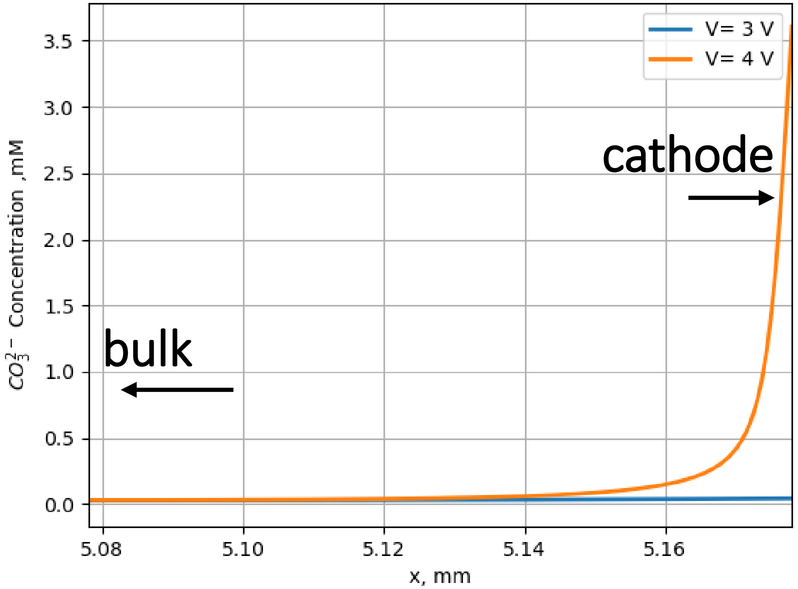
Dependancy on flow velocity is more pronounced on higher voltages. The reason is related to the fact that higher CO_2 feed rates is more impactful when there are higher rates of carbon dioxide comsuption.

Results #3: L=0.25 cm , u_0=0.067 m/s @ V= 3 V , 4 V









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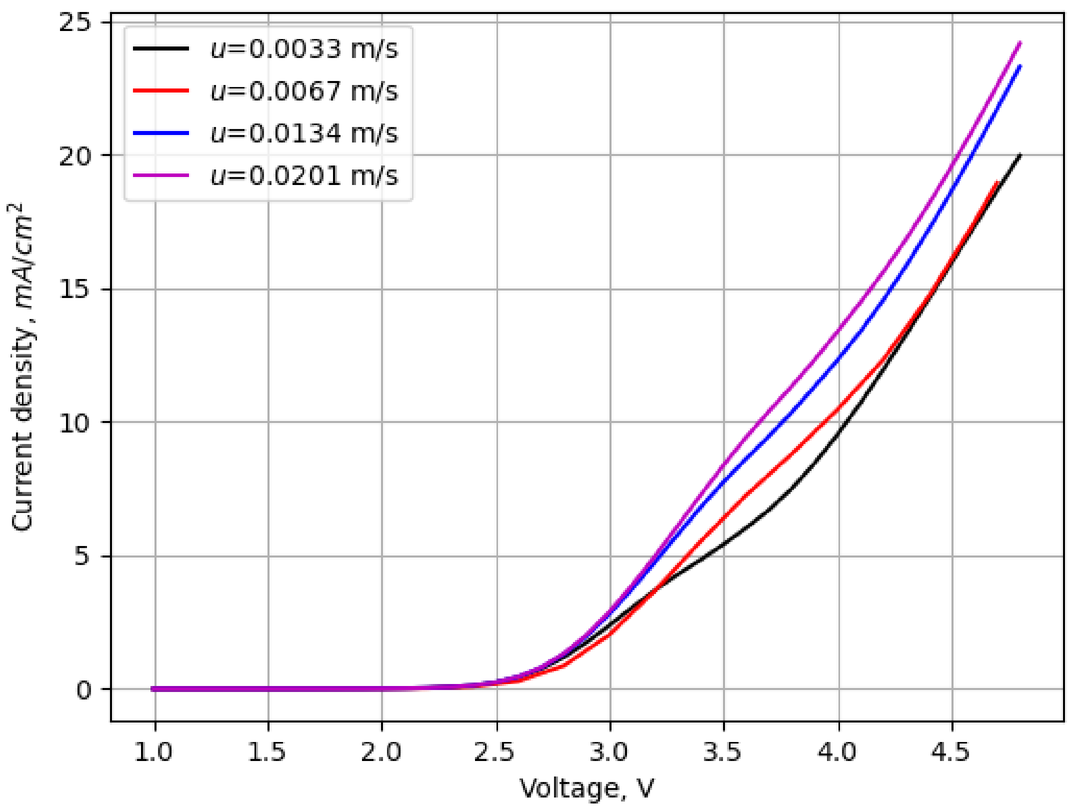
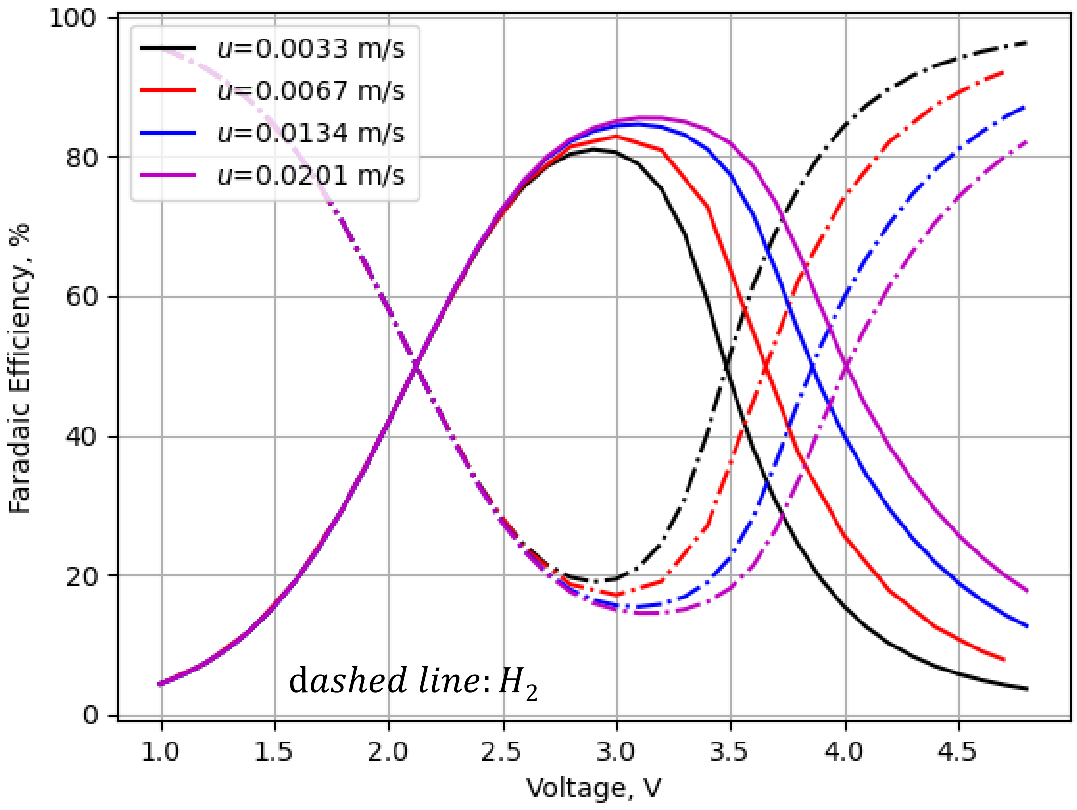
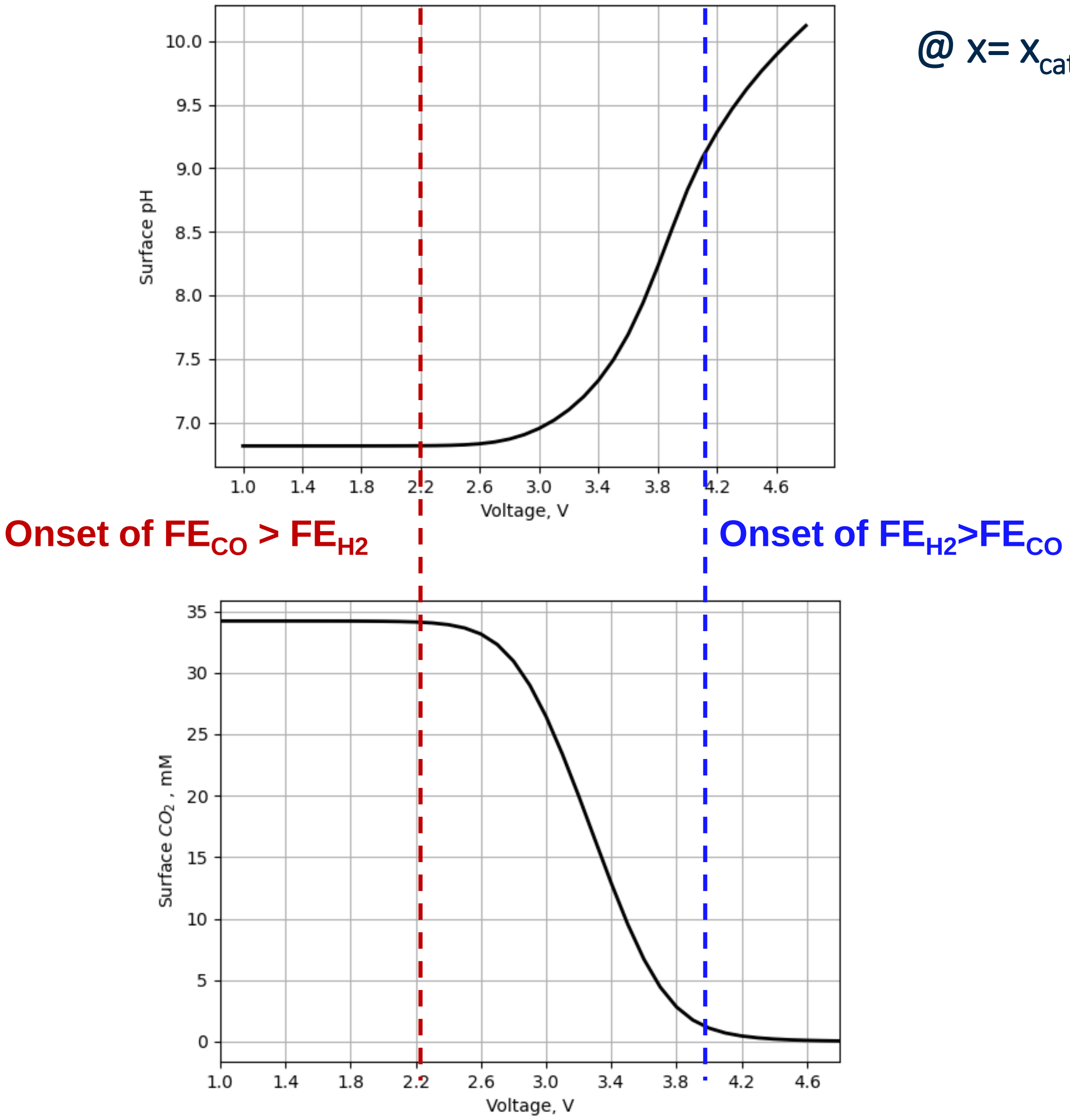




Results #4: L=0.25 cm , u_0=0.067 m/s

@ x= $x_{cathode}$



@ membrane surface