Optimizing electrochemical conversion of CO_2 to C2 products via multi-physics simulations

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COMSOL CONFERENCE
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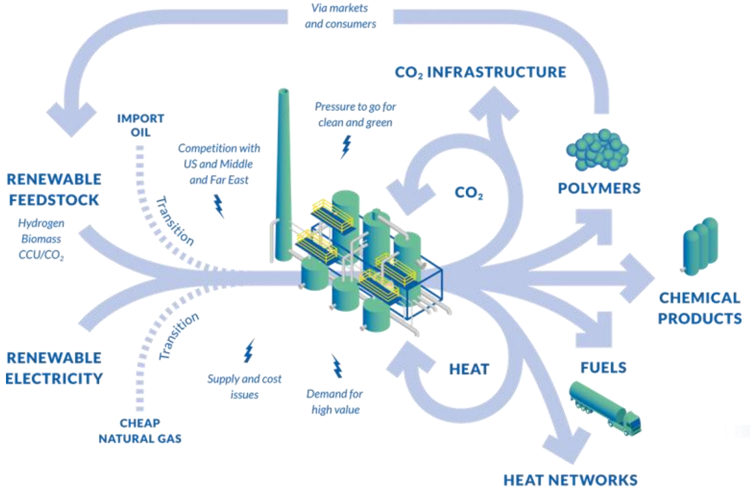
TNO innovation for life

About TNO

- **TNO: Netherlands Organization for Applied Scientific Research**
  - **>4200 employees**, several locations in the Netherlands
  - Independent not-for-profit organization for research in between academia and industry
  - From public-private collaborative projects (NL, EU) to contract research
  - Six main research units
- **Energy & Materials Transition unit**
  - **R&D division focusing on industrial processes**
- From 2015 **VOLTACHEM** Program **for accelerating industrial electrification**

VOLTA CHEM
Powered by TNO

https://www.voltachem.com/



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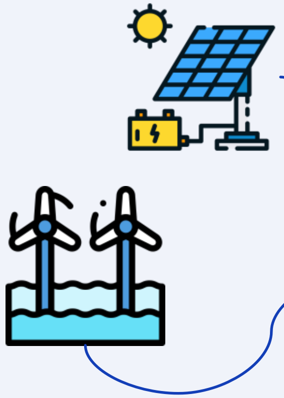
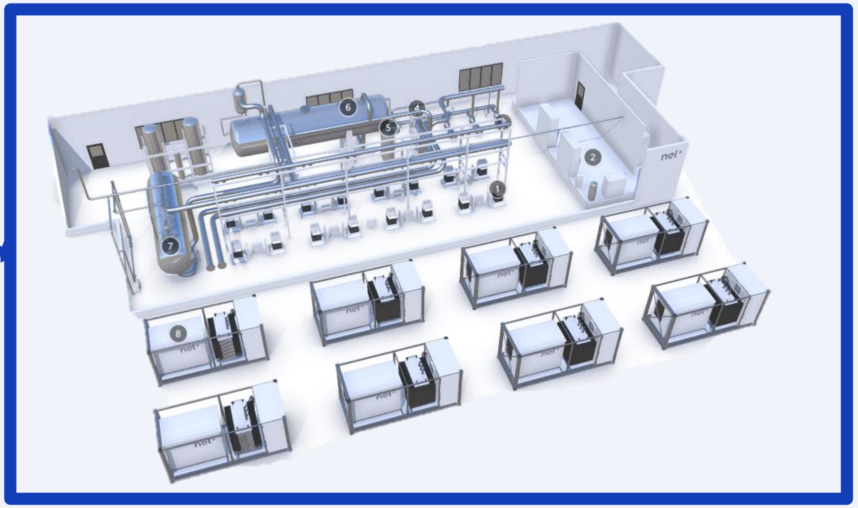
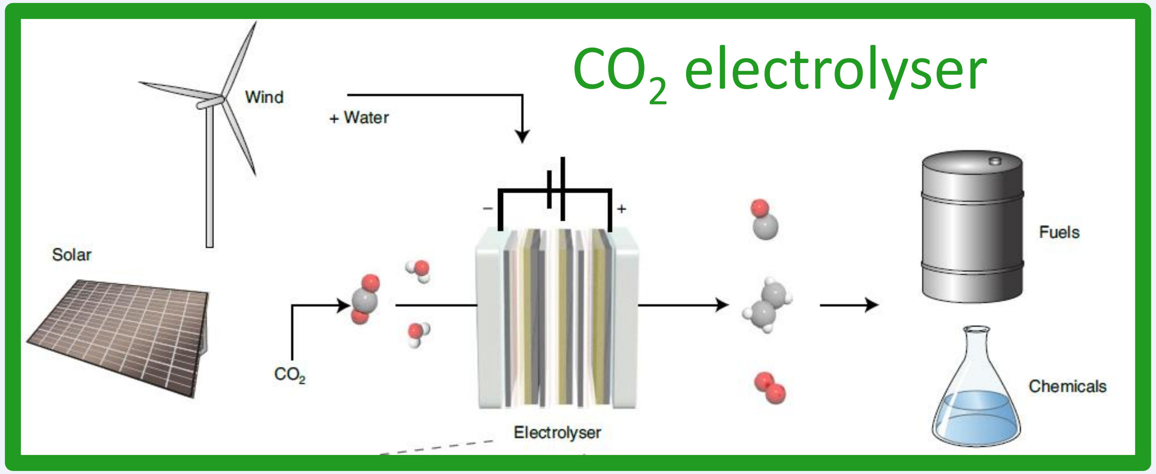
Multi-scale **Electrochemical Flow** Modelling

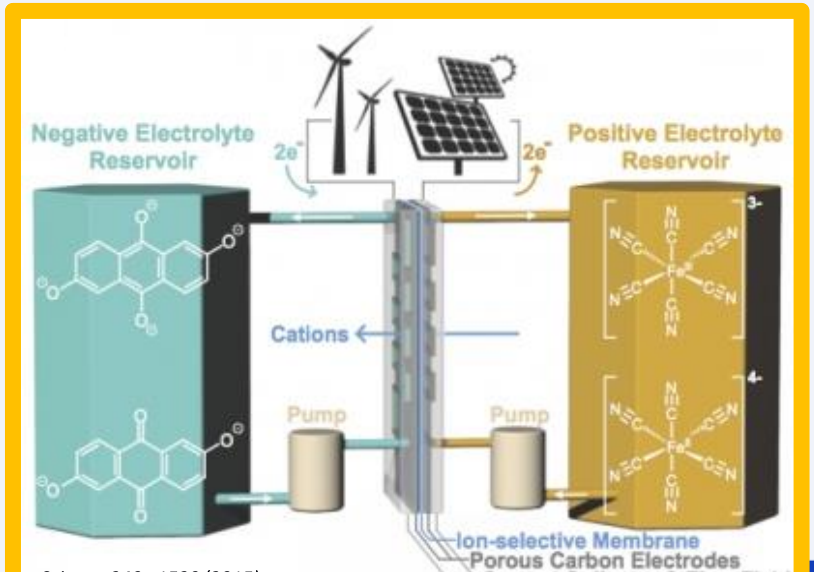




Water electrolyser



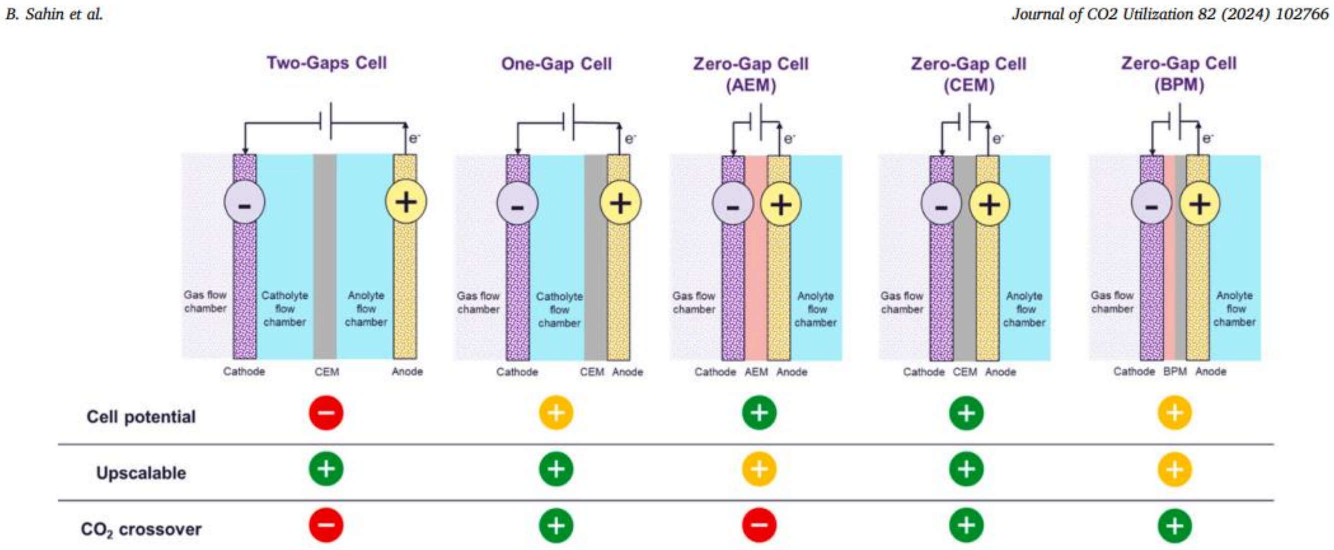
Redox Flow Battery



Science 349, 1529 (2015)

There are a lot of different configurations

- Current TNO focus: one-gap flow cell or membrane-electrode-assembly (MEA) with zero-gap, using AEM



Multi-physics modelling to guide cell design

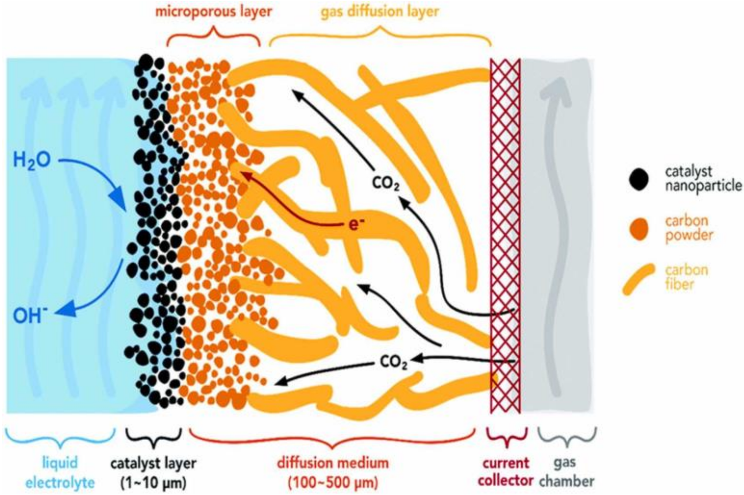
Models needed to quickly screen different designs and operating conditions

1D models developed based on pioneering works of Weng, Bell, Weber and recent study of Ehlinger *et al.*

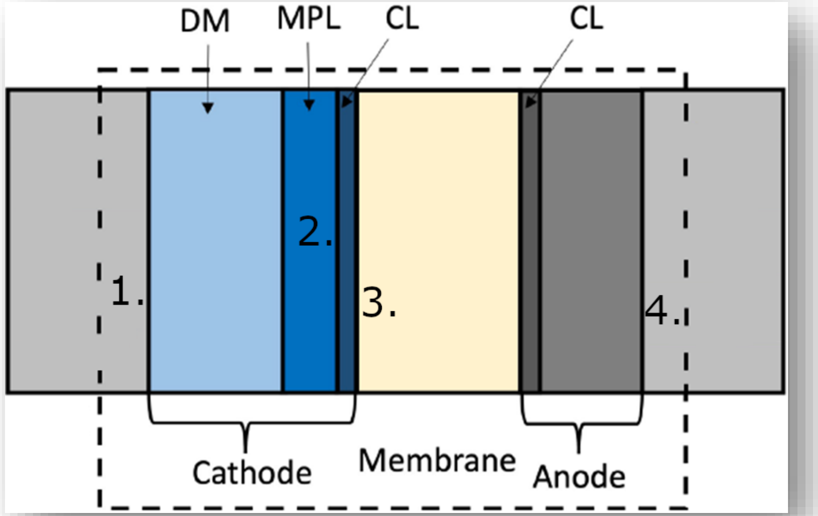
Steady-state and isothermal simulations of coupled phenomena at cell-level:

- **Flow**
  - Darcy's law, simplified 2-phase using saturation curves
- **Species transport** (12 species)
  - Gaseous species transport using multicomponent diffusion
  - Aqueous species using Nernst-Planck
  - Donnan potential included in transport across AEM for MEA configuration
- **Reactions** (7+5 heterogeneous + homogeneous)

- <u>Outputs</u>: I-V curve, Faraday efficiency, spatial distributions of key quantities



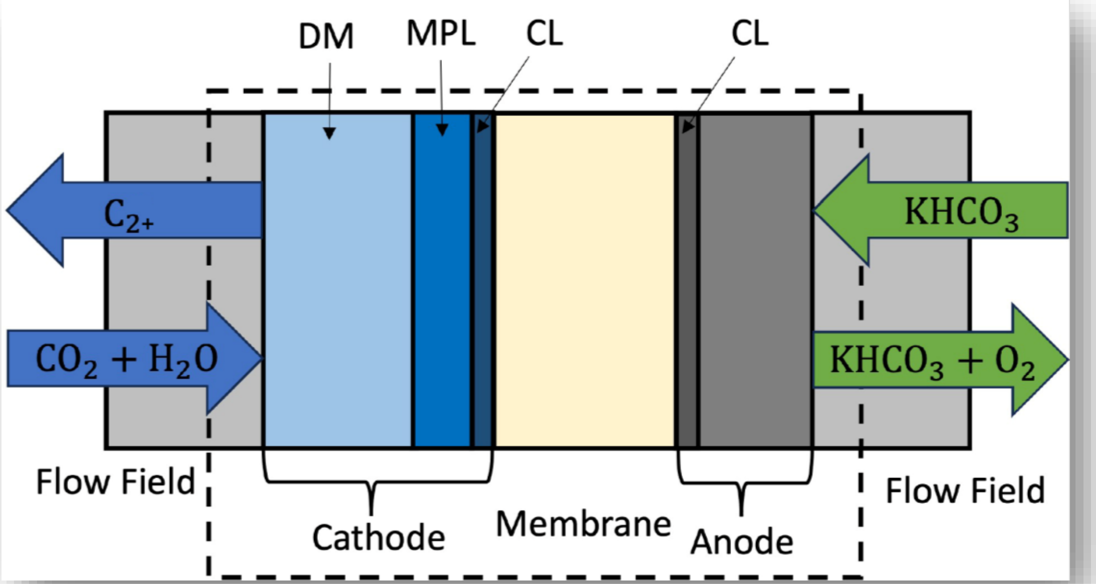
Weng, Bell, Weber *PCCP* (2018), *En. Env. Sci.* (2019), *En. Env. Sci.* (2020)



Ehlinger *et al.*, ChemElectroChem 11 (2024)

1D MEA model

- Tertiary Current Distribution
  - Porous Electrode: DM,MPL,CL
  - Porous Electrode Reactions: CL
  - Ion Exchange Membrane: Membrane



Butler-Volmer or Tafel kinetics

CO_2R

$$CO_2 + H_2O + 2e^- \longrightarrow CO + 2OH^-$$
$$CO_2 + 2H_2O + 2e^- \longrightarrow HCOOH + 2OH^-$$
$$CO_2 + 6H_2O + 8e^- \longrightarrow CH_4 + 8OH^-$$
$$2CO_2 + 8H_2O + 12e^- \longrightarrow C_2H_4 + 12OH^-$$
$$2CO_2 + 9H_2O + 12e^- \longrightarrow C_2H_5OH + 12OH^-$$
$$3CO_2 + 13H_2O + 18e^- \longrightarrow C_3H_7OH + 18OH^-$$

HER

$$2H^+ + 2e^- \longrightarrow H_2$$
$$2HCO_3^- + 2e^- \longrightarrow H_2 + CO_3^{2-}$$
$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$$

OER

$$2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$$
$$4OH^- \longrightarrow O_2 + 2H_2O + 4e^-$$

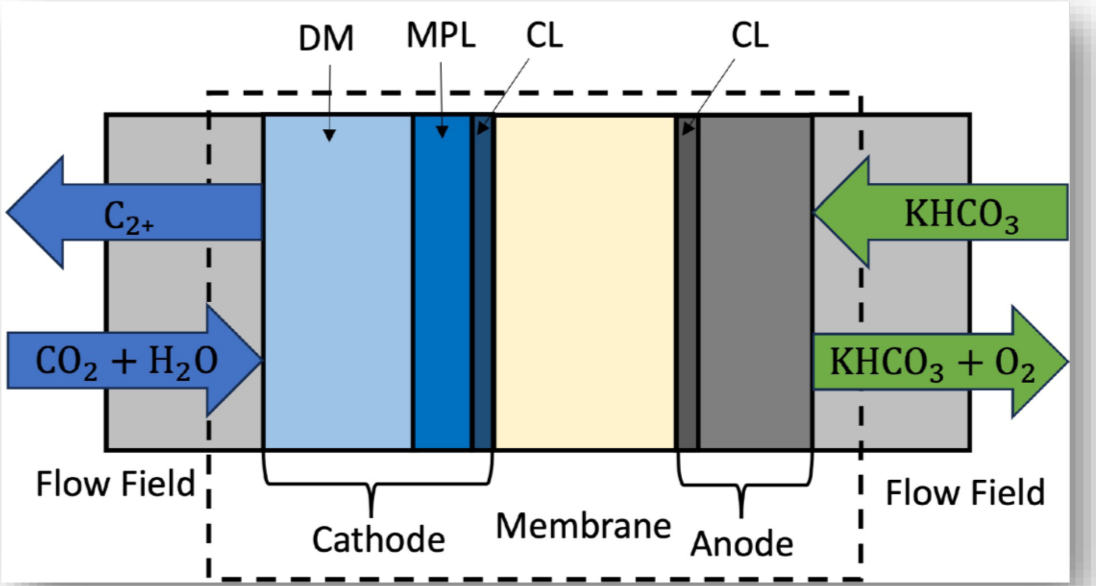
Law of mass action

Homogeneous reactions

Reaction	Equilibrium Constant	Forward Rate Constant
$CO_2 + H_2O \leftrightarrow H^+ + HCO_3^-$	$K_1 = 10^{-6.37}$ M	k_1 =3.71e−2 s^{-1}
$HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$	$K_2 = 10^{-10.32}$ M	k_2 = 59.44 s^{-1}
$CO_2 + OH^- \leftrightarrow HCO_3^-$	$K_3 = K_1/K_w$	k_3 =2.23e3 $M^{-1}s^{-1}$
$HCO_3^- + OH^- \leftrightarrow H_2O + CO_3^{2-}$	$K_4 = K_2/K_w$	k_4 =6e9 $M^{-1}s^{-1}$
$H_2O \leftrightarrow H^+ + OH^-$	$K_w = 10^{-14}$ M^2	k_w =1.4e−3 M s^{-1}

1D MEA model

- Tertiary Current Distribution
  - Porous Electrode: DM,MPL,CL
  - Porous Electrode Reactions: CL
  - Ion Exchange Membrane: Membrane



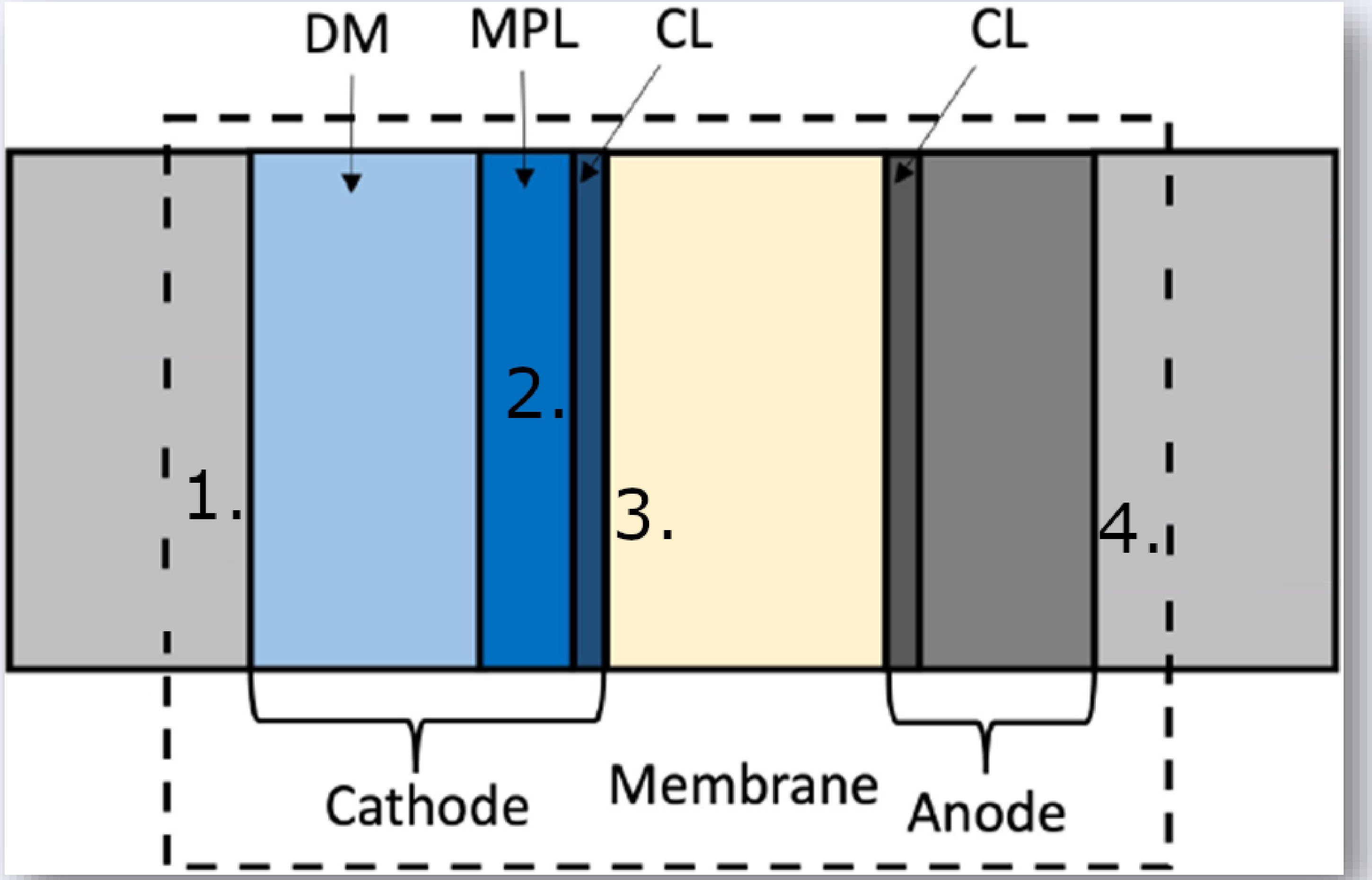
- Transport of Concentrated Species in Porous Media
  - Cathode DM, MPL, CL

- Darcy's law
  - Cathode DM, MPL, CL

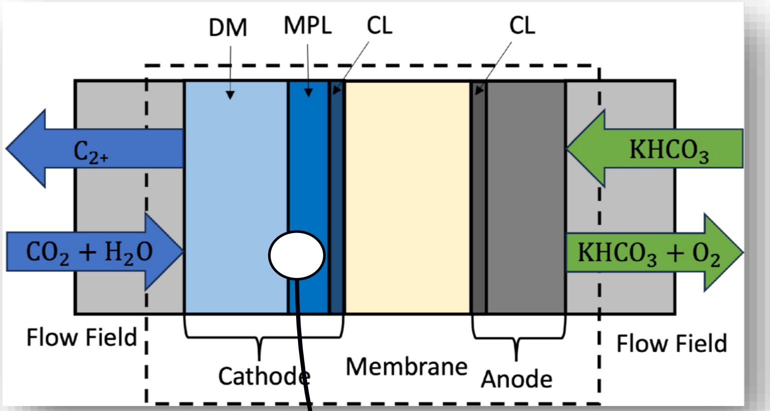
Physics

Boundary conditions

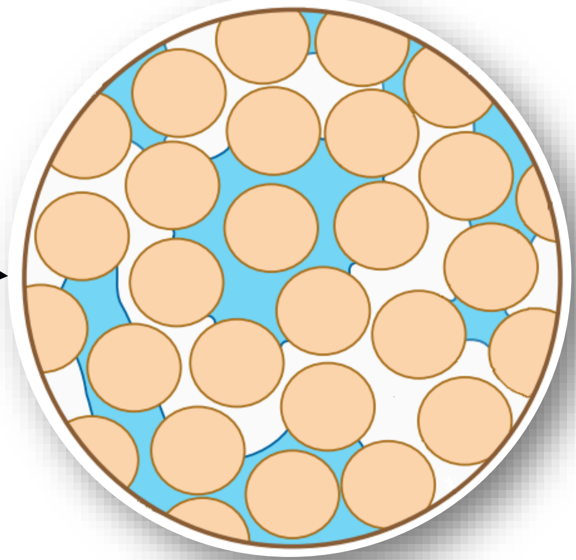
1. Gas channel | Cathode Diffusion Medium:
   - P = 1 atm
   - $\omega_{CO2} = 0.94$, $\omega_{H2O} = 0.04$, $\omega_{H2} = 0.01$, $\omega_{CO} = 0.01$
   - $\phi_s = 0$ V
2. Microporous Layer | Cathode Catalyst Layer:
   - $J_{aq} = 0$
3. Cathode Catalyst Layer | Membrane:
   - $J_{gas} = 0$
4. Anode Diffusion Medium | Anolyte:
   - $c_i = c_{equi}$
   - $\phi_s = \phi_{applied}$



Modelling electrode flooding

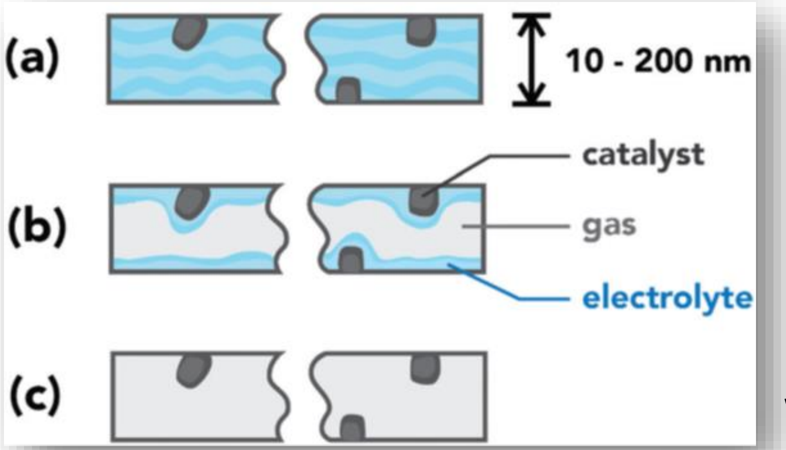


Multiphase flow in porous media



Simplified to parameter S

S: pore saturation



(a) S = 1, flooded case

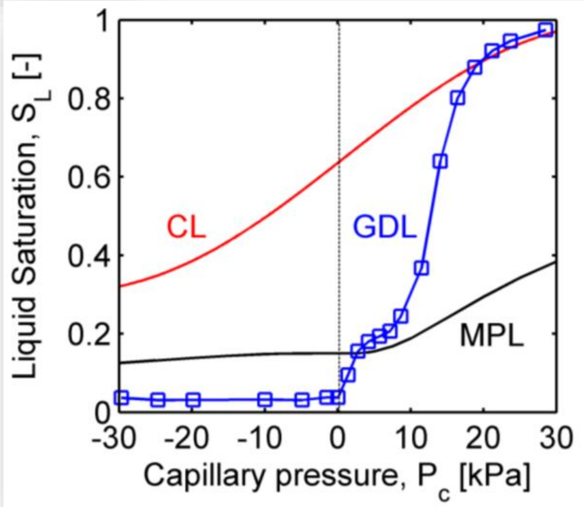
(b) 0 < S < 1, wetted case

(c) S = 0, dry case

Weng et al. (2018)

It depends on local conditions

Capillary pressure = $p_l - p_g$



Zenyuk et al. (2015)

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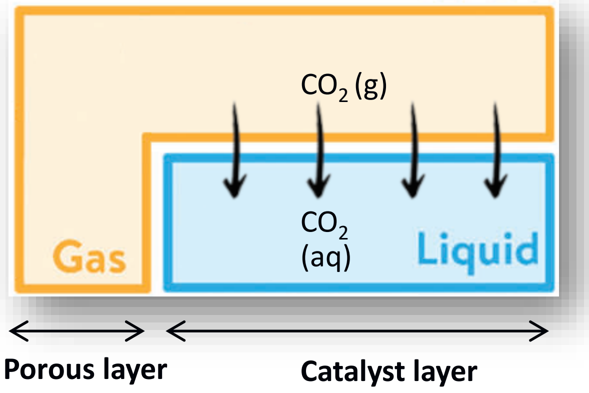
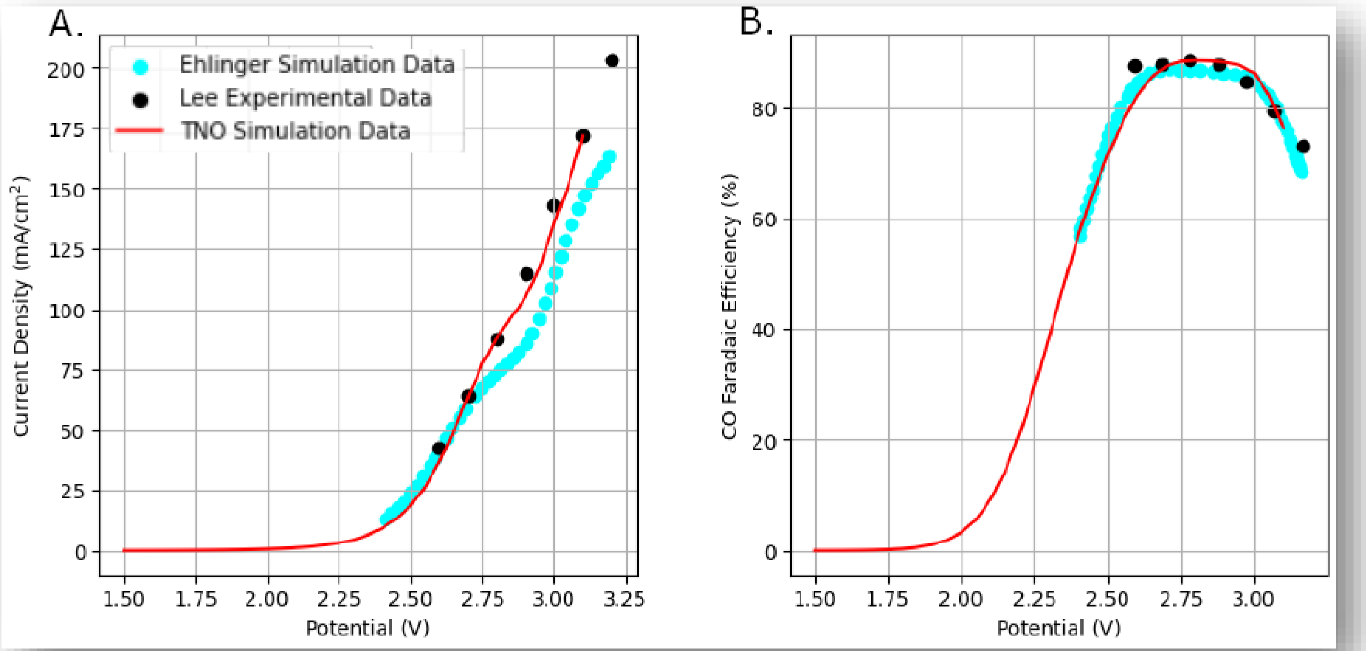
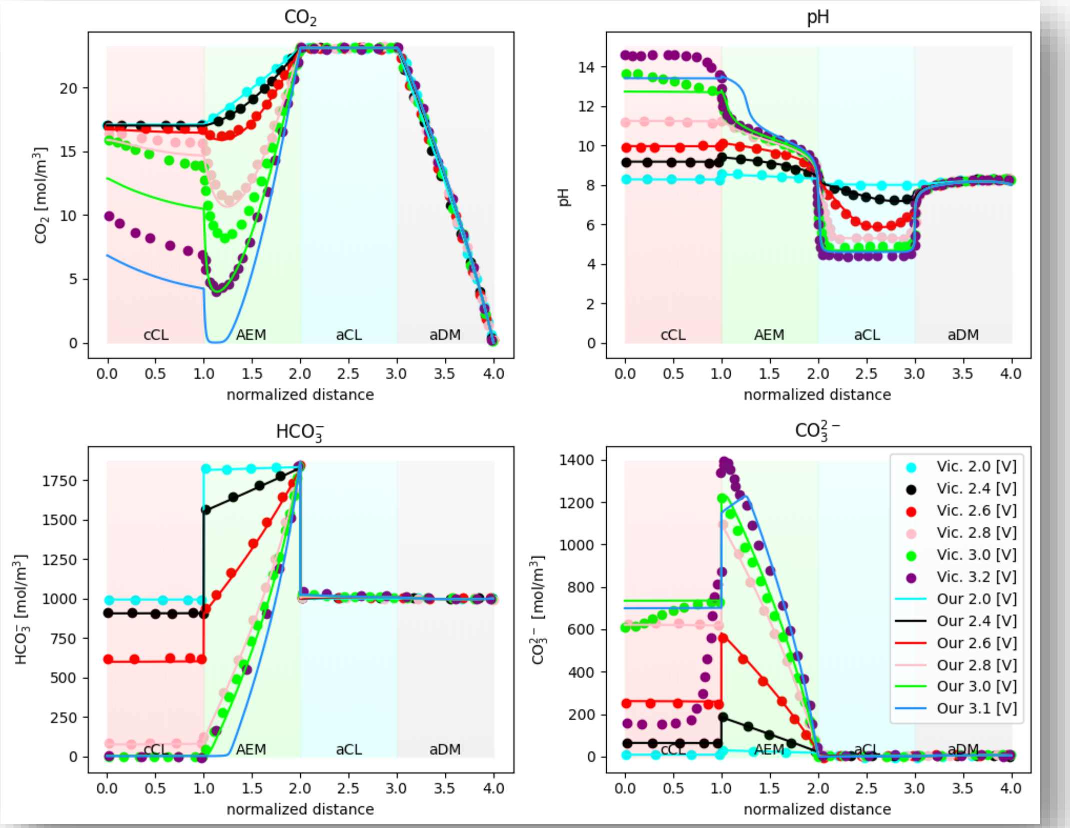
Model validation (for CO_2 to CO)

- Focus on gas-liquid behavior in cathode
- Accurate saturation curves crucial to capture decrease in Faradaic efficiency
- Several complex coupled phenomena: implementation details matter!



CO_2 dissolution in CL described as source term





We thank Victoria Ehlinger for useful correspondence

Extending the model to ethylene

- Include additional reactions to C2+ products
- Good agreement with previous literature (for “ideal” wetting of S=0.64)

$$CO_2 + H_2O + 2\,e^- \longrightarrow CO + 2\,OH^-$$
$$CO_2 + 2\,H_2O + 2\,e^- \longrightarrow HCOOH + 2\,OH^-$$
$$CO_2 + 6\,H_2O + 8\,e^- \longrightarrow CH_4 + 8\,OH^-$$
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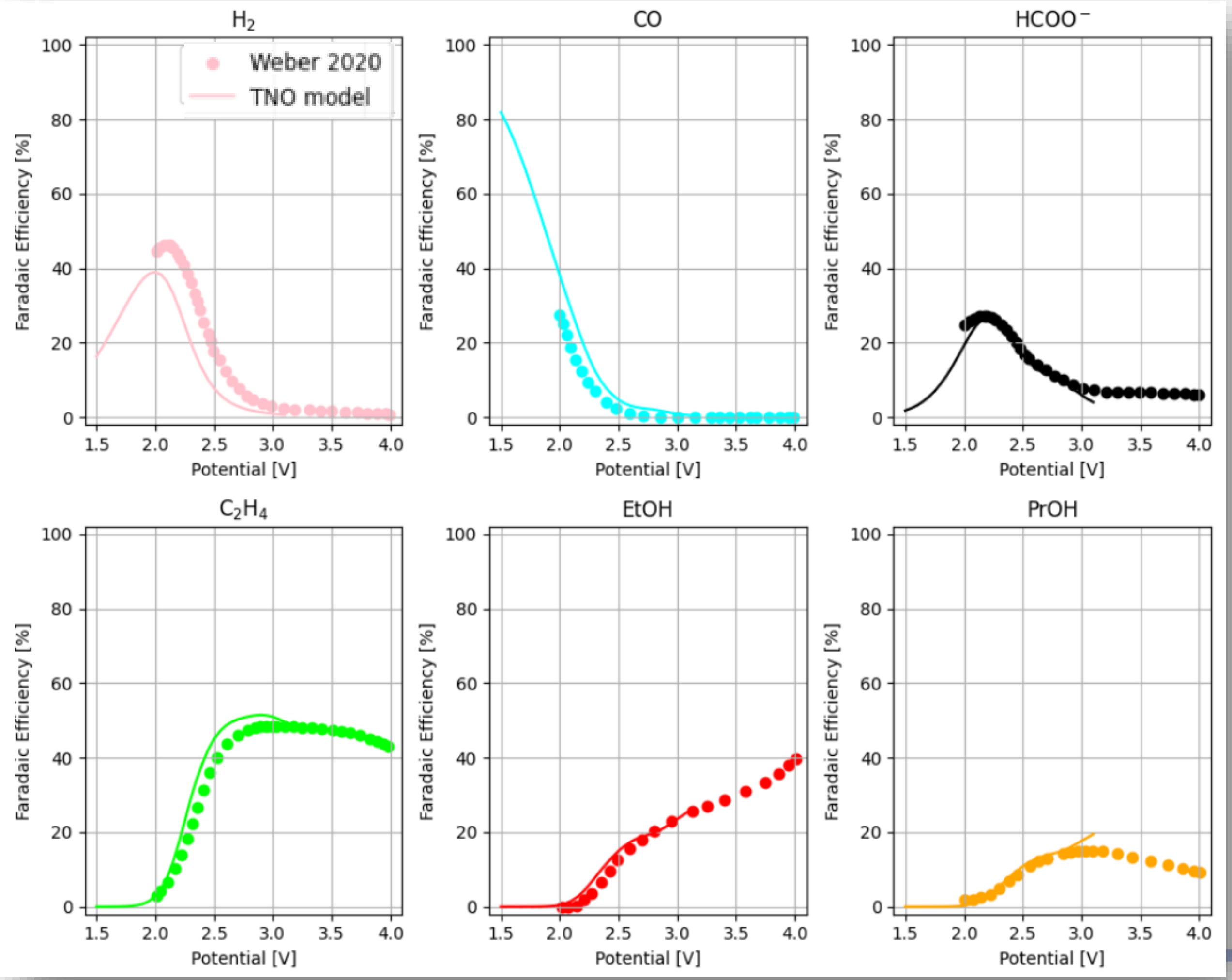
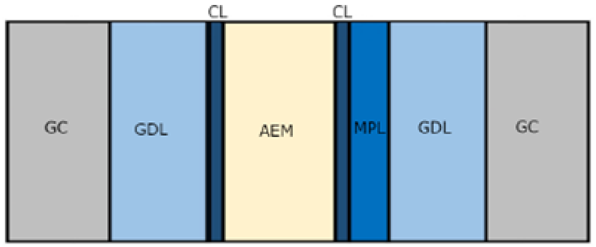
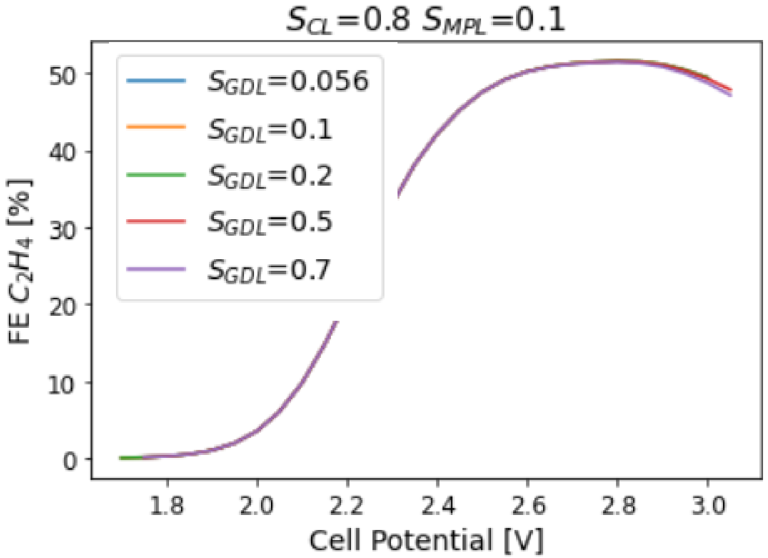


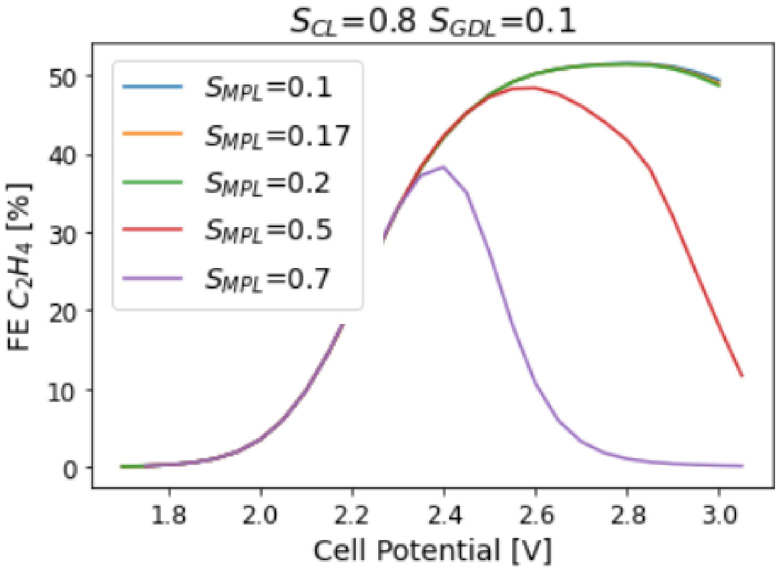
1D simulation results: gas-liquid management

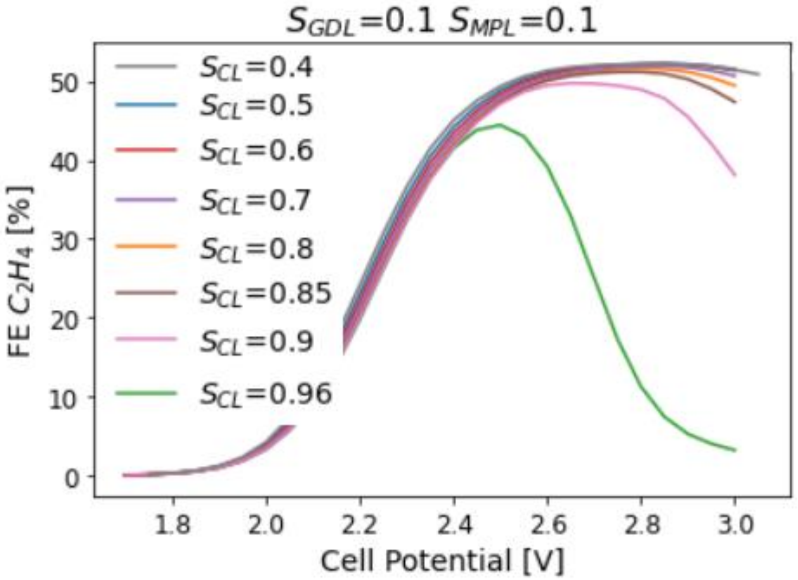
- Impact of (average) saturation level of the different cathode layers on Faradaic efficiency
  - GDL has minor impact
  - Flooding of MPL can also be detrimental
  - Catalyst layer is the most important one



cathode







2D simulations to address upscaling challenges

- Much less done in literature for 2D, especially for CO_2 to C_2H_4
  - Few studies on planar electrodes, microfluidic and GDE flow cells

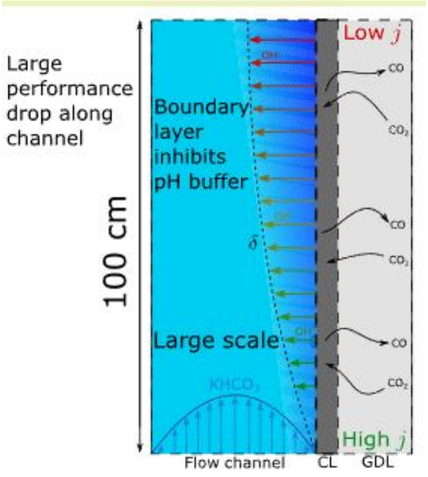
    Qiu et al., Env. Chem. Lett. (2023), Yang et al. ACS Sus. Chem. Eng. (2020), Kas et al. ACS Sus. Chem. Eng. (2021)

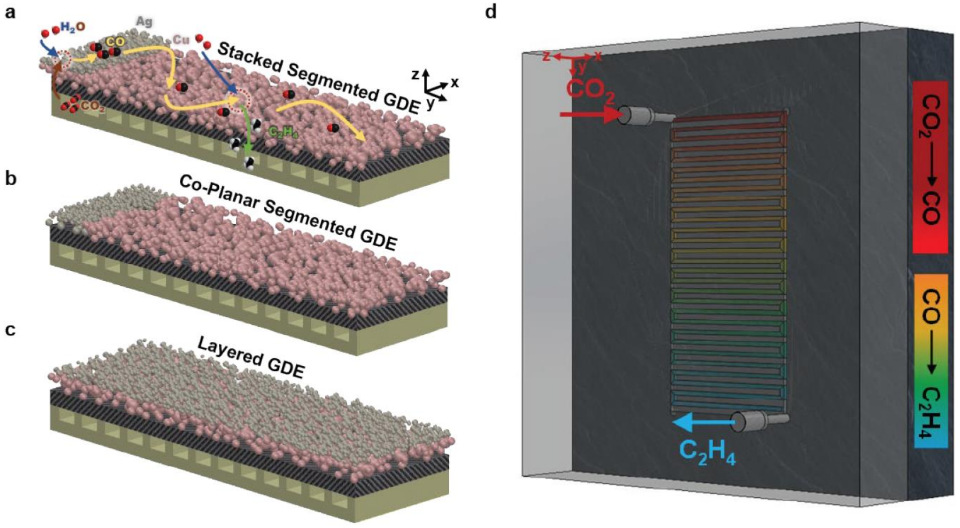
- 2D simulations to understand **limitations to single-pass conversion**
  - Blake *et al.* shown limitations in 1m-long CO_2->CO GDE flow cell, related to inhomogeneities in catalyst local environment

- 2D simulations to **optimize catalyst distribution**
  - **Segmented GDE:** two types of catalysts (silver + copper) to promote in-situ tandem reaction (CO_2->CO->C_2H_4)

  - What about **non-uniform** catalyst distribution?

Blake *et al.*, *ACS Sust. Chem. Eng.*, 11, 2840, (2023)





Zhang *et al.*, *Nat. Catal.*, 5, 201, (2022)

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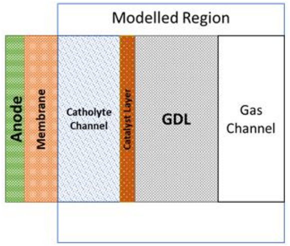
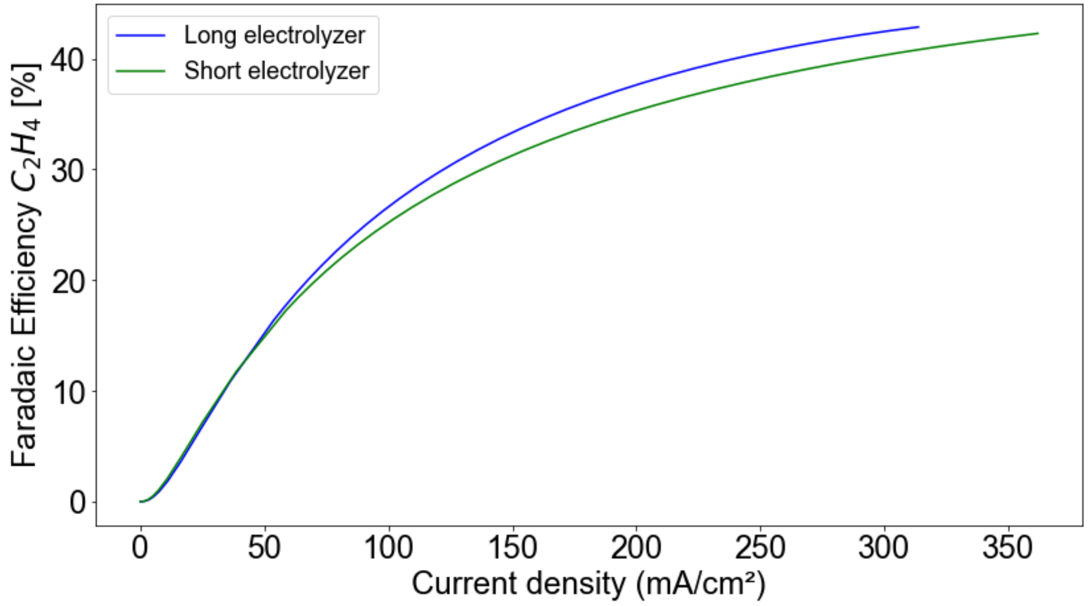
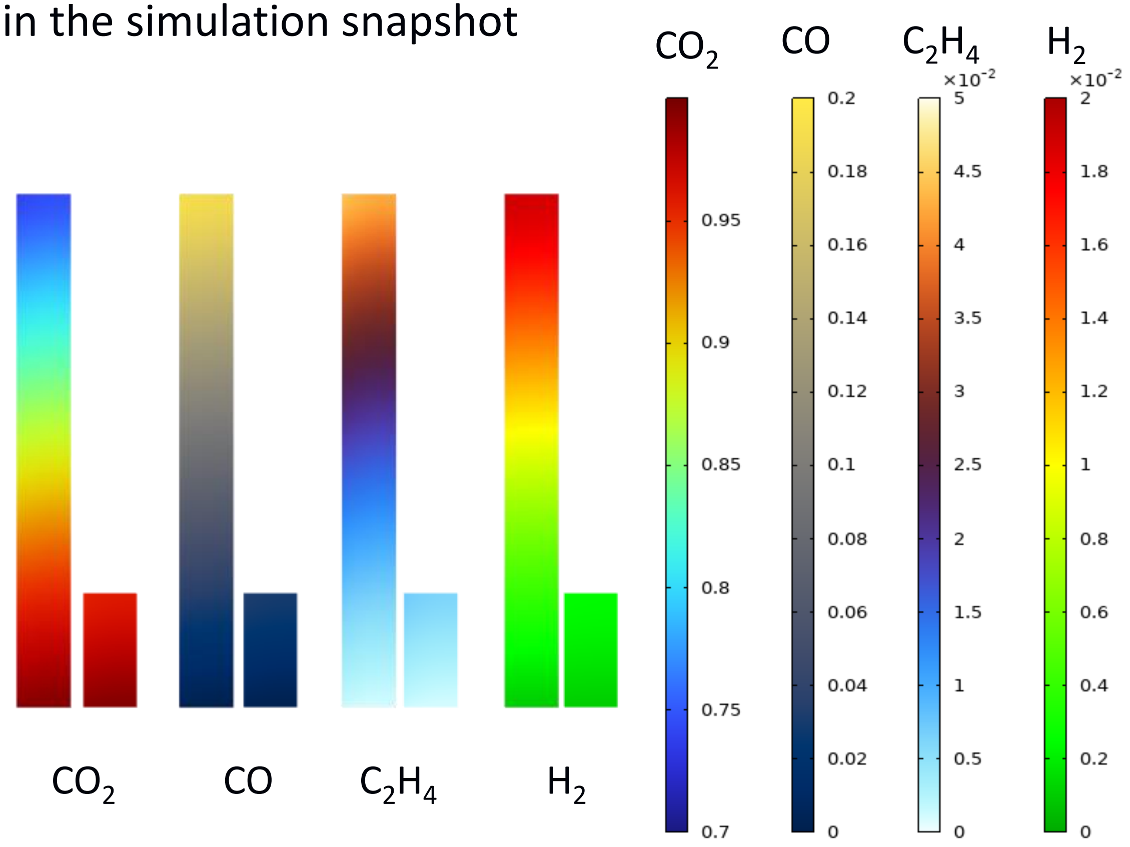
(ongoing) 2D simulations: counteracting inhomogeneities



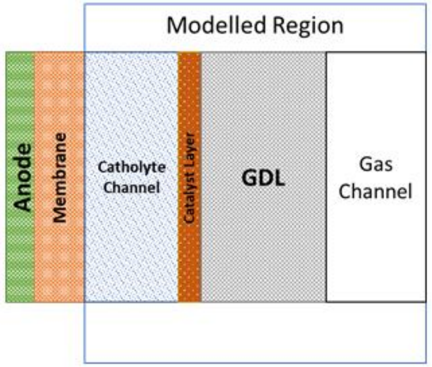
- Upto 10 cm long channel simulated
- High current density (300 mA/cm^2)
- For long channels, large **mass fraction gradients** seen in the simulation snapshot
- Performance is influenced due to inhomogeneity.



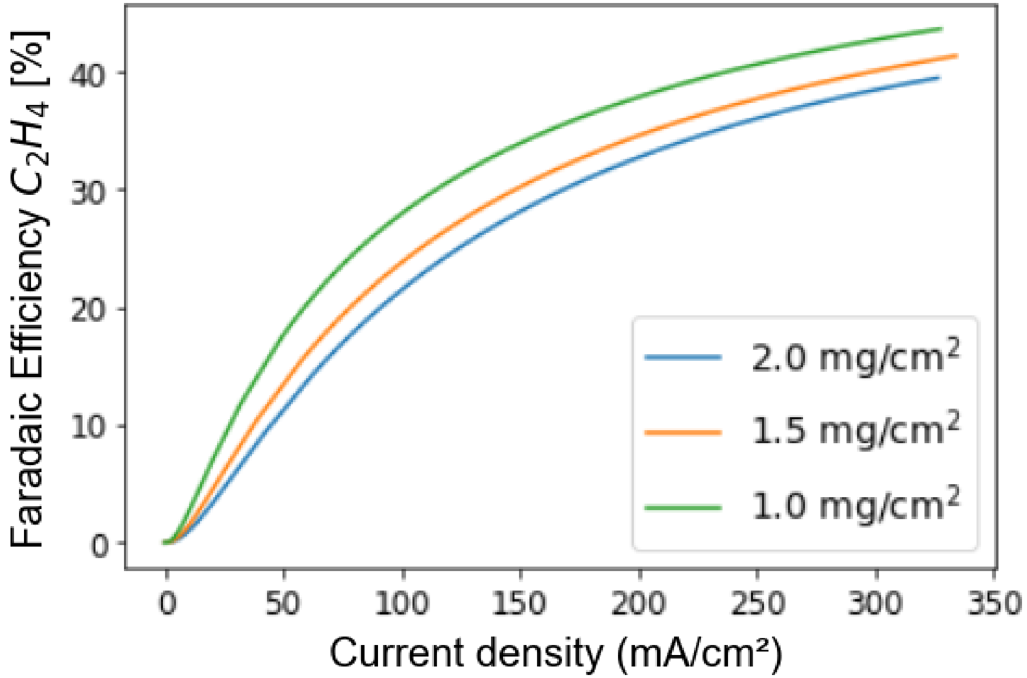


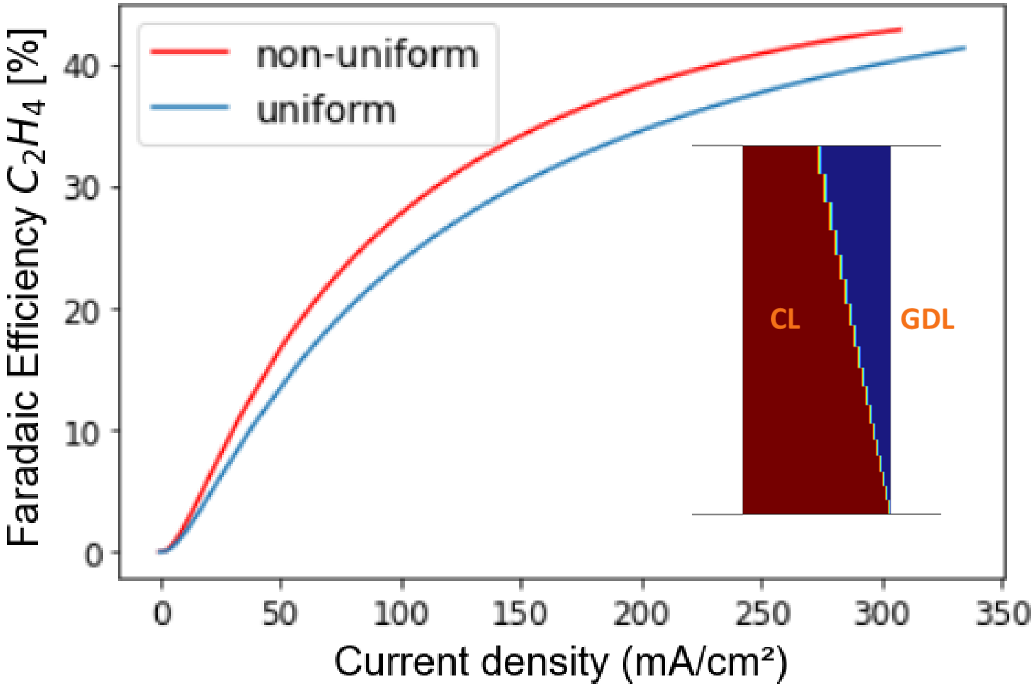
Shown mass fractions in gas channel (3mm wide)

(ongoing) 2D simulations: tuning catalyst loading

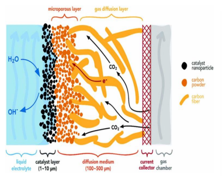
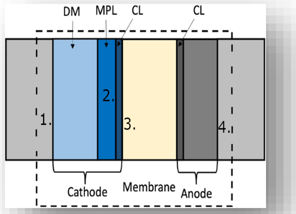


- Depending on manufacturing process, changes in catalyst loading can affect catalyst layer porosity, thickness, active surface area…
- **For a 10cm cell, decreasing (uniform) catalyst loading can improve performance**

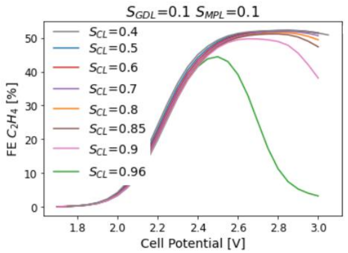




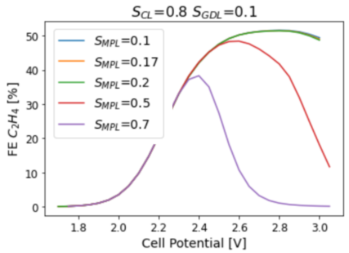
CONCLUSIONS

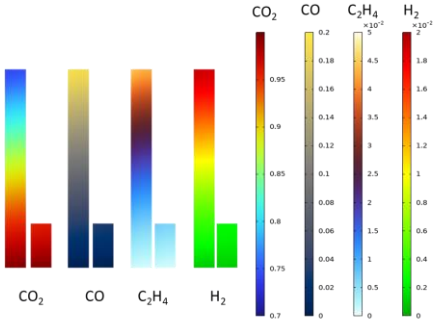
- We model different electrolyzer configurations: MEA and one gap configuration
- Catalyst layer design is crucial for performance of CO2 electrolyzer



- MPL could also be detrimental

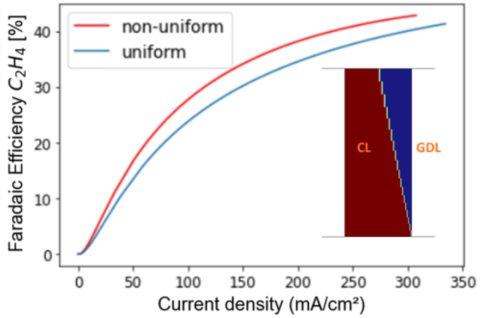


- There are large inhomogeneties in long electrolyzers



Shown mass fractions in gas channel (3mm wide)

- Catalyst loading can be tuned to improve performance



Thank you for your attention!

For more info, collaborations, internships/vacancies:
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