Multiphysics model for design optimization of a monolithic photoelectrochemical cell device

Elise Bérut, Damien Gloriod, Fabrice Micoud, Estelle Le Baron

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Funded by the European Union

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Introduction

The FreeHydroCells project

Funded by the European Union

OBJECTIVE:

Create a novel tandem **monolithic photoelectrochemical (PEC) cell**
to split water unassisted → **cheap, efficient and modular H_2 generating solution**

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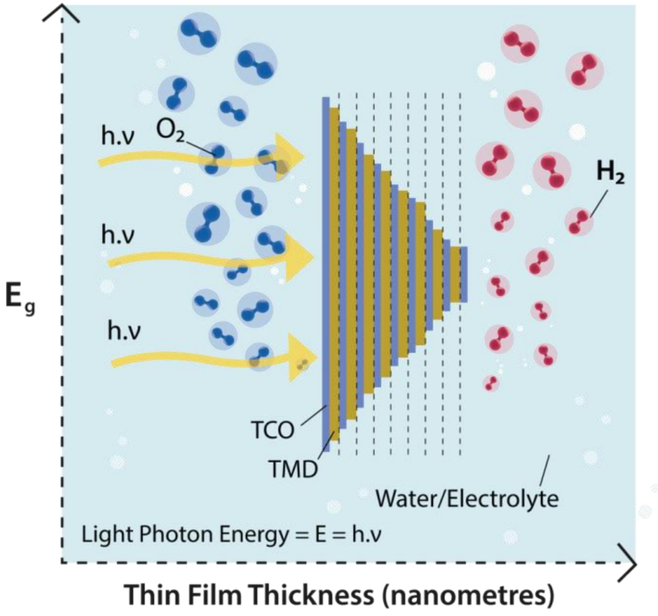

University College Cork, Ireland
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Ireland, coordinator

Consiglio Nazionale delle Ricerche

Italy

RWTH AACHEN UNIVERSITY

Germany

AMO

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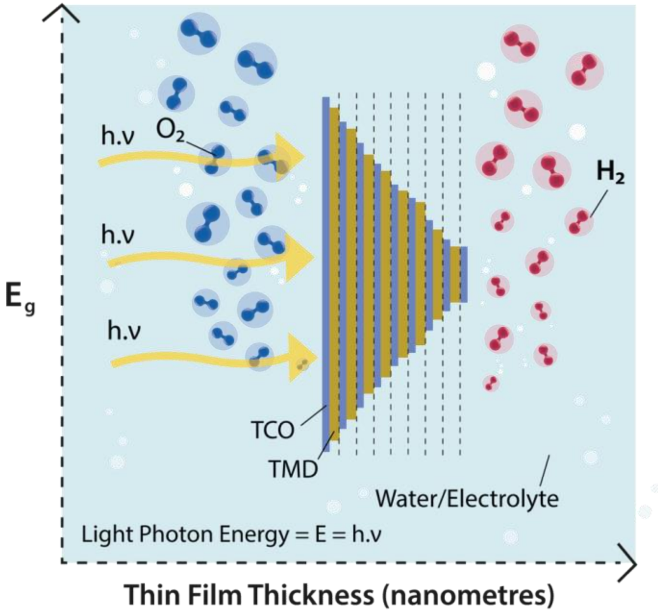

Novel materials:
- doping TCOs and TMDs as N-type or P-type semiconductors
- thickness, bandgap, conductivity
- recombination reduction through defect saturation
- solar absorption optimization

Monolithic PEC cell engineering:
- integration in multilayer PN-junctions
- cascading bandgap alignment, redox alignment
- maximum light absorption and STH efficiency

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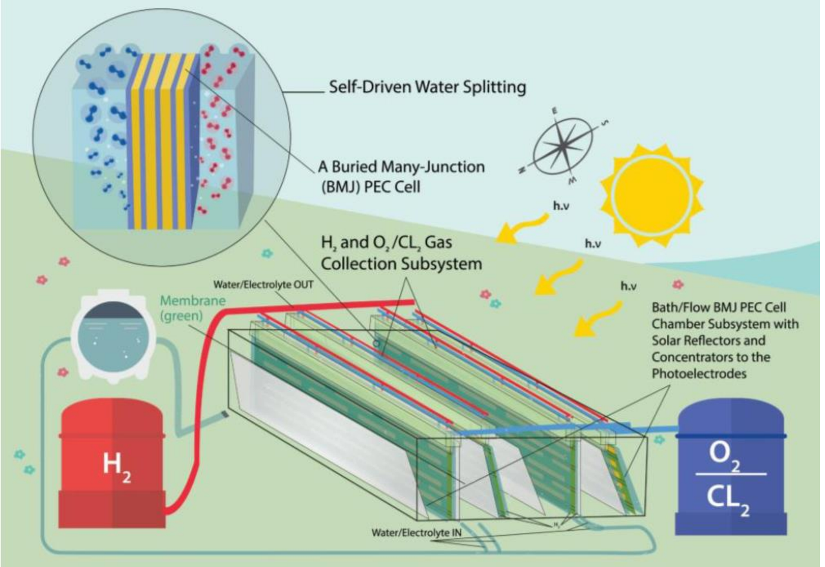

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BARDS
A Sound Approach to Chemical Analysis

Ireland

France

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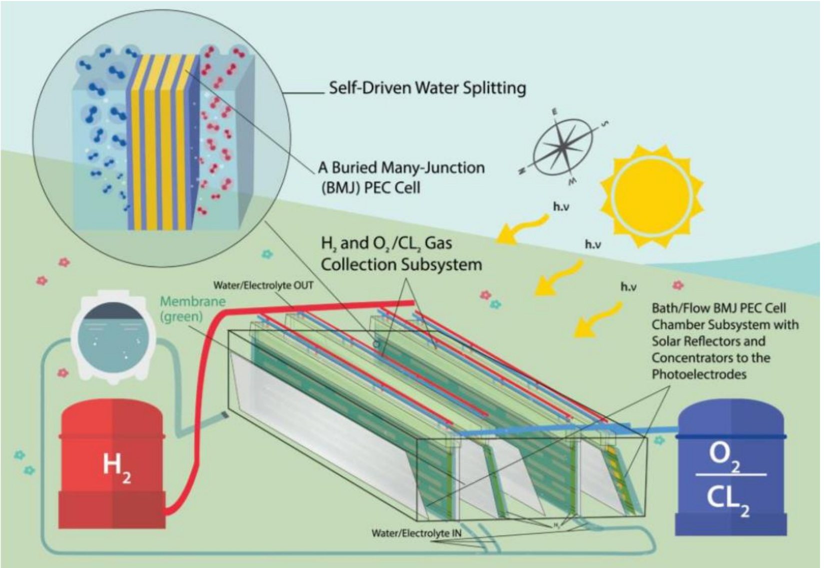

Device engineering:
- monolithic cell integration
- good STH efficiency
- durable system with long service life
- optimization of design and operating conditions

Upscaling and commercialization:
- environmentally-benign
- cost-effective production
- scalable, modular expansion

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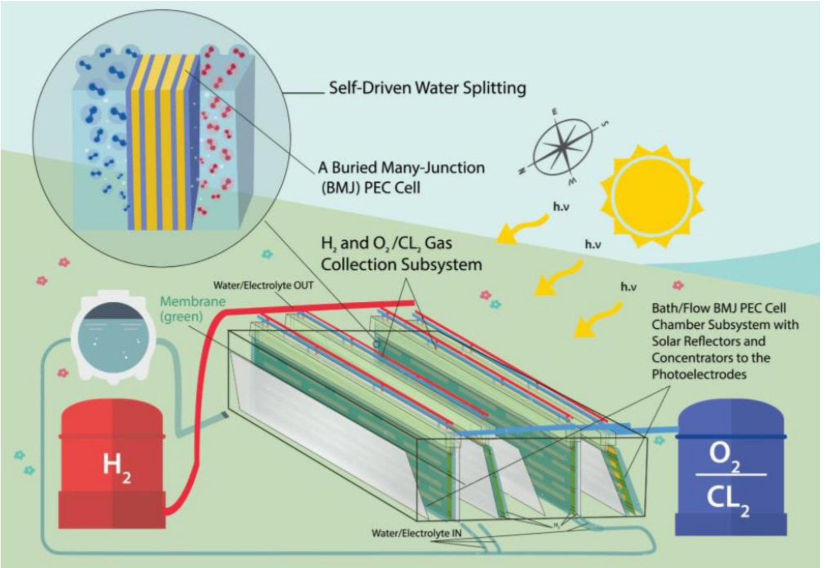

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- Consortium: 7 European partners
- Duration: 40 months (nov. 2022 - feb. 2026)
- EU funding: 3.8 million €

UCC University College Cork, Ireland Coláiste na hOllscoile Corcaigh

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UCC ACADEMY

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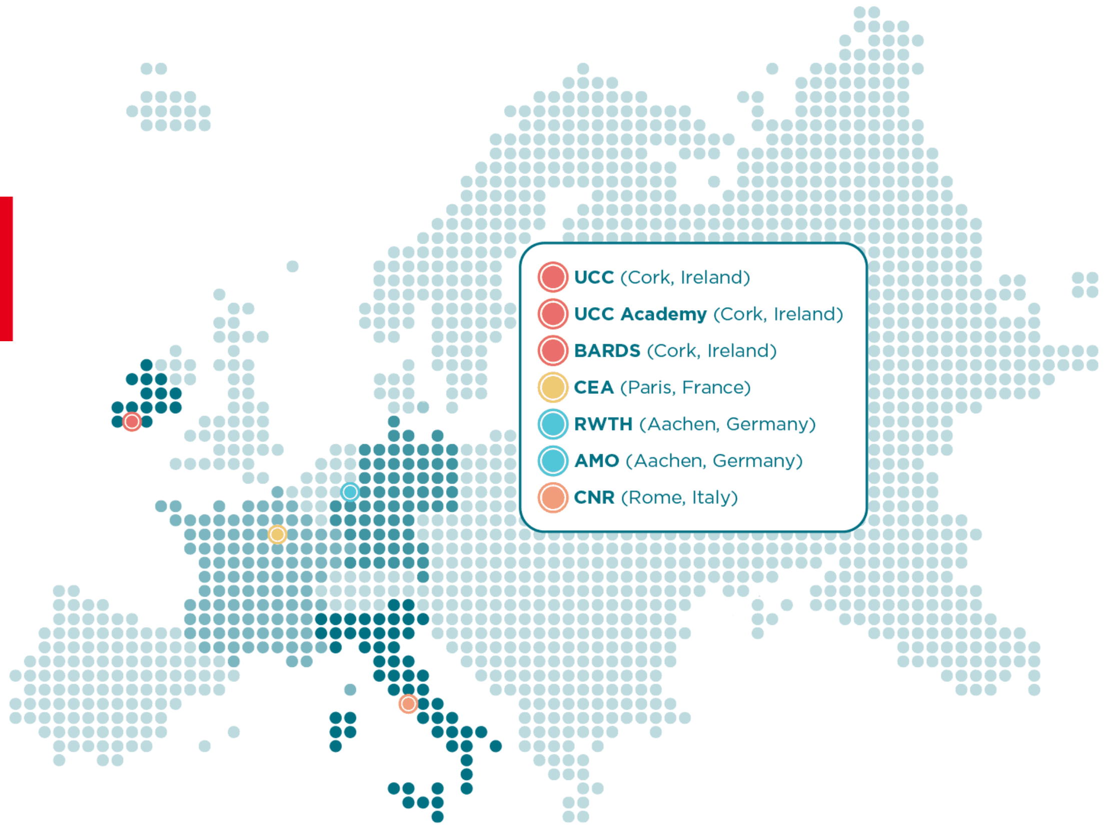

Numerical model description

Physical description

OBJECTIVE

Optimization of PEC system design and operating conditions to:

- minimize the (optical and ohmic) impact of **bubbles**
- enhance **ionic transport** between compartments

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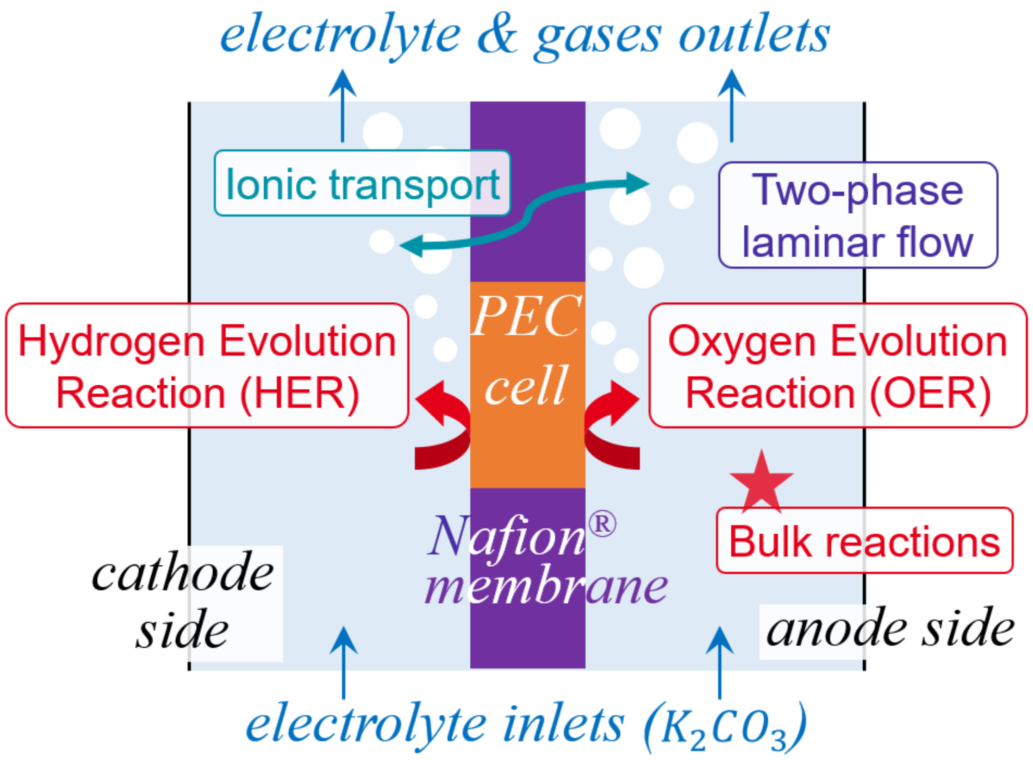

2D steady system-scale model including:

- two-phase laminar flow (mixture model from Schillings[1])
- ionic transport by convection, diffusion and migration
- HER / OER reactions (Butler-Volmer with mass-transport)
- bulk reactions and water self-ionization

[1] Schillings *et al.* (2015) Int. J. Heat Mass Transf. 85, 292-299

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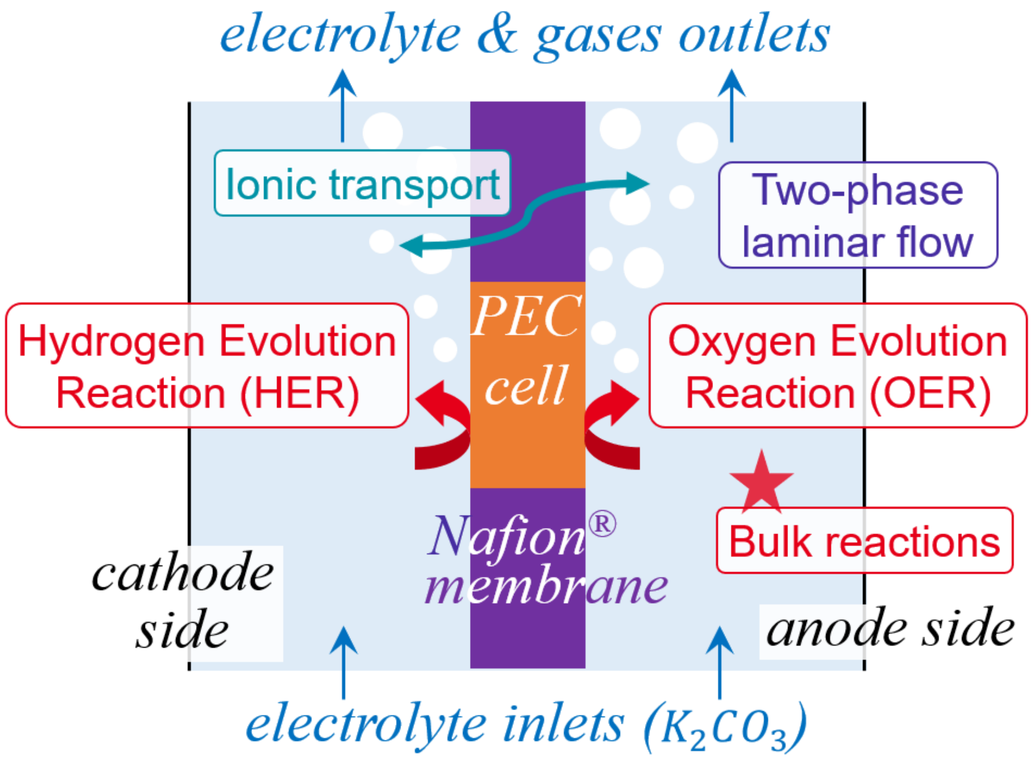

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$$2H_2O + 2e^- \rightarrow \boldsymbol{H_2} + 2OH^- \quad \text{(HER)}$$

$$2OH^- \rightarrow 1/2\,\boldsymbol{O_2} + H_2O + 2e^- \quad \text{(OER)}$$

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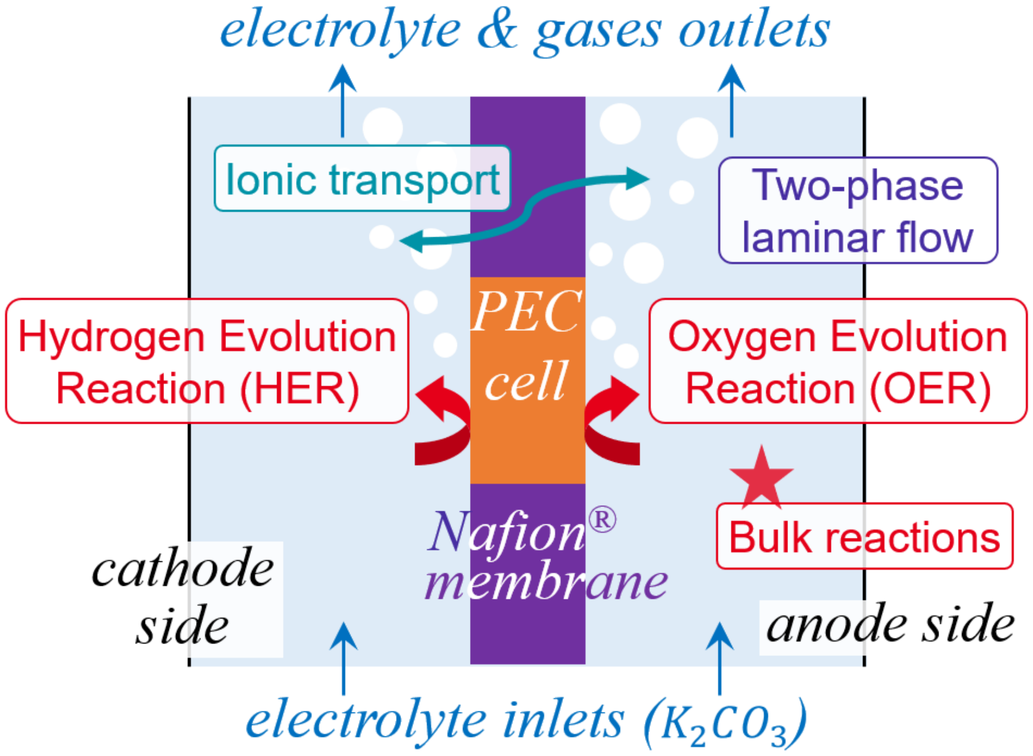

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$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \qquad CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^-$$

$$CO_2 + OH^- \rightleftharpoons HCO_3^- \qquad HCO_3^- + OH^- \rightleftharpoons H_2O + CO_3^{2-}$$

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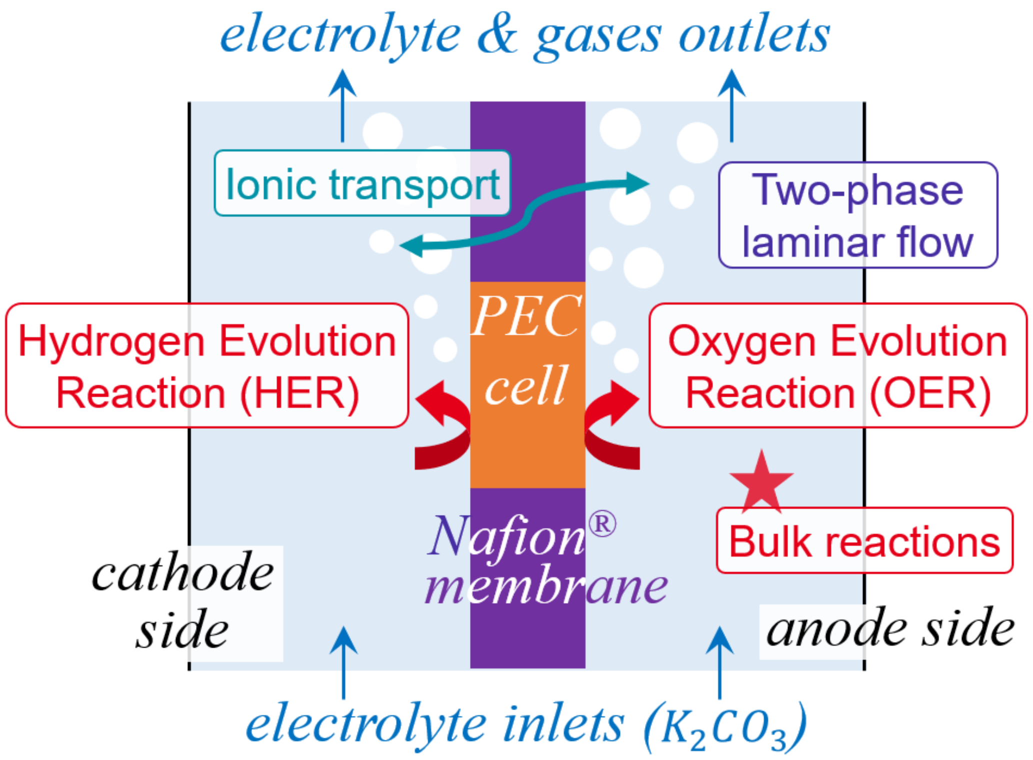

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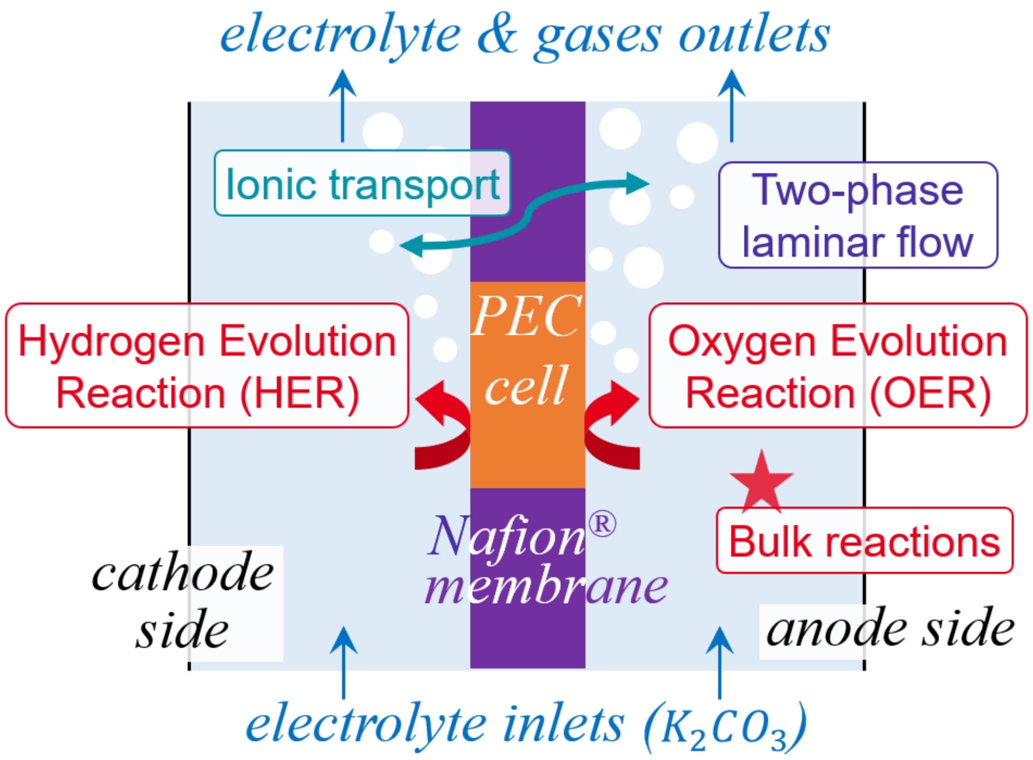

! Dark electrolyzer

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Comparison with existing models of two-phase hydrodynamics in (photo)electrochemical reactors

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- Methods for **two-phase flow modeling**: discrete phase, two-fluid or ***mixture model**
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➔ Originality lies in **system configuration**

literature	present model
mostly 2D steady	2D steady
mostly dark electrolyzers (few photo-reactors)	dark electrolyzer
wired cells	monolithic cell
mostly membrane-less	Nafion membranes

Numerical model description

Main input and output parameters

COMSOL

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geometry
operating conditions
bubble radius
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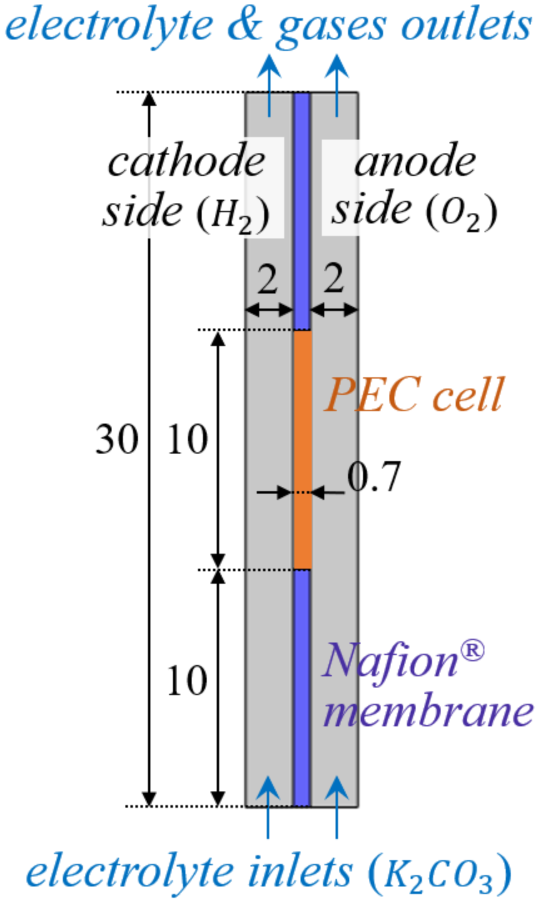

input variable	value
E_{cell}	1.8 V
pH_{in}	12
$\dot{Q}_l$	0.1 L/min
P_{op}	101325 Pa
T_{op}	25 °C
r_b	30 µm
$i_{0,OER}$	10^{-4} A/m²
$i_{0,HER}$	10 A/m²
α_{anode}	0.5
$\alpha_{cathode}$	0.5

state-of-the-art kinetic inputs[2]

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geometry
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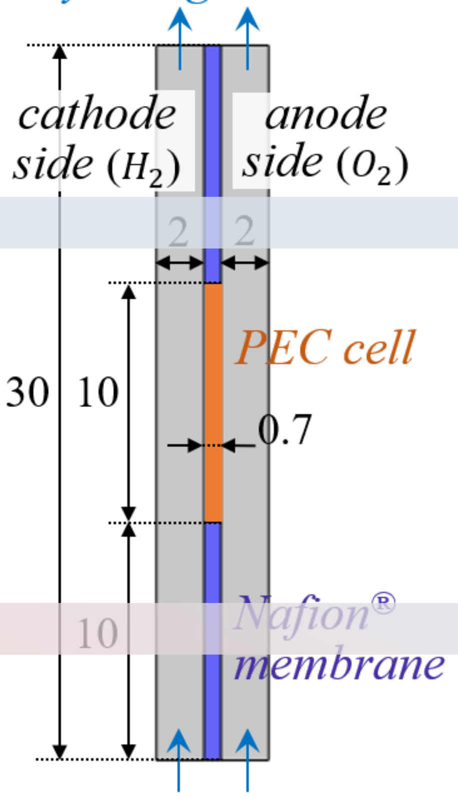
chemical kinetics

MAIN OUTPUTS
gas fraction, gas flow rates
ionic concentrations
electric potential, overpotentials
current densities, total current
electrolyte velocity, pressure
+ optical loss due to bubbles



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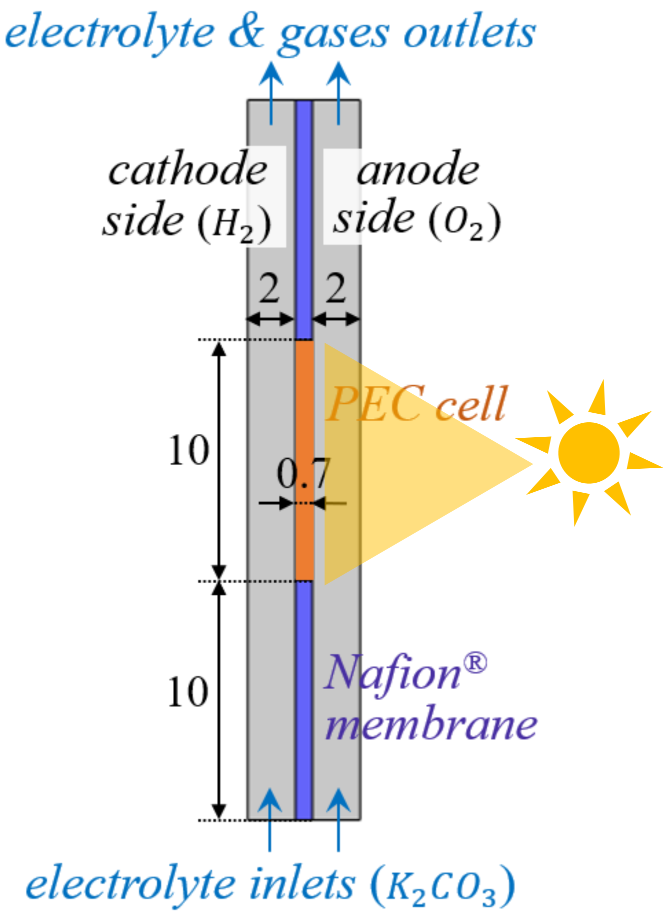

- **incident power**: $\Phi_{max} = L_{cell} D \int_{\lambda} \varphi_i d\lambda$ → incident spectral irradiance (AM1.5G)

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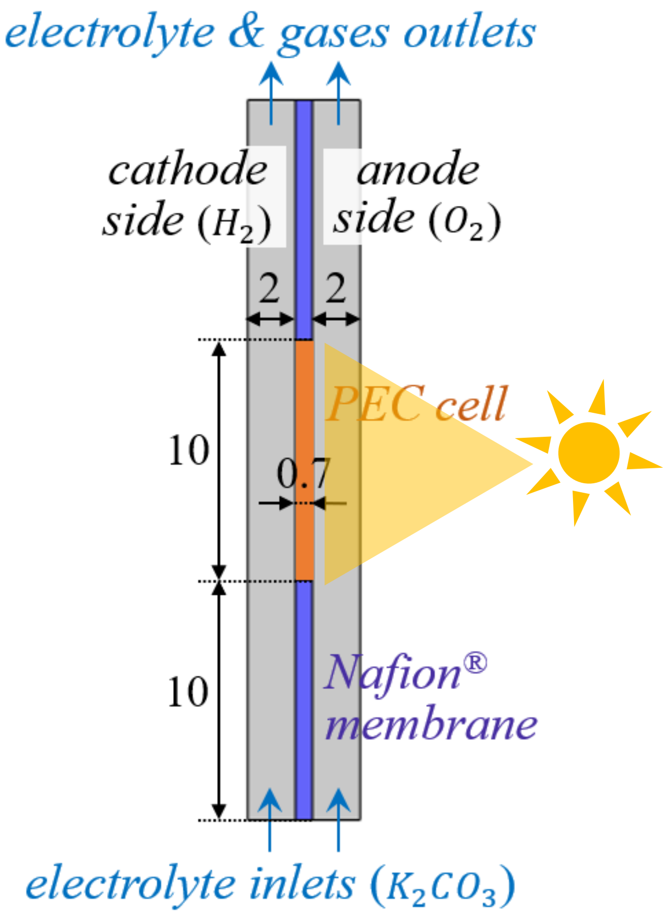

- **incident power**: $\Phi_{max} = L_{cell} D \int_\lambda \varphi_i d\lambda$ → incident spectral irradiance (AM1.5G)
- **power transmitted through the bubble plume**:

$$\Phi_b = D \int_{L_{cell}} \int_\lambda f(\alpha, r_b, t_l) \varphi_i d\lambda dy$$

transmitted fraction:

$$f(\alpha, r_b, t_l) \underset{3}{=} \exp\left(-\frac{3C\bar{\alpha}t_l}{4r_b}\right)$$

bubble radius (r_b), gas fraction (α), liquid thickness (t_l)

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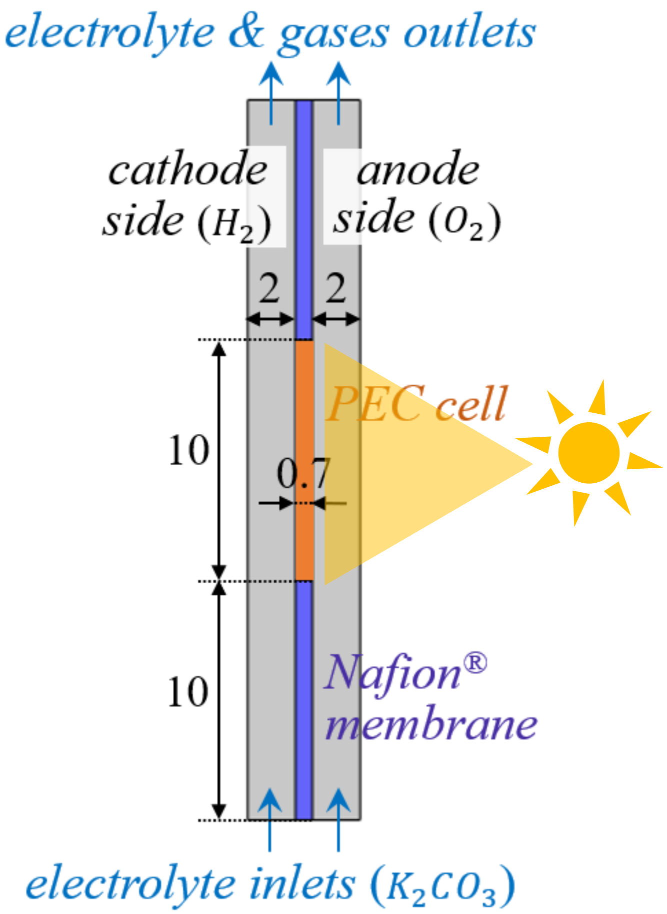

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(gas fraction: α; bubble radius: r_b; liquid thickness: t_l)

- **power transmitted through bubbles + liquid:**

$$\Phi_{lb} = D \int_{L_{cell}} \int_{\lambda} \tau_i f(\alpha, r_b, t_l) \varphi_i \, d\lambda dy$$

τ_i → transmittance of electrolyte

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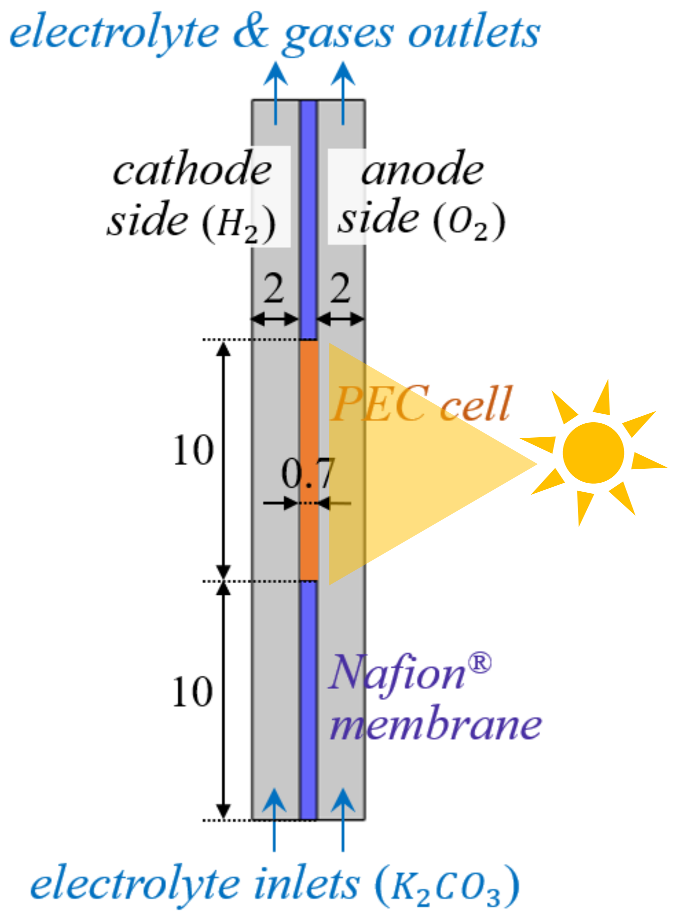

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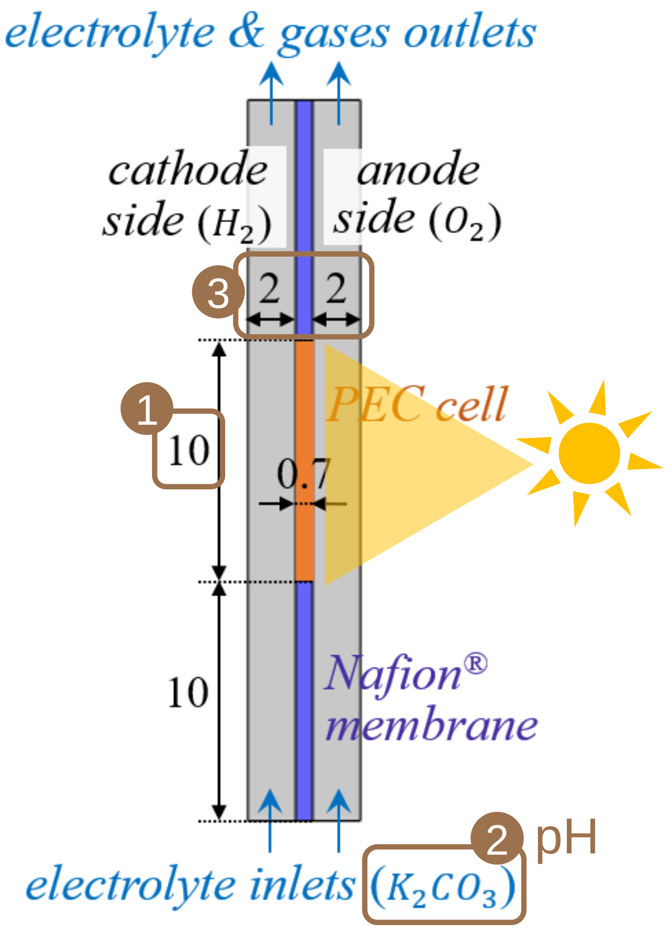

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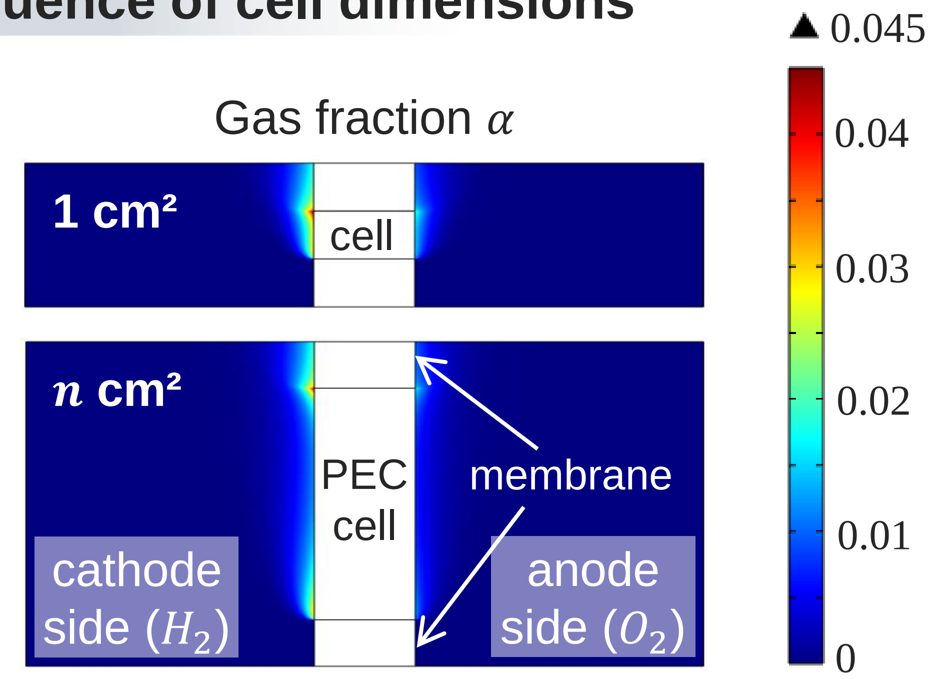
Results and discussion

Influence of cell dimensions



- **Reduced H_2 flux** when cell size increases

1 cm² → 3.4 mL/h/cm²

n cm² (confidential) → 0.8 mL/h/cm² -76%

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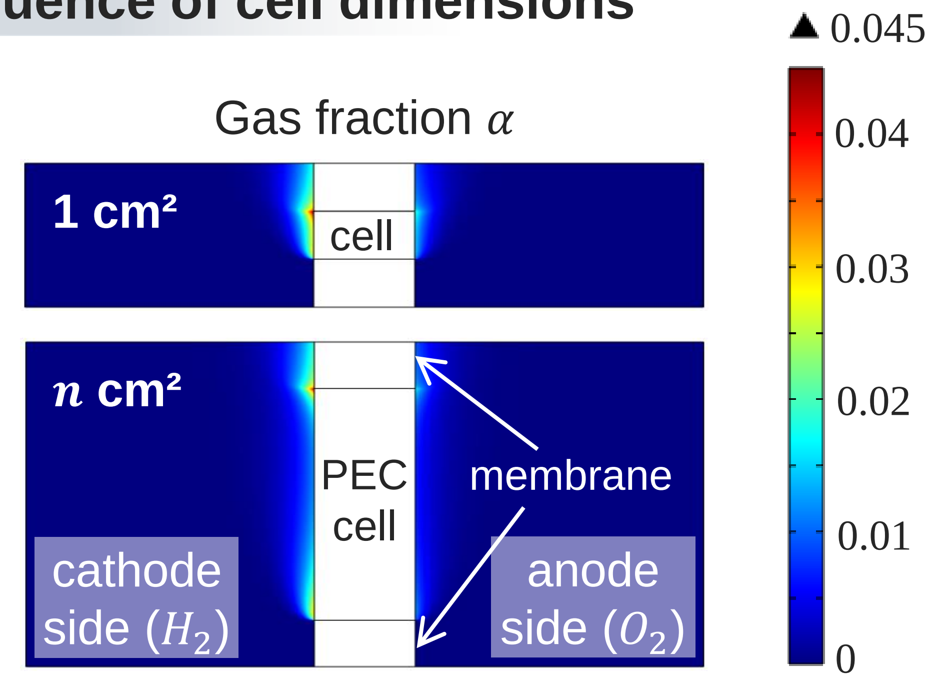
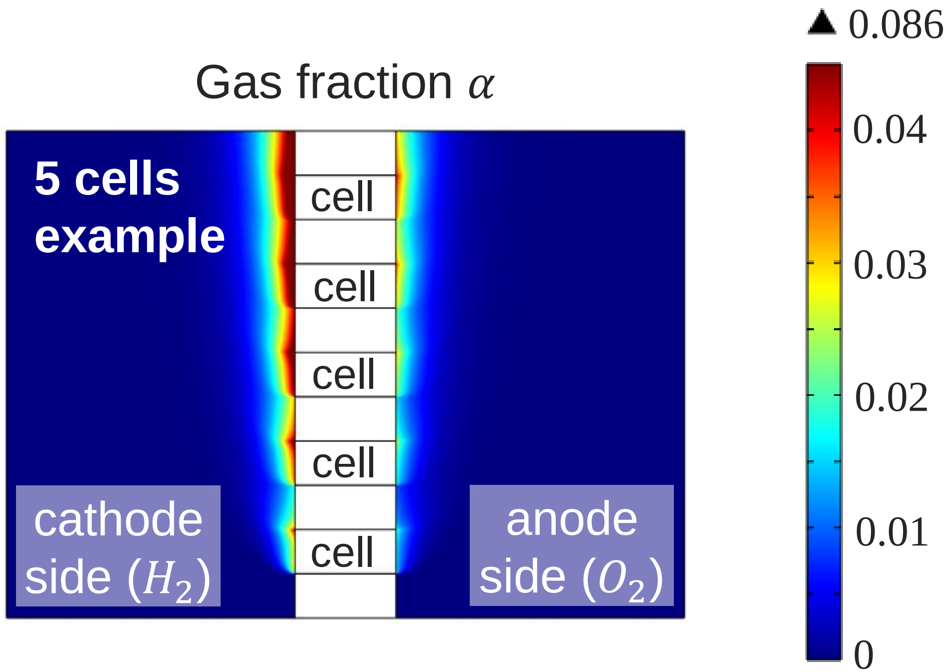




- **Reduced H_2 flux** when cell size increases

1 cm² → 3.4 mL/h/cm²
n cm² (confidential) → 0.8 mL/h/cm² **-76%**

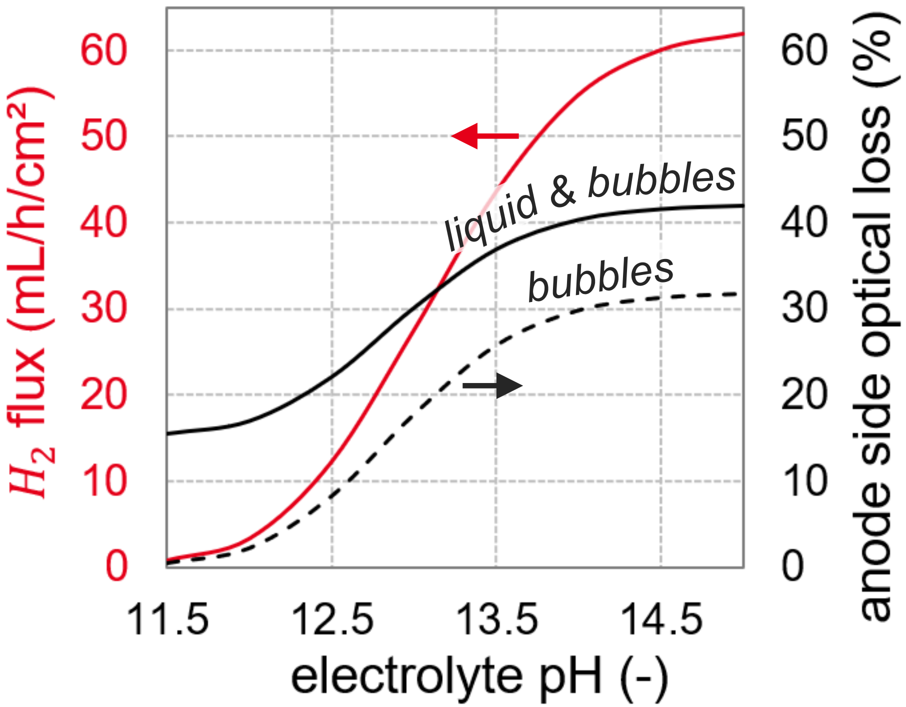
- Better to **couple multiple small cells**

n cells of 1 cm² → 3.1 mL/h/cm² **H_2 flux x 4**

BUT **increased optical loss** due to bubbles
n cm² → 4% VS n cells of 1 cm² → 10%

Results and discussion

Influence of inlet pH



- ***H_2* flux** significantly **increases with pH** up to a plateau
- **High pH influence** in the range [11.5-14.5]

➡ At low pH, low OH^- concentration at anode hinders the OER reaction

- **Optical losses increase with pH** up to a plateau (due to increased gas generation)

❗ Non-negligible optical losses for high H_2 flux (40%)

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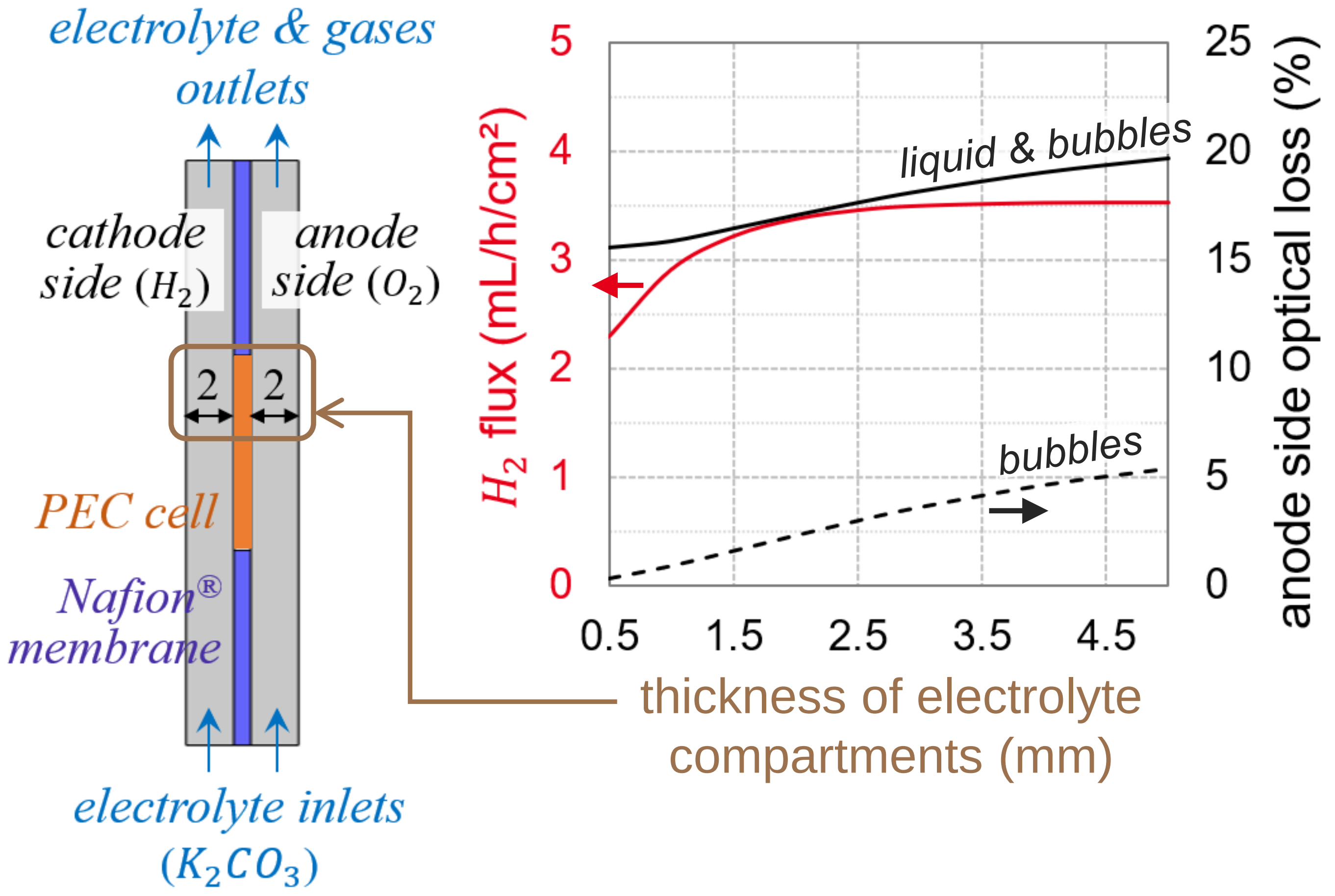
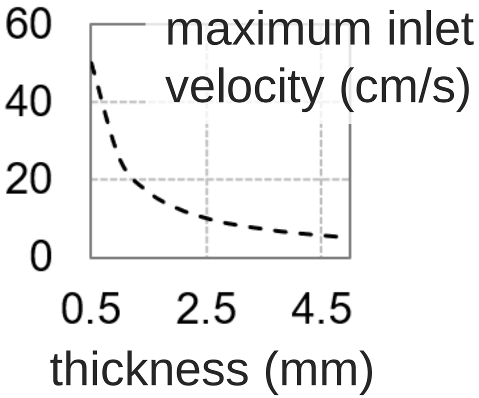
Influence of electrolyte thickness at constant flow rate



- H_2 **flux increases** with thickness **up to a plateau**
- **Monotonic increase of optical losses** with thickness (due to increased gas generation and bubble accumulation)



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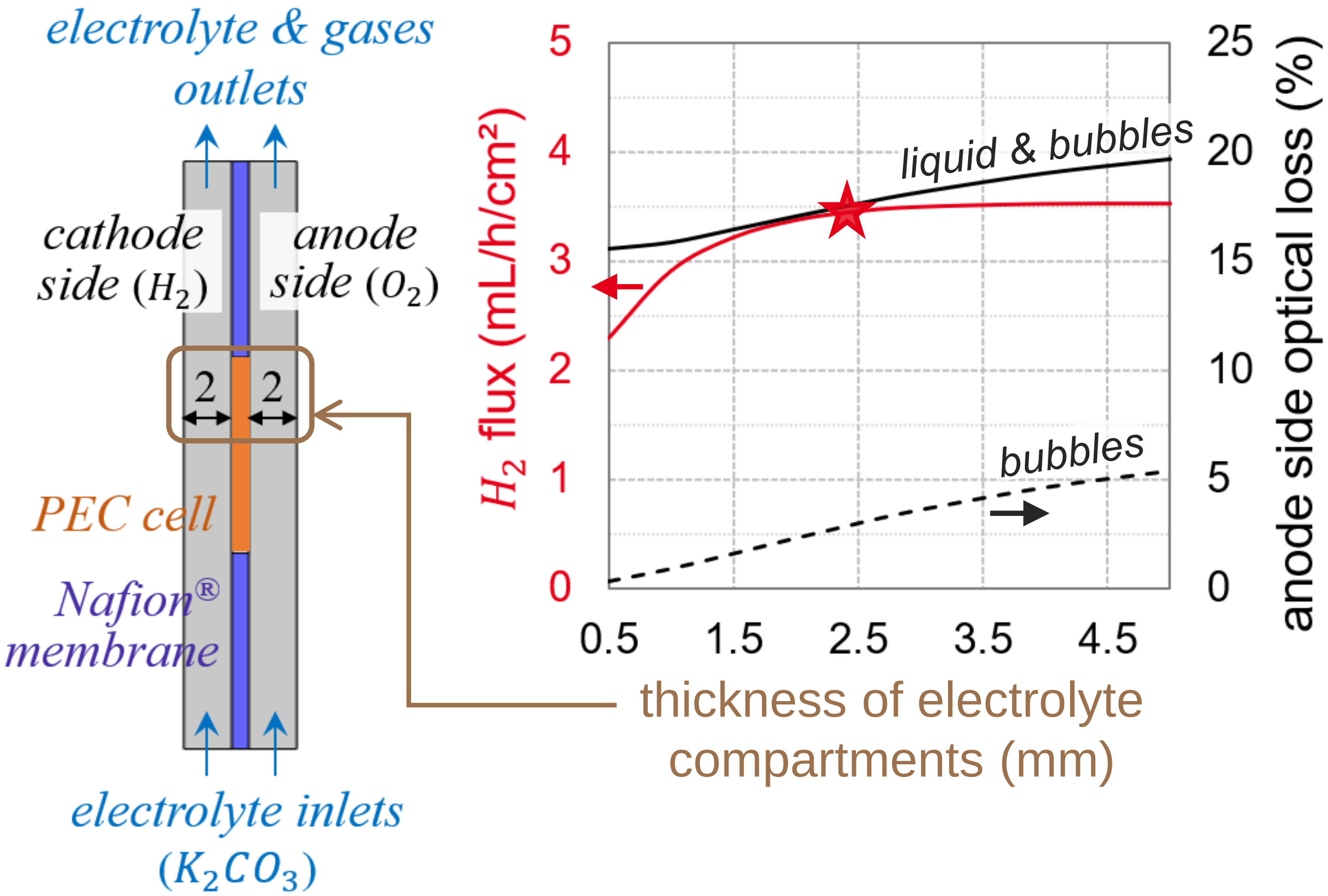

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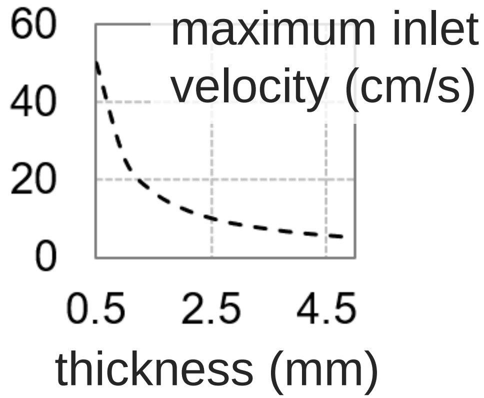

➡ **Optimum** ★ determination

Conclusion

Numerical results

- **Coupling multiple small cells** is recommended for increased H_2 flux ❗ increased optical losses
- **Optimal electrolyte thickness** and **inlet pH** can be determined for a given set of inputs

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Future work

- **Experimental validation** using literature data (monolithic cell under development)
- Comparison of **several electrolytes and membrane types**
- Influence of **membrane dimensions**
- Photocurrent estimation & additional coupling considering optical losses?

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Thank you!

Questions?

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Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or CINEA. Neither the European Union nor the granting authority can be held responsible for them.

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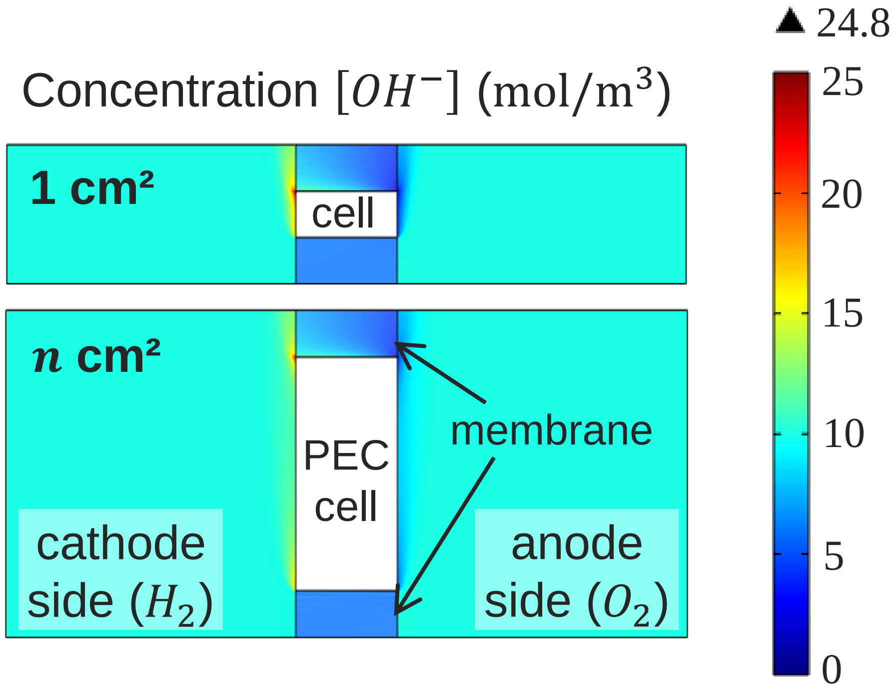

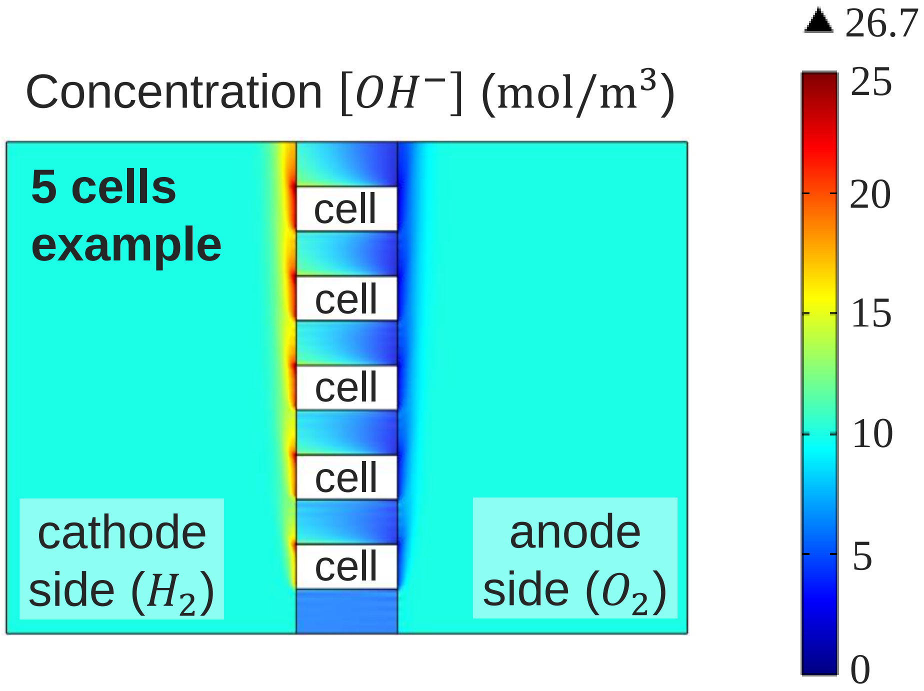

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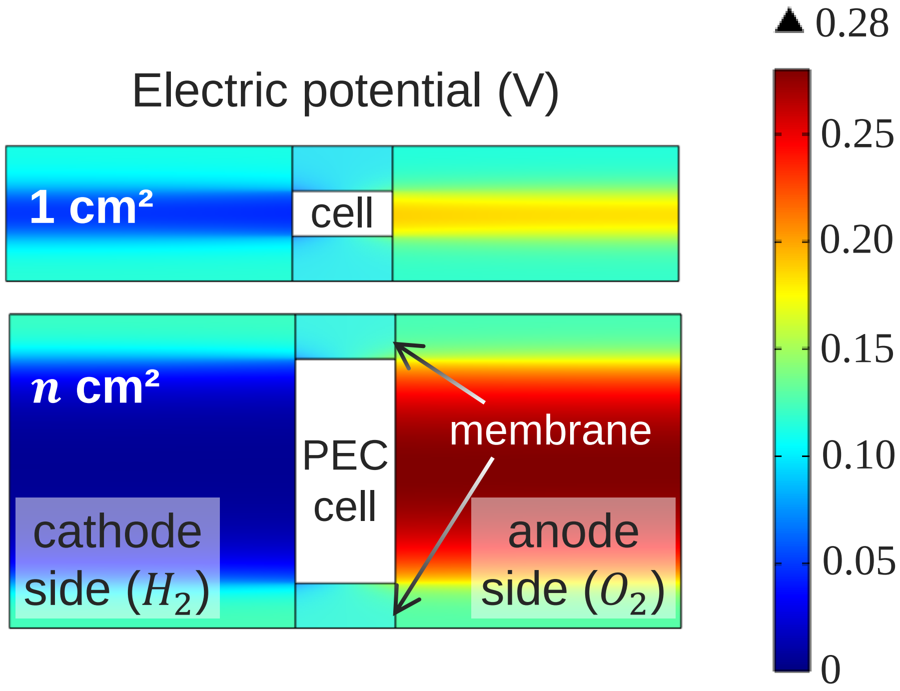
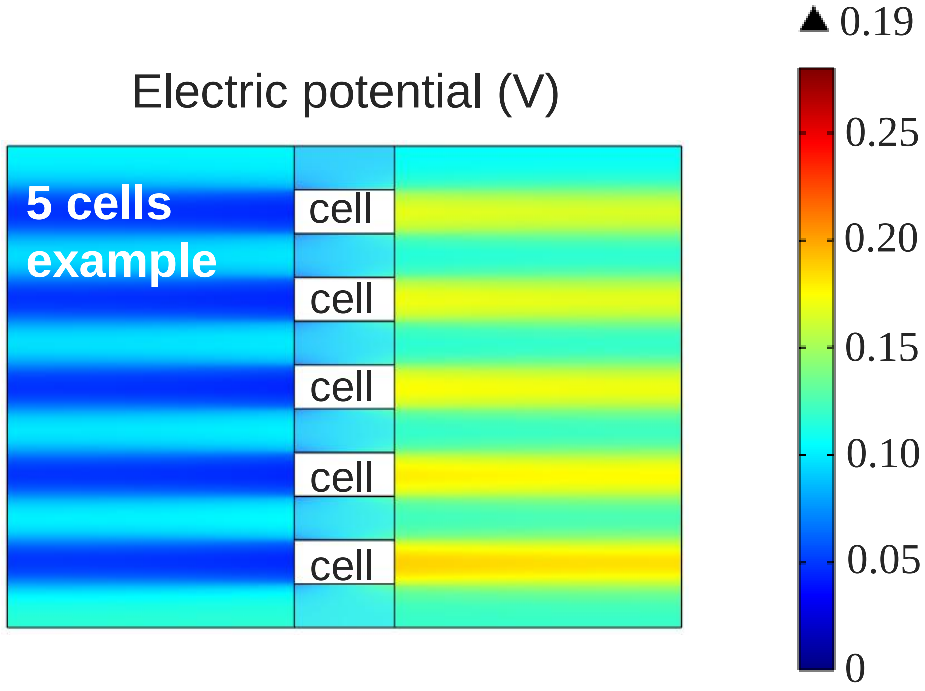
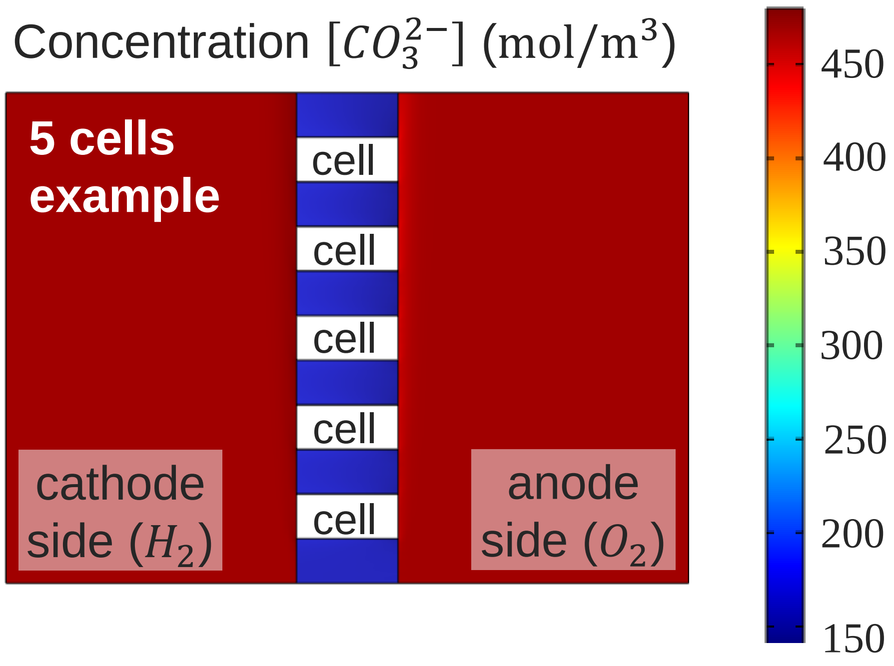
Influence of cell dimensions

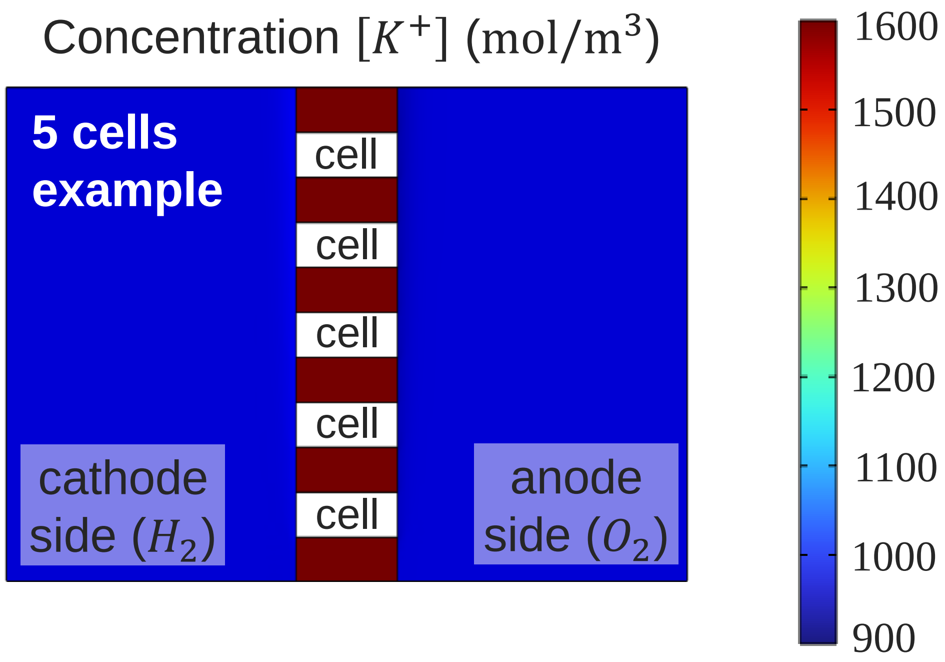




Results and discussion

Influence of cell dimensions





Results and discussion

Influence of inlet pH