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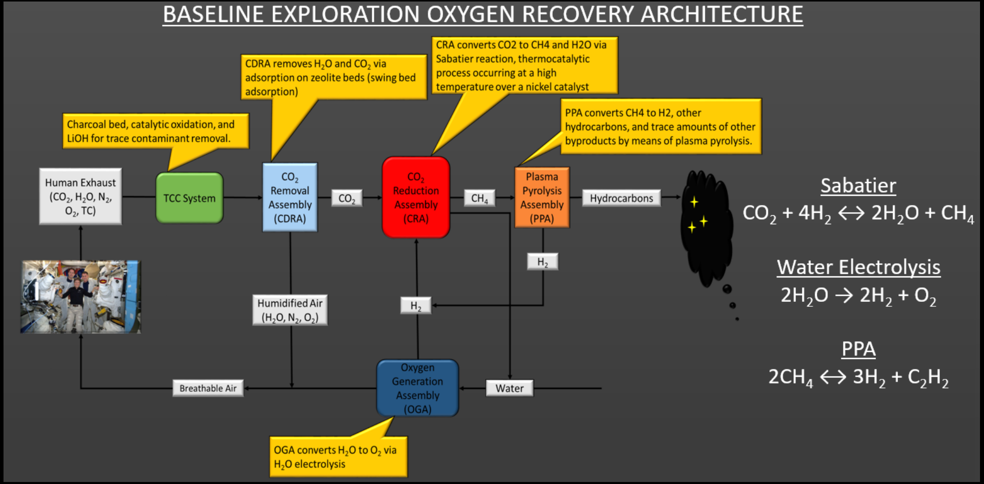
NASA Marshall Space
Flight Center (MSFC)

Modeling Electrolytic Conversion of Metabolic CO_2 and Optimizing a Microfluidic Electrochemical Reactor for Advanced Closed Loop Life Support Systems

Jesus A. Dominguez (Jacobs JSEG), Brittany Brown (NASA Marshall)
Brian Dennis (UTA), Wilaiwan Chanmanee (UTA)
Lorlyn Reidy (Jacobs JSEG), Peter Curreri (NASA Marshall),
Ellen M. Rabenberg (NASA Marshall), Kenneth A. Burke (NASA Glenn),

O_2 recovery from metabolic CO_2 at ISS

Current architecture via Sabatier approach coupled with water electrolysis



BASELINE EXPLORATION OXYGEN RECOVERY ARCHITECTURE

Charcoal bed, catalytic oxidation, and LiOH for trace contaminant removal.

CDRA removes H_2O and CO_2 via adsorption on zeolite beds (swing bed adsorption)

CRA converts CO2 to CH4 and H2O via Sabatier reaction, thermocatalytic process occurring at a high temperature over a nickel catalyst

PPA converts CH4 to H2, other hydrocarbons, and trace amounts of other byproducts by means of plasma pyrolysis.

OGA converts H_2O to O_2 via H_2O electrolysis

Sabatier

$$CO_2 + 4H_2 \leftrightarrow 2H_2O + CH_4$$

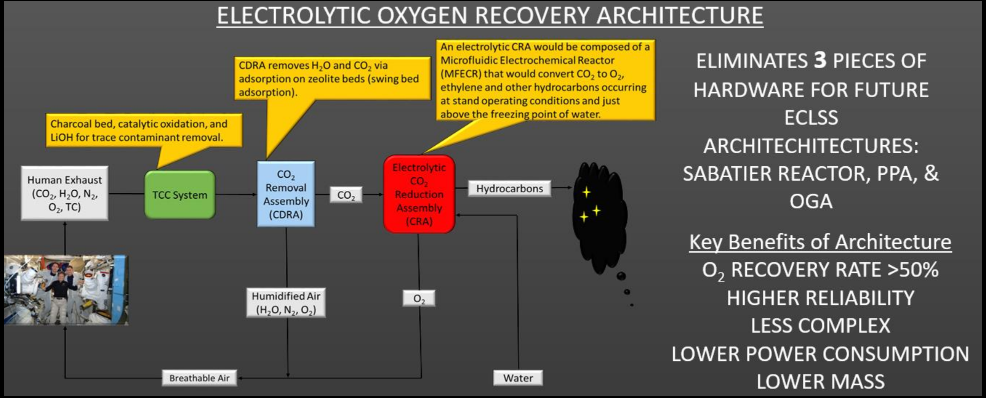
Water Electrolysis

$$2H_2O \rightarrow 2H_2 + O_2$$

PPA

$$2CH_4 \leftrightarrow 3H_2 + C_2H_2$$

Alternative architecture via electrolytic reduction of CO_2 to O_2 and C_2H_4



ELECTROLYTIC OXYGEN RECOVERY ARCHITECTURE

Charcoal bed, catalytic oxidation, and LiOH for trace contaminant removal.

CDRA removes H_2O and CO_2 via adsorption on zeolite beds (swing bed adsorption).

An electrolytic CRA would be composed of a Microfluidic Electrochemical Reactor (MFECR) that would convert CO_2 to O_2, ethylene and other hydrocarbons occurring at stand operating conditions and just above the freezing point of water.

ELIMINATES **3** PIECES OF HARDWARE FOR FUTURE ECLSS ARCHITECHITECTURES: SABATIER REACTOR, PPA, & OGA

Key Benefits of Architecture

O_2 RECOVERY RATE >50%

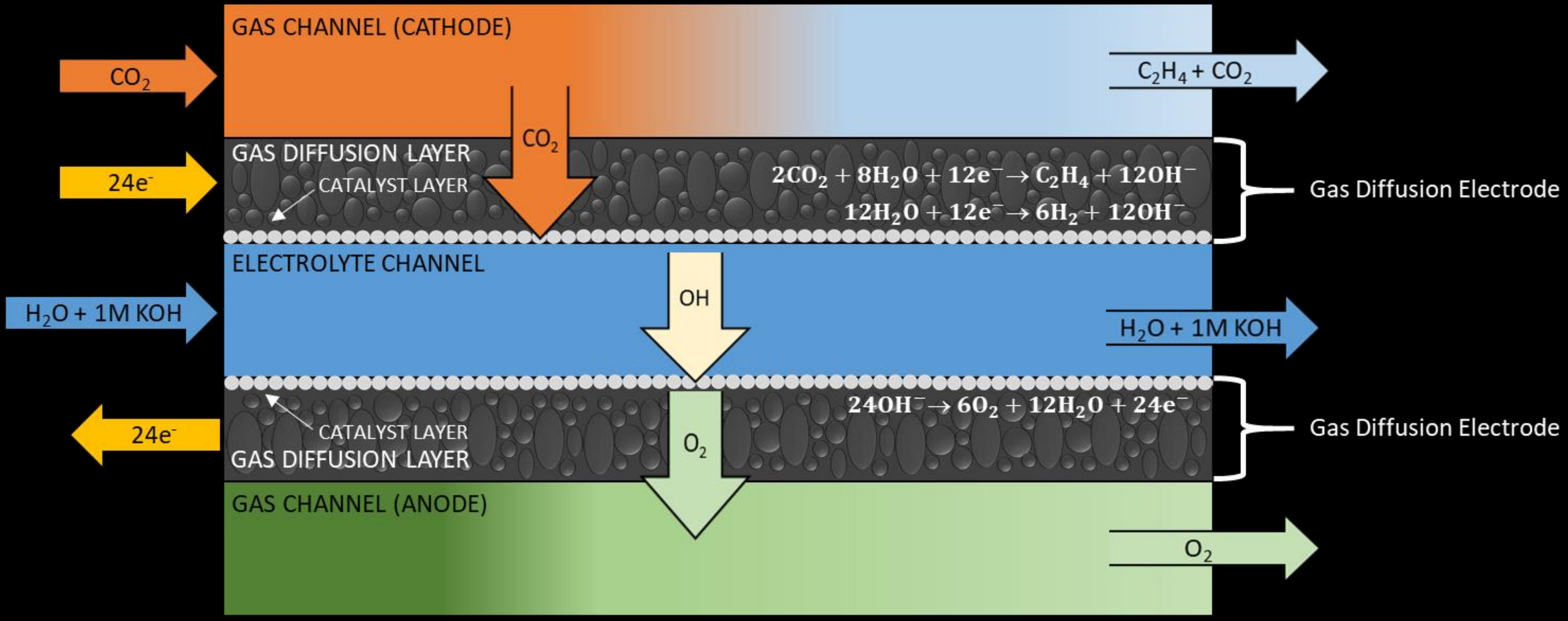
HIGHER RELIABILITY

LESS COMPLEX

LOWER POWER CONSUMPTION

LOWER MASS

O_2 recovery from metabolic CO_2 via selective electrolysis



GAS CHANNEL (CATHODE)

CO_2

CO_2

$C_2H_4 + CO_2$

GAS DIFFUSION LAYER

CATALYST LAYER

$24e^-$

$2CO_2 + 8H_2O + 12e^- \rightarrow C_2H_4 + 12OH^-$

$12H_2O + 12e^- \rightarrow 6H_2 + 12OH^-$

Gas Diffusion Electrode

ELECTROLYTE CHANNEL

H_2O + 1M KOH

OH

H_2O + 1M KOH

$24OH^- \rightarrow 6O_2 + 12H_2O + 24e^-$

$24e^-$

CATALYST LAYER

GAS DIFFUSION LAYER

O_2

Gas Diffusion Electrode

GAS CHANNEL (ANODE)

O_2

$$2CO_2 + 8H_2O \rightarrow C_2H_4 + 6H_2 + 6O_2$$

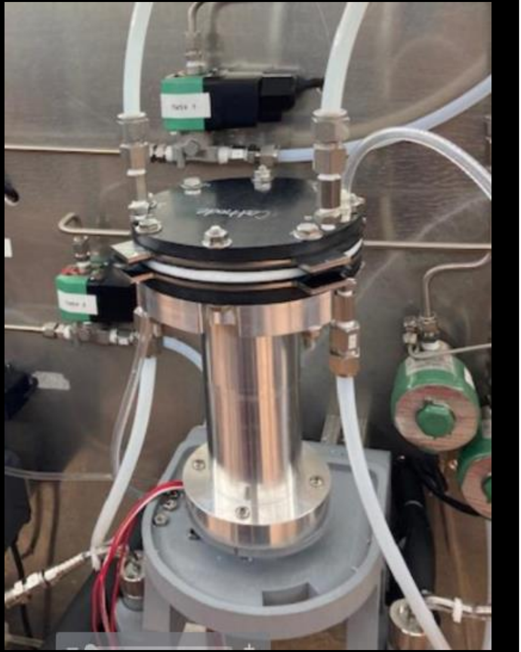
EDU’s model scope

- The model has the foundation and rigor to simulate the Engineering Design Unit (EDU) electrochemical (EC) process and optimize the design and operation of the EDU allowing efficient metabolic CO_2 reduction to C_2H_4 generating H_2 and O_2 as byproduct at ambient conditions.

- The EDU is installed in a test stand at NASA Marshall Space Flight Center (MSFC) equipped with all the instrumentation and sensors that will allow fully validation of the model including determination of the kinetics parameters for the key EC reactions.

EDU's test stand

Assembled EDU's elements



EDU installed in test stand

Test stand

EDU’s model domains

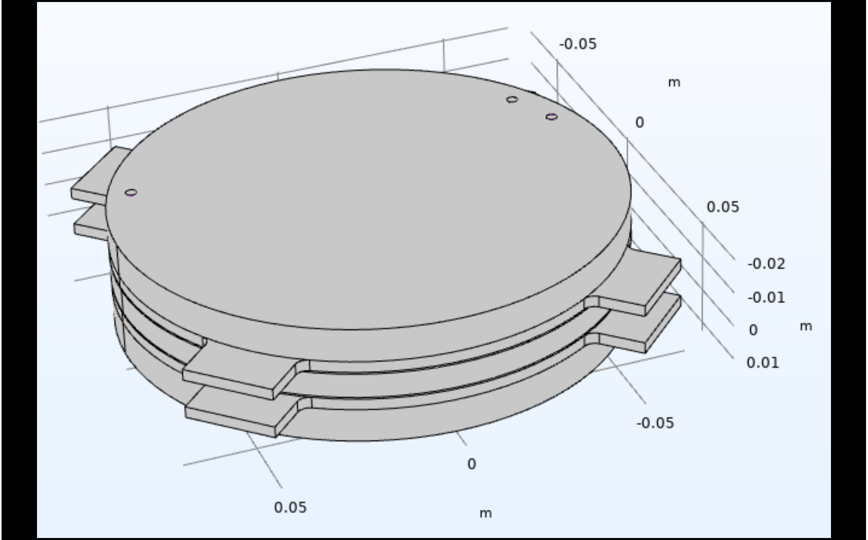
End plate

Electrode

Electrolyte

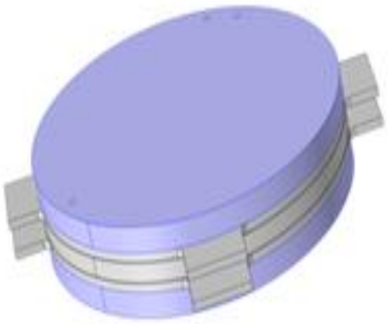
EDU’s elements

Assembled EDU’s elements

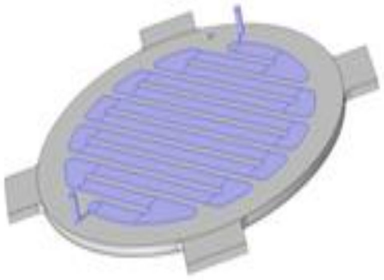


3D model at EDU’s scale

EDU's material and flow domains

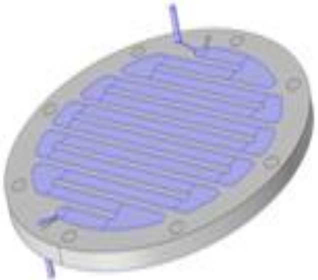


top and bottom endplates

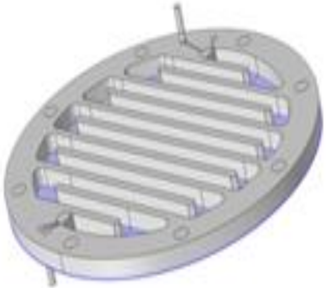


cathode channel and CO_2 flow

cathode GDE

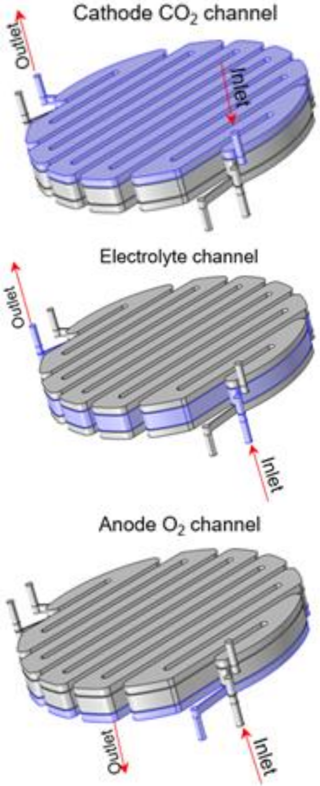


electrolyte channel and
KOH solution flow



anode GDE

anode channel and O_2 flow



EDU's model fundamentals

Multi-physics approach

- Electronic charge balance (Ohm's law)
- Ionic charge balance (Ohm's law)
- Concentration-dependent Butler-Volmer and Tafel charge transfer kinetics
- Flow distribution in gas and liquid channels (Navier-Stokes)
- Flow in the porous GDEs (Brinkman equations)
- Mass balances in gas phase in both gas channels and porous electrodes (Maxwell-Stefan diffusion and convection)
- Evaporation and condensation of water on the GDLs and gas channels
- Temperature (energy balance equation) via three types of heat transfer mechanisms,
  1) conductive within EDU's components,
  2) convective within the channel flows,
  3) radiative between EDU surface and ambient
- Heat generation/source via Joule heating effect.

EDU’s model fundamentals

Electrochemical reactions

CO_2 Conversion to C_2H_4 with H_2 as byproduct

Acid Electrolyte	**E° (V)**
Cathode	
$2CO_2 + 12H^+ + 12e^- = C_2H_4 + 4H_2O$	-0.35
$12H^+ + 12e^- = 6H_2$	0.00
Anode	
$12H_2O = 24H^+ + 24e^- + 6O_2$	-1.23
Total	
$2CO_2 + 8H_2O = C_2H_4 + 6H_2 + 6O_2$	-1.58

Alkaline Electrolyte	
Cathode	
$2CO_2 + 8H_2O + 12e^- = C_2H_4 + 12OH^-$	-1.18
$12H_2O + 12e^- = 6H_2 + 12OH^-$	-0.40
Anode	
$12OH^- = 6H_2O + 12e^- + 3O_2$	-0.83
Total	
$2CO_2 + 8H_2O = C_2H_4 + 6H_2 + 6O_2$	-2.41

H_2O Electrolysis

Acid Electrolyte	**E° (V)**
Cathode	
$4H^+ + 4e^- = 2H_2$	0.00
Anode	
$2H_2O = 4H^+ + 4e^- + O_2$	-1.23
Total	
$2H_2O = 2H_2 + O_2$	-1.23

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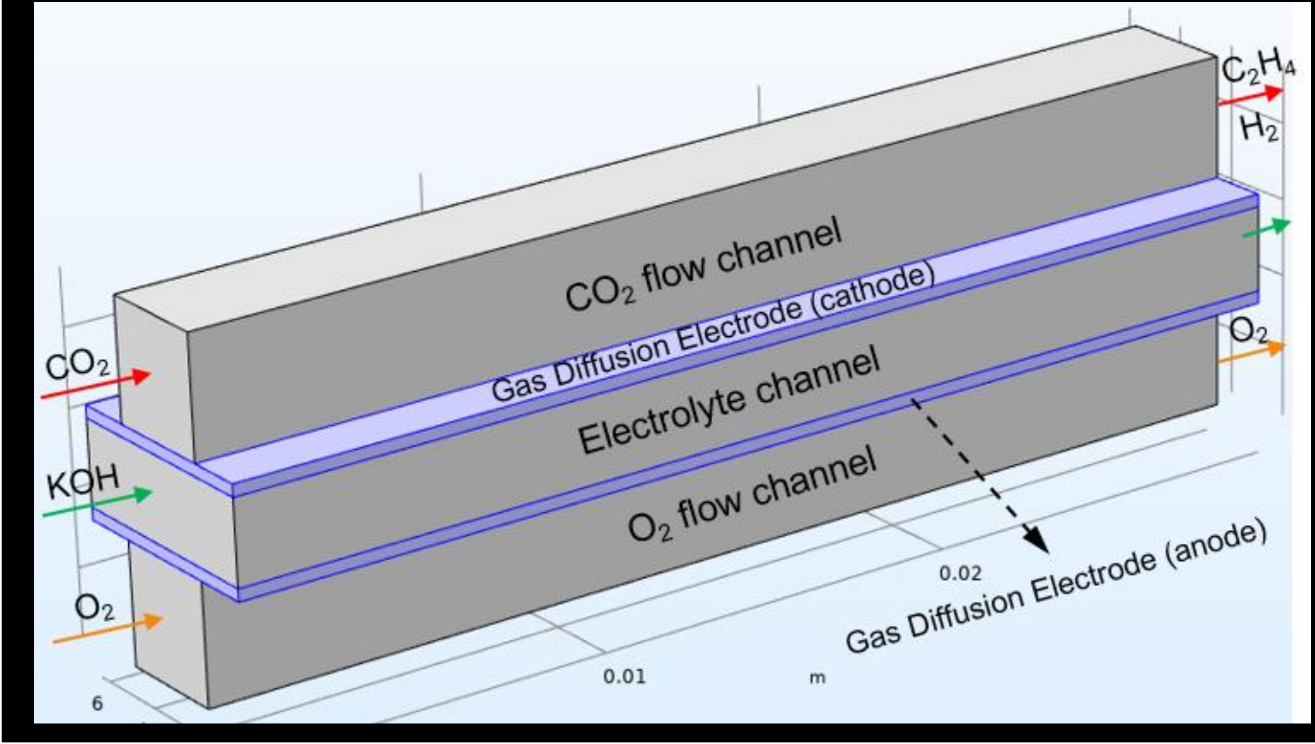
EDU’s model fundamentals

Electrochemical reaction domains



Alkaline Electrolyte

Cathode

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Anode

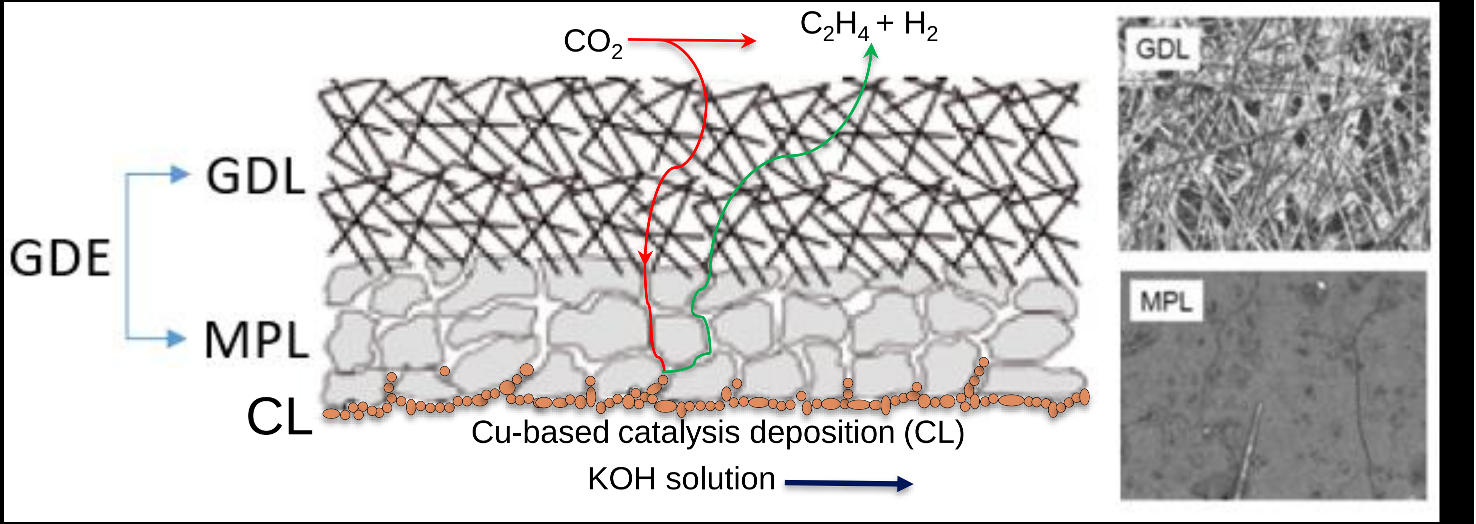
$12OH^- = 6H_2O + 12e^- + 3O_2$

Total

$2CO_2 + 8H_2O = C_2H_4 + 6H_2 + 6O_2$

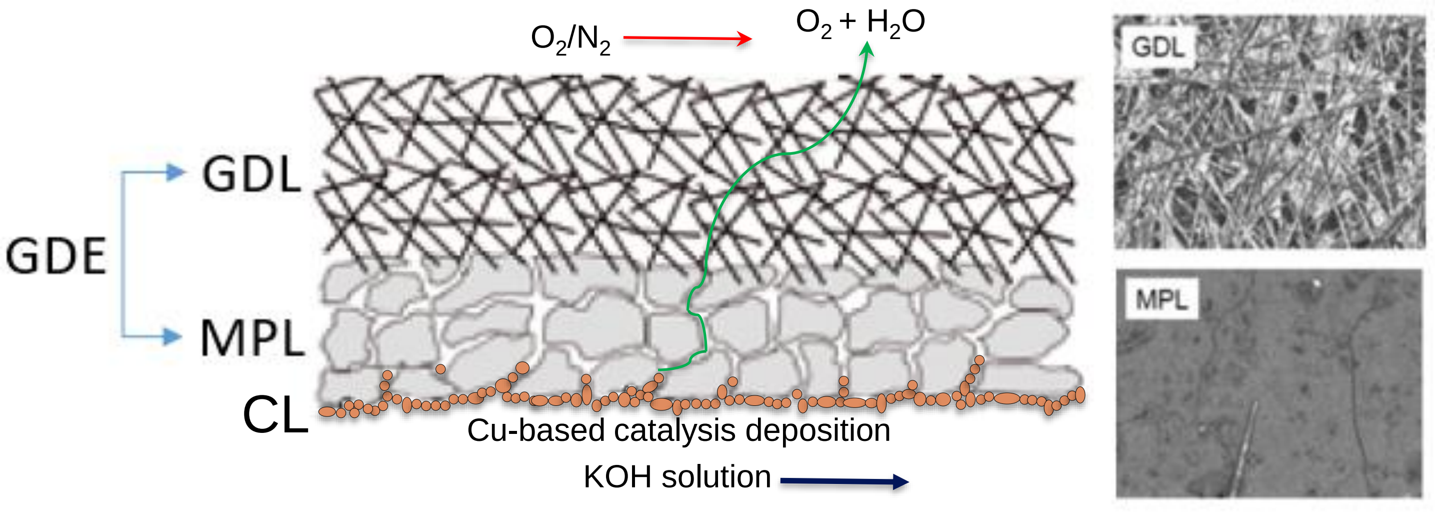
EDU’s model fundamentals

Cathode GDL



EDU’s model fundamentals

Anode GDL

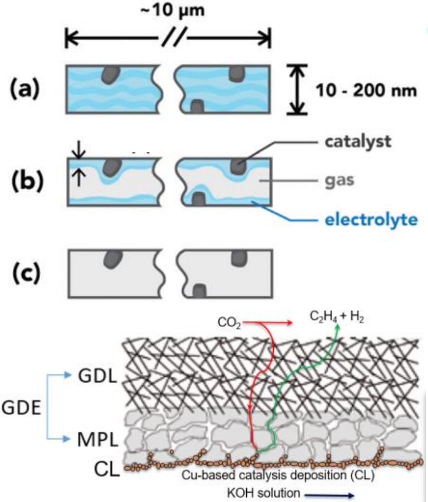


EDU’s model fundamentals

Electrochemical CO_2 reduction approach

- The exact microstructure of the CL is not well known.
- Many have argued that the high current densities achievable with GDEs is due to a high concentration of CO_2 at the gas/solid interface overcoming the low solubility of CO_2 in water.
- Recent experimental and theoretical work have demonstrated the importance of water and hydrated cations on the elementary processes involved in CO_2R superseding the role of CO_2 gas phase within the GDLs.
- Therefore, researchers have proposed that it is necessary for the catalyst to be covered with electrolyte in order to be active. This means that although CO_2 is supplied to the GDE from the gas phase, the reactant at the catalyst site is still dissolved CO_2.

- The performance of a GDL greatly depends on the local environment within the CL and the balance between transport phenomena and reaction kinetics.
- Based on the capillary pressure, CL pore-size distribution and their wettability, the pores can be a) flooded, b) wetted or c) dry.



Gas dissolution $CO_2\,(g) \leftrightarrow CO_2\,(aq)$

$$R_{CO_2(aq)} = R_{CO_2(g)} = a_{gl}\,K_{GL} M_{CO_2}\left[\frac{P_{CO_2(g)}}{H_{CO_2}} - C_{CO_2(l)}\right]$$

a_{gl} = specific gas-liquid interface area

H_{CO_2} = Henry constant for CO_2 in electrolyte

K_{GL} = Overall mass transfer coefficient = $1\text{x}10^{-4}$ m.s^{-1}

M_{CO_2} = CO_2 molecular weight = 44 g/mol

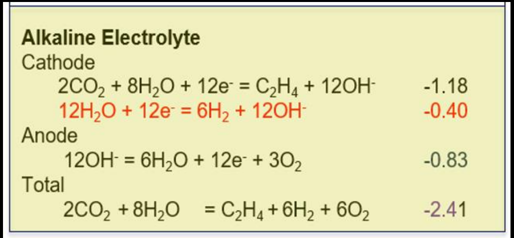
$P_{CO_2(g)}$ = CO_2 partial pressure (gas phase)

$C_{CO_2(l)}$ = CO_2 concentration (liquid phase)

$$i_{co_2} = -i_{o,co_2}^{ref}\left[\frac{C_{CO_2(aq)}}{C_{CO_2(aq)}^{ref}}\right]\exp\left[-\frac{\beta_{co_2}F\eta}{RT}\right] \quad \text{(Tafel kinetics)}$$

EDU’s model fundamentals

Water phase change and transportation on GDLs



Alkaline Electrolyte

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Anode

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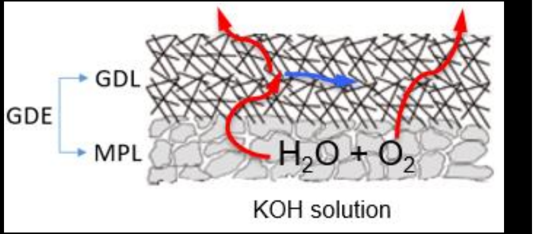
Total

$2CO_2 + 8H_2O = C_2H_4 + 6H_2 + 6O_2$	-2.41

8 moles of water consumed on the cathode
6 moles of water generated on the anode



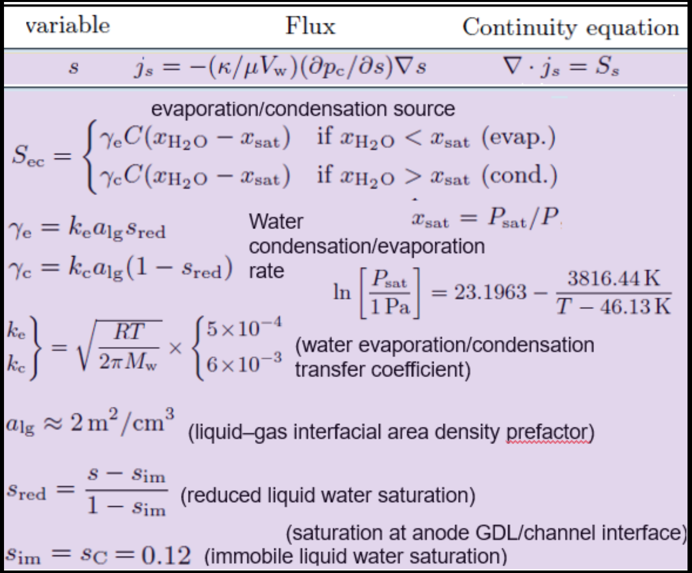
- A capillary pressure formulation of Darcy’s law is used to model the transport of liquid water in the cathode:
  - Saturation level, s, is dependent variable
- The liquid water flux, j_s, is defined as

  $$j_s = -\frac{\kappa}{\mu V_w}\frac{\partial p_c}{\partial s}\nabla s$$

  μ = viscosity and V_w = molar volume of liquid water

  κ = permeability and p_c = capillary pressure, both depend on s
- An evaporation-condensation rate expression is added as source term to account for the liquid water-vapor phase transfer

How much water is condensed within the GDL?



variable	Flux	Continuity equation
s	$j_s = -(\kappa/\mu V_\mathrm{w})(\partial p_\mathrm{c}/\partial s)\nabla s$	$\nabla \cdot j_s = S_s$

evaporation/condensation source

$$S_\mathrm{ec} = \begin{cases} \gamma_\mathrm{e} C(x_\mathrm{H_2O} - x_\mathrm{sat}) & \text{if } x_\mathrm{H_2O} < x_\mathrm{sat} \text{ (evap.)} \\ \gamma_\mathrm{c} C(x_\mathrm{H_2O} - x_\mathrm{sat}) & \text{if } x_\mathrm{H_2O} > x_\mathrm{sat} \text{ (cond.)} \end{cases}$$

$$\gamma_\mathrm{e} = k_\mathrm{e} a_\mathrm{lg} s_\mathrm{red}$$

$$\gamma_\mathrm{c} = k_\mathrm{c} a_\mathrm{lg} (1 - s_\mathrm{red})$$

Water condensation/evaporation rate

$$x_\mathrm{sat} = P_\mathrm{sat}/P$$

$$\ln\left[\frac{P_\mathrm{sat}}{1\,\mathrm{Pa}}\right] = 23.1963 - \frac{3816.44\,\mathrm{K}}{T - 46.13\,\mathrm{K}}$$

$$\left.\begin{matrix} k_\mathrm{e} \\ k_\mathrm{c} \end{matrix}\right\} = \sqrt{\frac{RT}{2\pi M_\mathrm{w}}} \times \begin{cases} 5\times10^{-4} \\ 6\times10^{-3} \end{cases}$$

(water evaporation/condensation transfer coefficient)

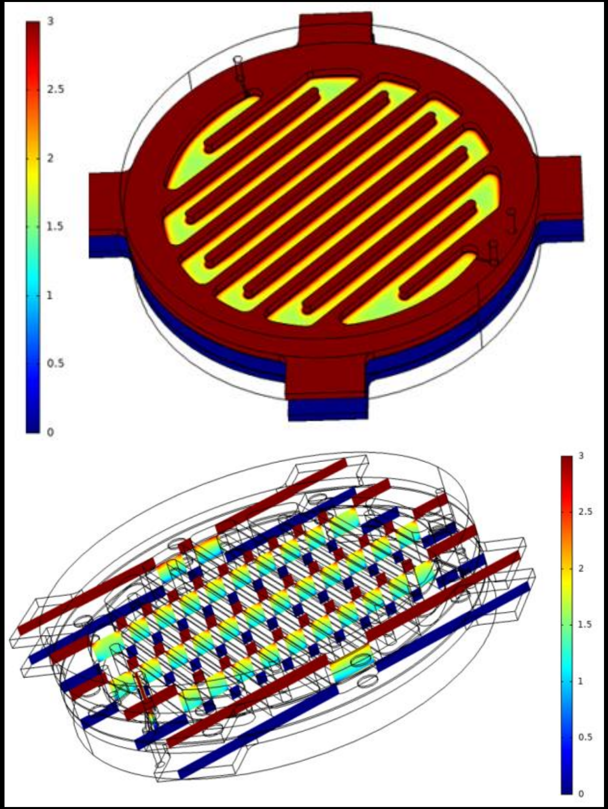
$a_\mathrm{lg} \approx 2\,\mathrm{m}^2/\mathrm{cm}^3$ (liquid–gas interfacial area density prefactor)

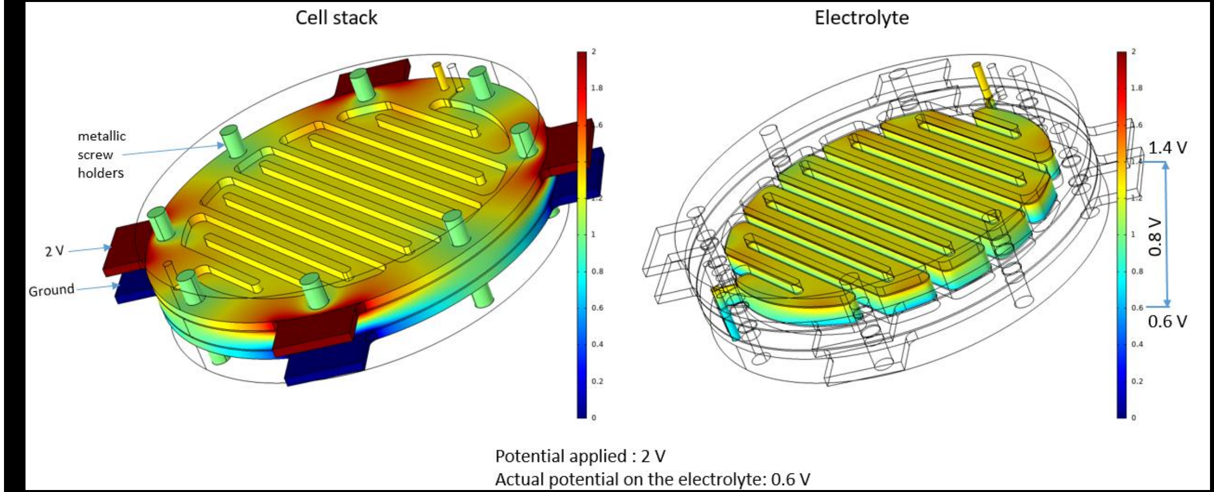
$s_\mathrm{red} = \frac{s - s_\mathrm{im}}{1 - s_\mathrm{im}}$ (reduced liquid water saturation)

(saturation at anode GDL/channel interface)

$s_\mathrm{im} = s_\mathrm{C} = 0.12$ (immobile liquid water saturation)

EDU’s model outcome
Electrical potential



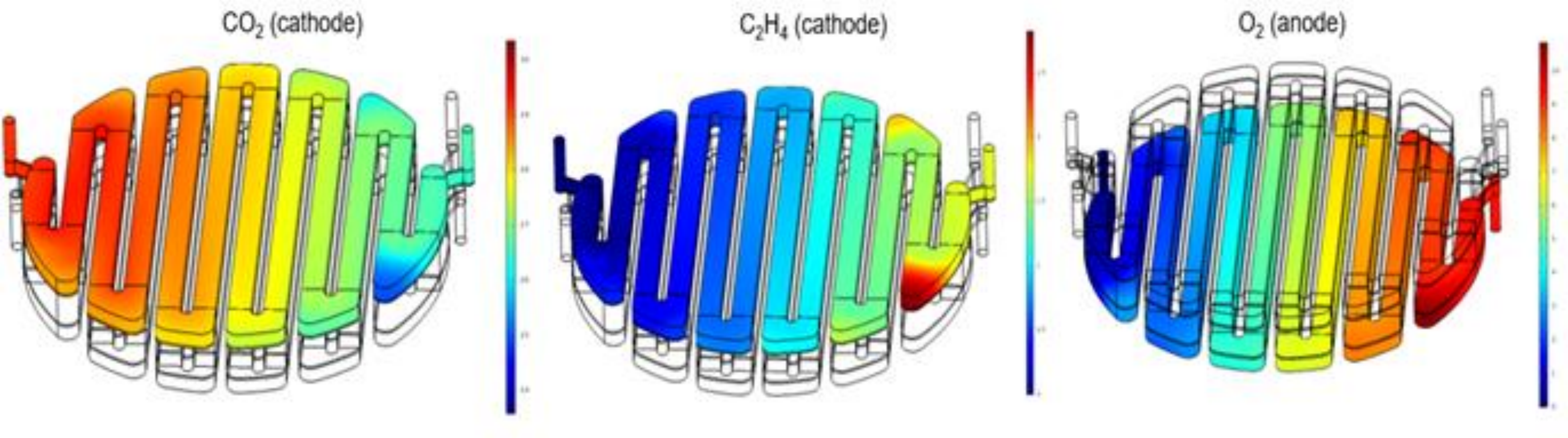


Potential applied : 2 V
Actual potential on the electrolyte: 0.6 V

Worst case scenario for potential application to the cell: Metallic screw holders no insulated

EDU’s model outcome

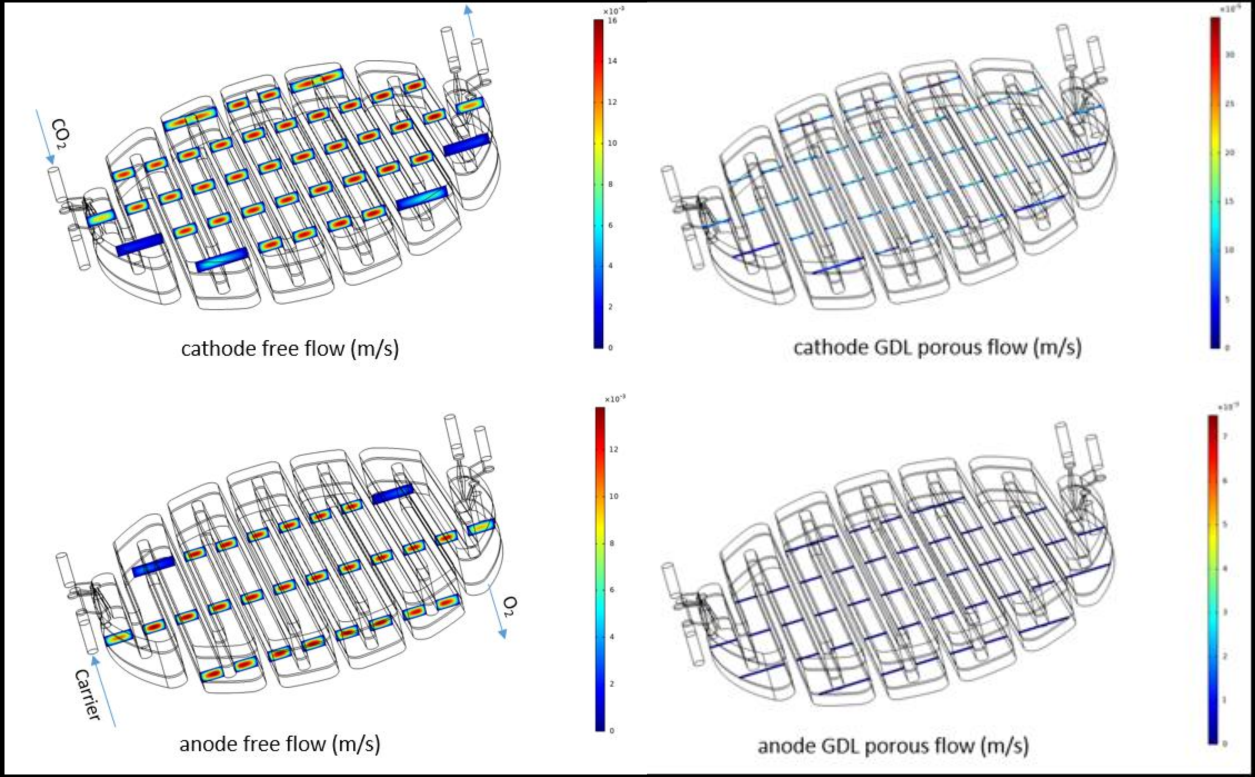
Mass concentration



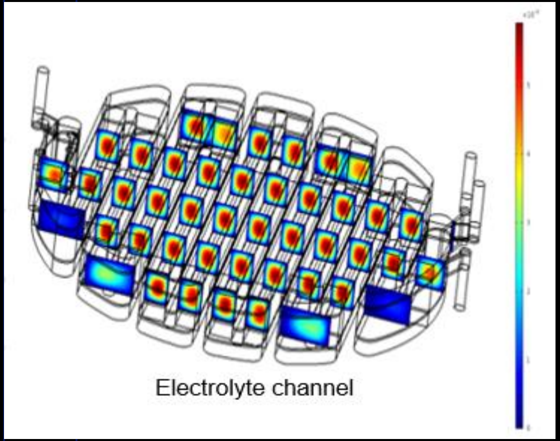
Component mass concentration

EDU's model outcome

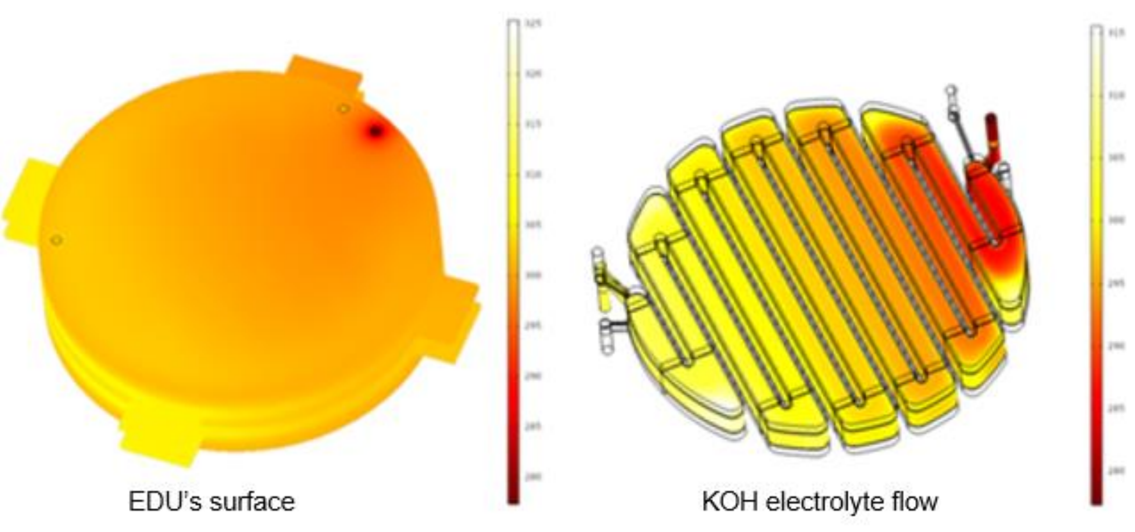
Flow velocity



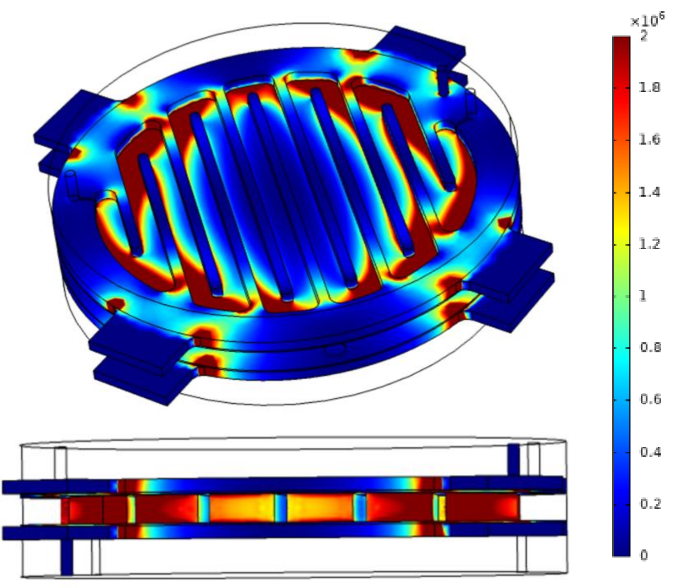
Flow velocity



EDU's model outcome
Temperature and Joule heating

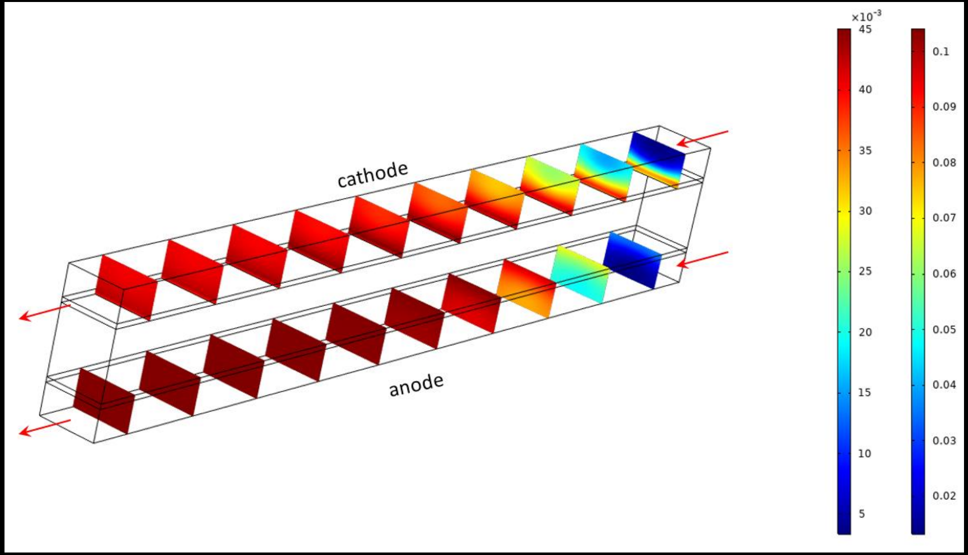


Temperature

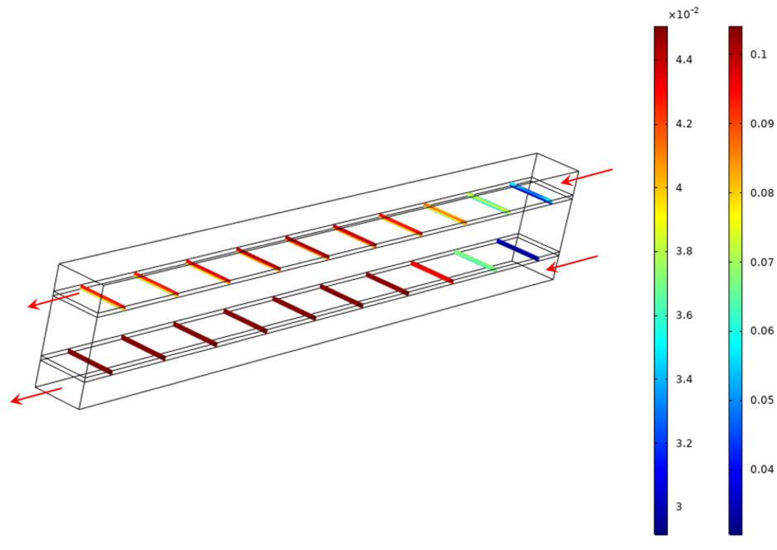


Joule Heating

EDU’s model outcome
Water (liquid/vapor) transport

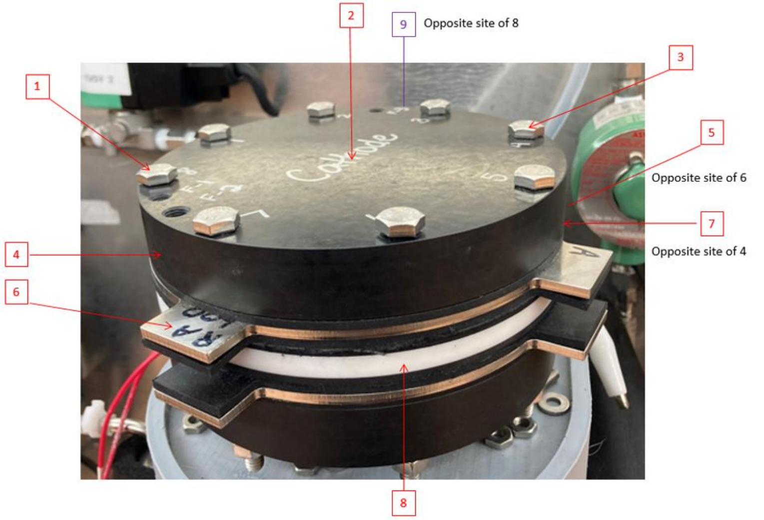


Water vapor on channels and GDLs

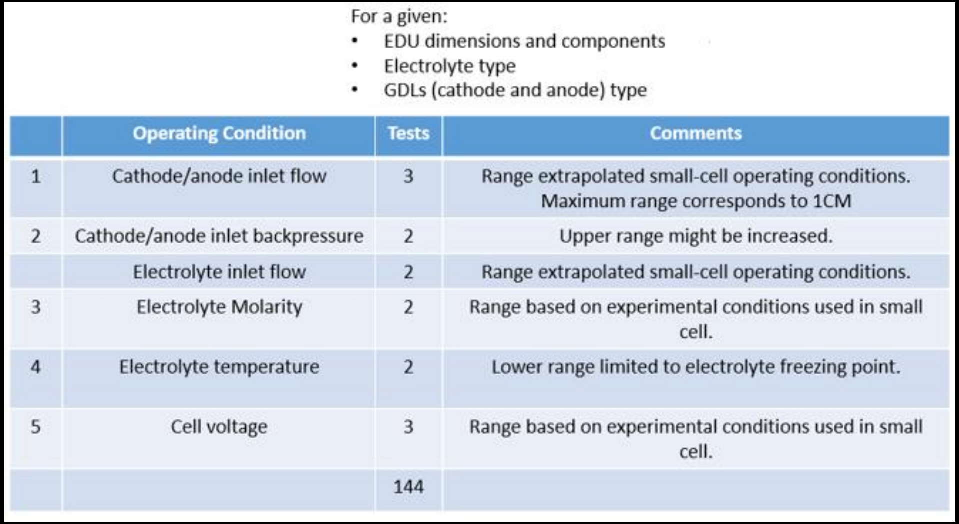


Water liquid on GDLs

Next: Model Validation



Estimation of natural convection coefficient via least-square temperature error minimization (Levenberg–Marquardt algorithm)



For a given:
- EDU dimensions and components
- Electrolyte type
- GDLs (cathode and anode) type

	Operating Condition	Tests	Comments
1	Cathode/anode inlet flow	3	Range extrapolated small-cell operating conditions. Maximum range corresponds to 1CM
2	Cathode/anode inlet backpressure	2	Upper range might be increased.
	Electrolyte inlet flow	2	Range extrapolated small-cell operating conditions.
3	Electrolyte Molarity	2	Range based on experimental conditions used in small cell.
4	Electrolyte temperature	2	Lower range limited to electrolyte freezing point.
5	Cell voltage	3	Range based on experimental conditions used in small cell.
		144	

Experiment test matrix
Correlation evaluation via Independent Component analysis (ICA)

Acknowledge

- Special thanks to Dr. Enrique Jackson for his support and assistance on the use of a high-performance computational system (512 MB of RAM) that has allowed the authors to run the model in hours rather than days.
- We would like to thank Mr. Max McCall for his valuable contribution on the MFECR’s mechanical design and generation of the 3D model domains.
- We are also thankful to Matthew Russell, Allison Burns, Samantha Hall, and Christian Coris for their contribution on the development and implementation of the model during their internship at MSFC.

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NASA Marshall Space Flight Center (MSFC)

THANKS!!
Questions?