Role of ammonia decomposition in the operation of DA-SOFC: numerical and experimental study

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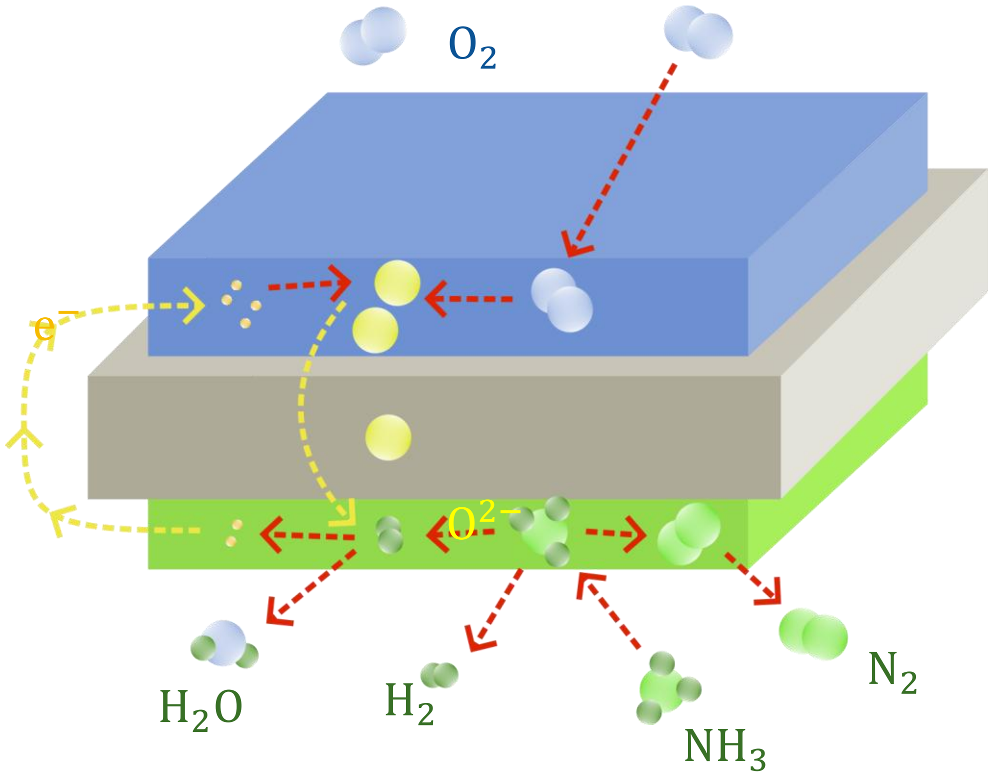
MOTIVATION

The promise of solid oxide fuel cells (SOFC)



Advantages | Driving force

High efficiency
Fuel flexibility

Disadvantages | Opportunities

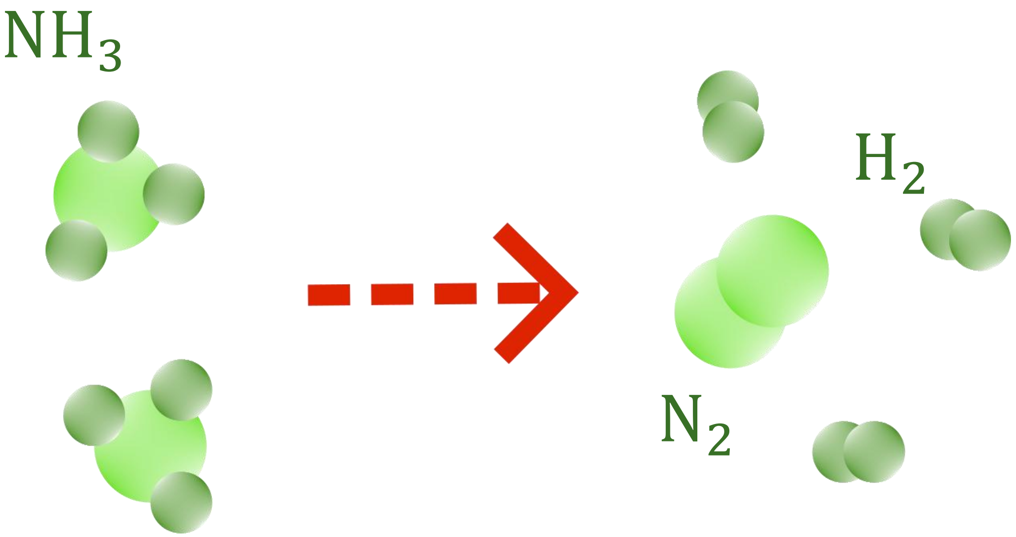
High temperature
High cost
Stability and degradation
Operational difficulties

Challenge | Objective

Reduce operating temperature while minimizing degradation and improving both efficiency and power output

MOTIVATION

Ammonia cracking



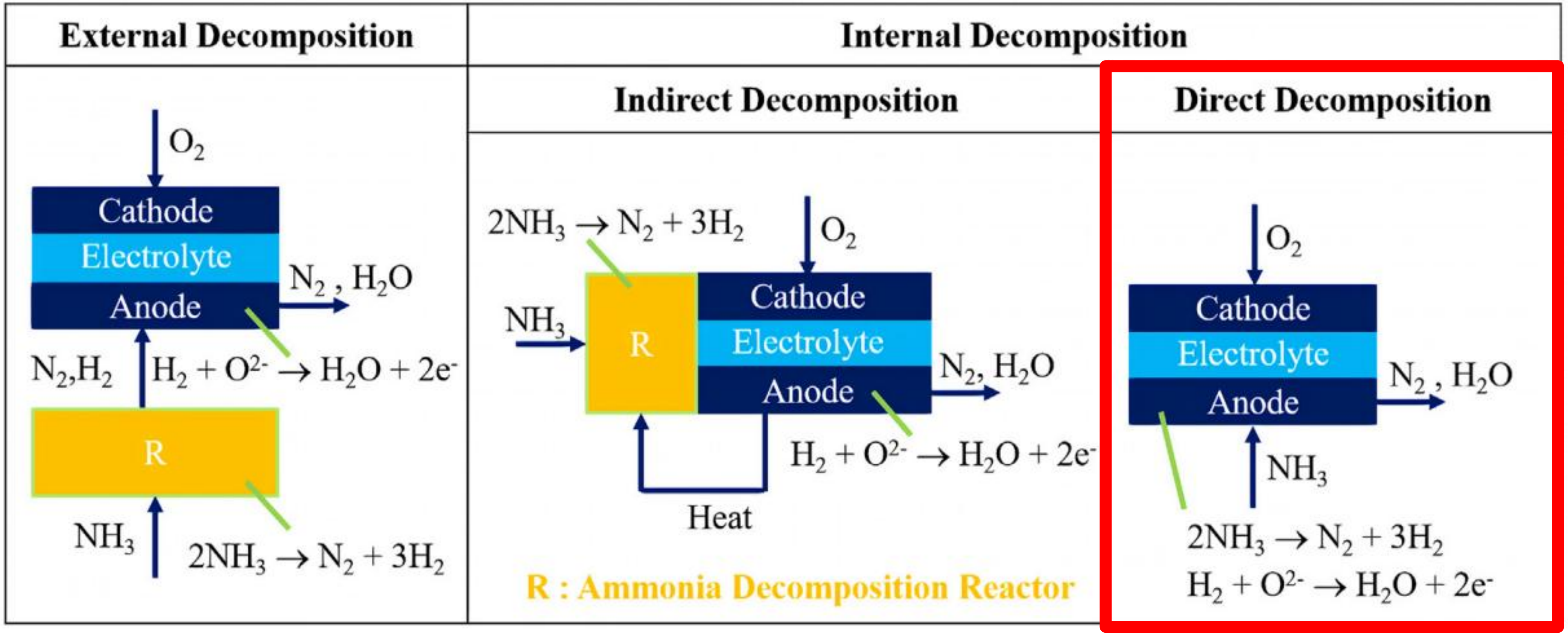
$$2\,NH_3 \longleftrightarrow N_2 + 3\,H_2$$

- Endothermic reaction.
- Occurs at high temperature ($T > 500$ °C)
- Catalysts are often used, Nickel being a popular choice.
- Many intermediate steps, simplification is desirable.
- Adsorption steps result in degradation (corrosion).

MOTIVATION

Types of ammonia SOFC

Classification according to location of ammonia cracking



Rathore et al. Int J Hydrogen Ener 2021, DOI: 10.1016/j.ijhydene.2021.08.092

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METHODS

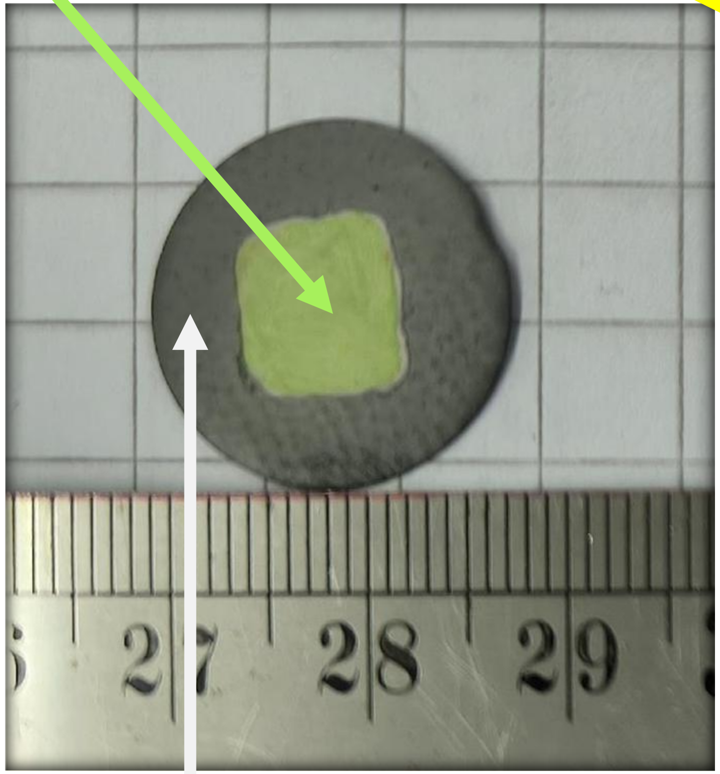
Experiment

Furnace

Anode: Ni-GDC

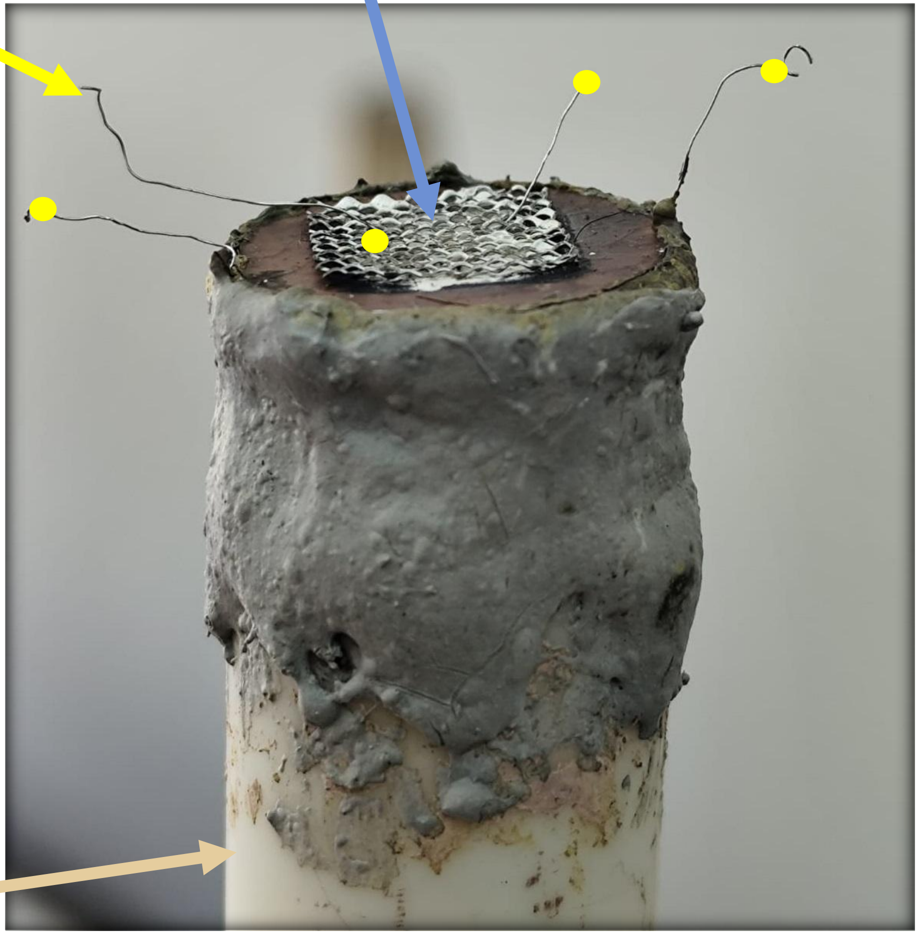
Current collectors

Cathode: $SrCo_{0.95}Re_{0.05}O_{(3-\delta)}$



Electrolyte: LSGM

Tubes: Alumina



Experimental setup @UACH (courtesy of prof. Loreto Troncoso)

METHODS

Experiment

Furnace

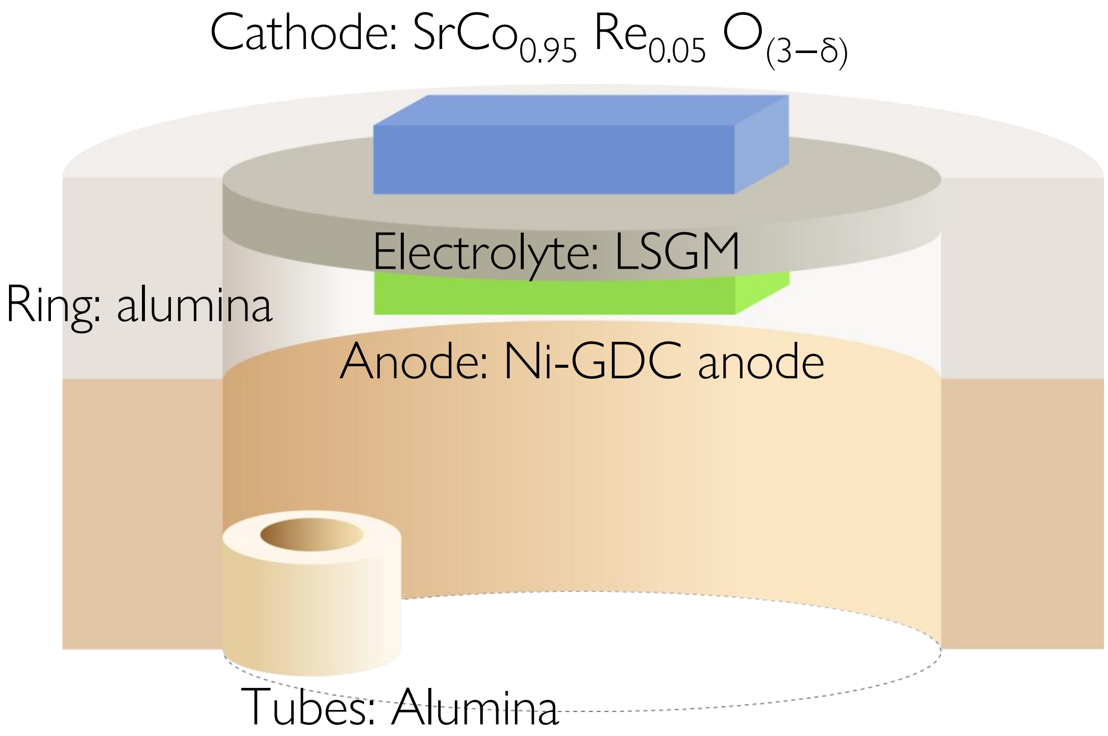
- Both pure H_2 and pure NH_3 used as fuel.
- Furnace temperature set to $T_{\text{fnc}} = 650\ °\text{C}$, $700\ °\text{C}$ and $750\ °\text{C}$.
- Applied a potential V_{cell} in the $0.22\ \text{V}$ ~ $1.1\ \text{V}$ range and measured current and power outputs.

CONTENTS

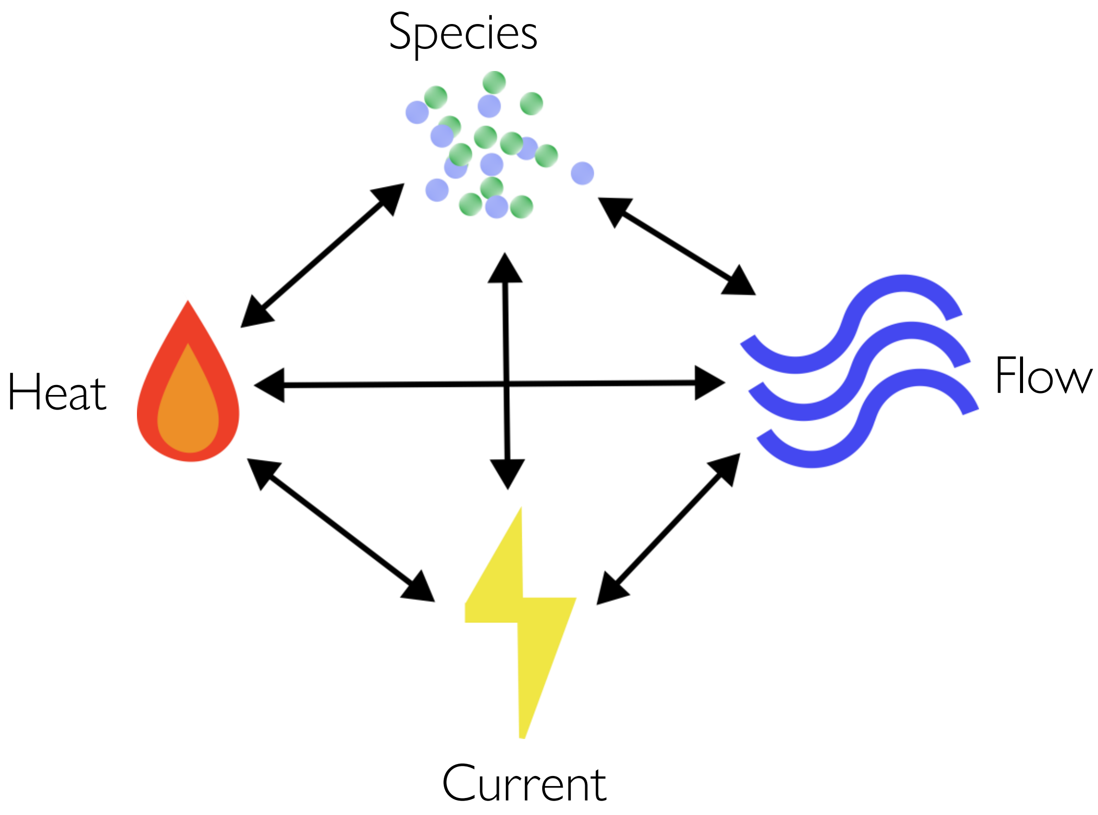
METHODS

Simulation

Full 3D geometry



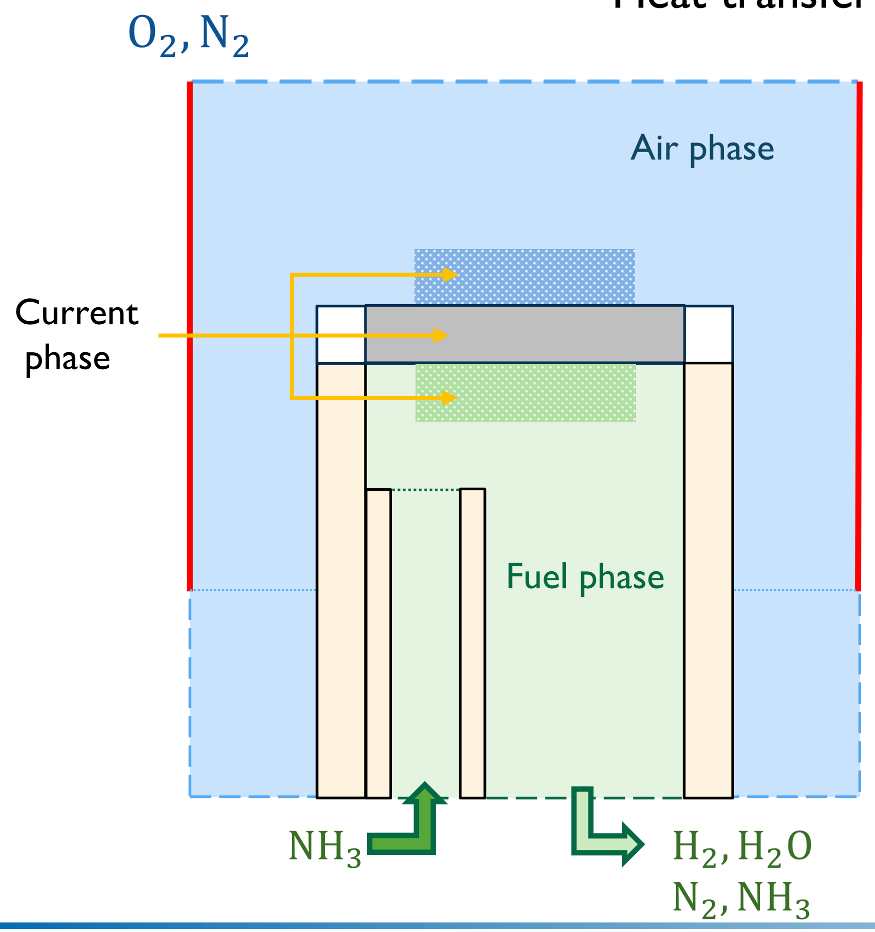
Multiphysics



METHODS

Simulation

Electrochemistry
- Current
- Species transport
- Fluid flow
- Heat transfer



Electrochemical reactions

$$H_2O + 2\,e \longleftrightarrow H_2 + O^{2-} \quad \text{in anode,}$$
$$O_2 + 4\,e \longleftrightarrow 2\,O^{2-} \quad \text{in cathode.}$$

Equilibrium potentials

$$E_{\text{eq},f} = E_{\text{eq,ref},f} - \frac{RT}{n_f F}\ln\left(\frac{c_{H_2}}{c_{H_2O}}\right)$$
$$E_{\text{eq},a} = E_{\text{eq,ref},f} + \frac{RT}{n_a F}\ln\left(c_{O_2}\right)$$

Overpotential

$$\eta := \phi_{\text{ele}} - \phi_{\text{ion}} - E_{\text{eq}}$$

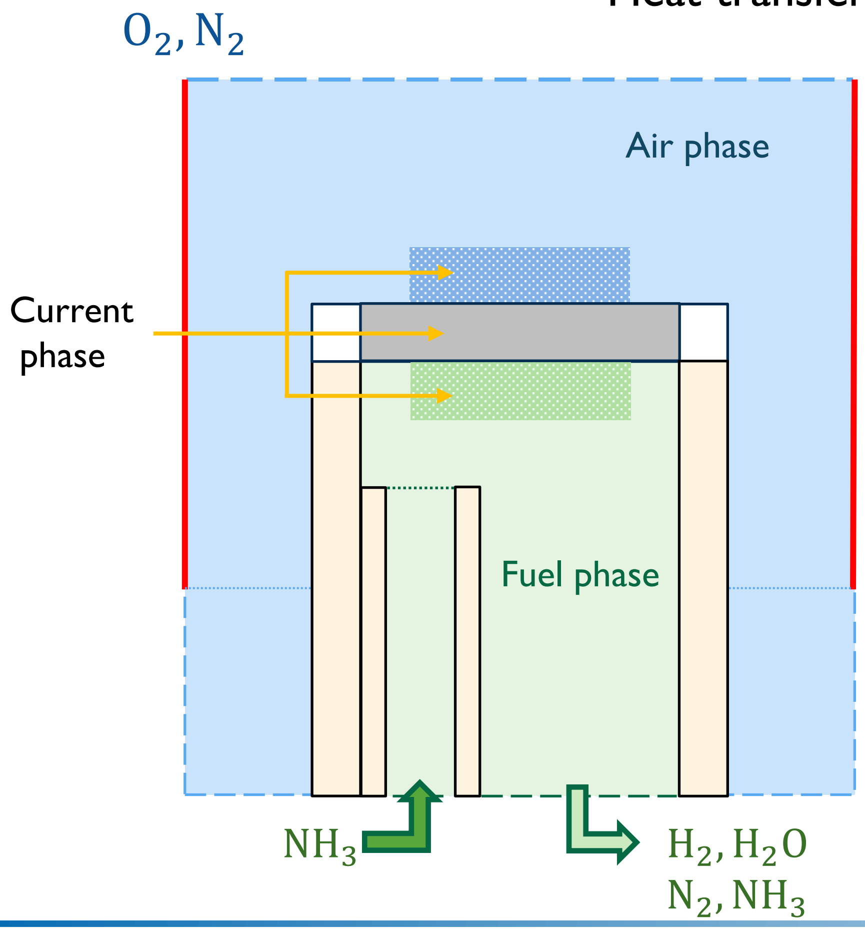
Current density

$$(\text{BV})\begin{cases} i_{\text{loc},f} = i_{0,f}\left(\exp\left(n_f\alpha_f\frac{F\eta}{RT}\right) - \exp\left(-n_f(1-\alpha_f)\frac{F\eta}{RT}\right)\right), \\ i_{\text{loc},a} = i_{0,a}\left(\exp\left(n_a\alpha_a\frac{F\eta}{RT}\right) - \exp\left(-n_a(1-\alpha_a)\frac{F\eta}{RT}\right)\right). \end{cases}$$

METHODS

Simulation

- Electrochemistry
- **Current**
- Species transport
- Fluid flow
- Heat transfer



Current source

$$S_{\text{current}} = \begin{cases} i_{v,f} & \text{in anode,} \\ i_{v,a} & \text{in cathode,} \\ 0 & \text{elsewhere.} \end{cases}$$

Ionic current

$$\begin{cases} \nabla \cdot \mathbf{i}_{\text{ion}} = S_{\text{current}} & \text{in current phase,} \\ \mathbf{i}_{\text{ion}} = -\sigma_{\text{ion}}^{\text{eff}} \nabla \phi_{\text{ion}} & \text{in current phase,} \\ -\mathbf{n} \cdot \mathbf{i}_{\text{ion}} = 0 & \text{on insulated walls.} \end{cases}$$

$$\sigma_{\text{ion}}^{\text{eff}} = \frac{\chi}{\tau} \sigma_{\text{ion}}$$

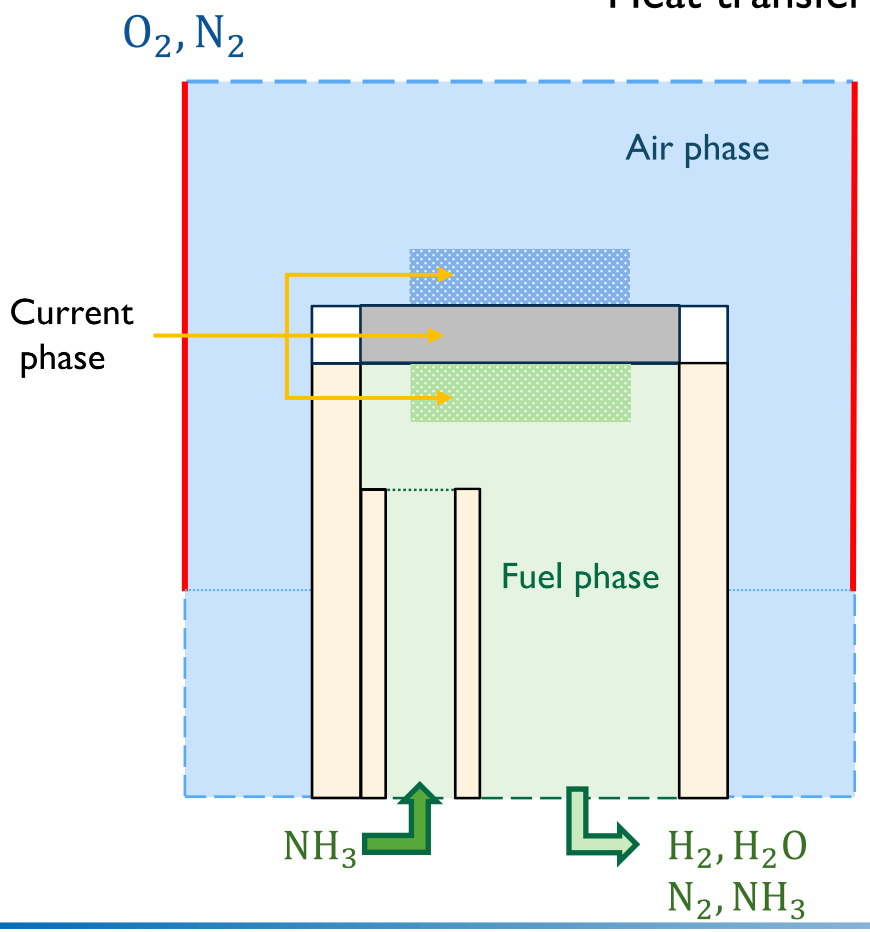
Electronic current

$$\begin{cases} \nabla \cdot \mathbf{i}_{\text{ele}} = -S_{\text{current}} & \text{in electrodes,} \\ \mathbf{i}_{\text{ele}} = -\sigma_{\text{ele}}^{\text{eff}} \nabla \phi_{\text{ele}} & \text{in electrodes,} \\ -\mathbf{n} \cdot \mathbf{i}_{\text{ele}} = 0 & \text{on electrode walls,} \\ \phi_{\text{ele}} = 0 & \text{on anode bottom,} \\ \phi_{\text{ele}} = V_{\text{cell}} & \text{on cathode top.} \end{cases}$$

METHODS

Simulation

- Electrochemistry
- Current
- **Species transport**
- Fluid flow
- Heat transfer



Fuel phase

$$\begin{cases} \rho(\mathbf{u}_f \cdot \nabla)\omega_i = -\nabla \cdot \mathbf{j}_i + S_i & \text{in fuel phase,} \\ \mathbf{n} \cdot \mathbf{j}_i = 0 & \text{on walls \& outlet,} \\ \omega_i = \omega_{0,i} & \text{at inlet.} \end{cases}$$

Air phase

$$\begin{cases} \rho(\mathbf{u}_a \cdot \nabla)\omega_i = -\nabla \cdot \mathbf{j}_i + S_i & \text{in air phase,} \\ \mathbf{n} \cdot \mathbf{j}_i = 0 & \text{on walls,} \\ \mathbf{n} \cdot \mathbf{j}_i = 0 & \text{at open boundary if } \mathbf{n} \cdot \mathbf{u}_a \geq 0, \\ \omega_i = \omega_{0,i} & \text{at open boundary if } \mathbf{n} \cdot \mathbf{u}_a < 0. \end{cases}$$

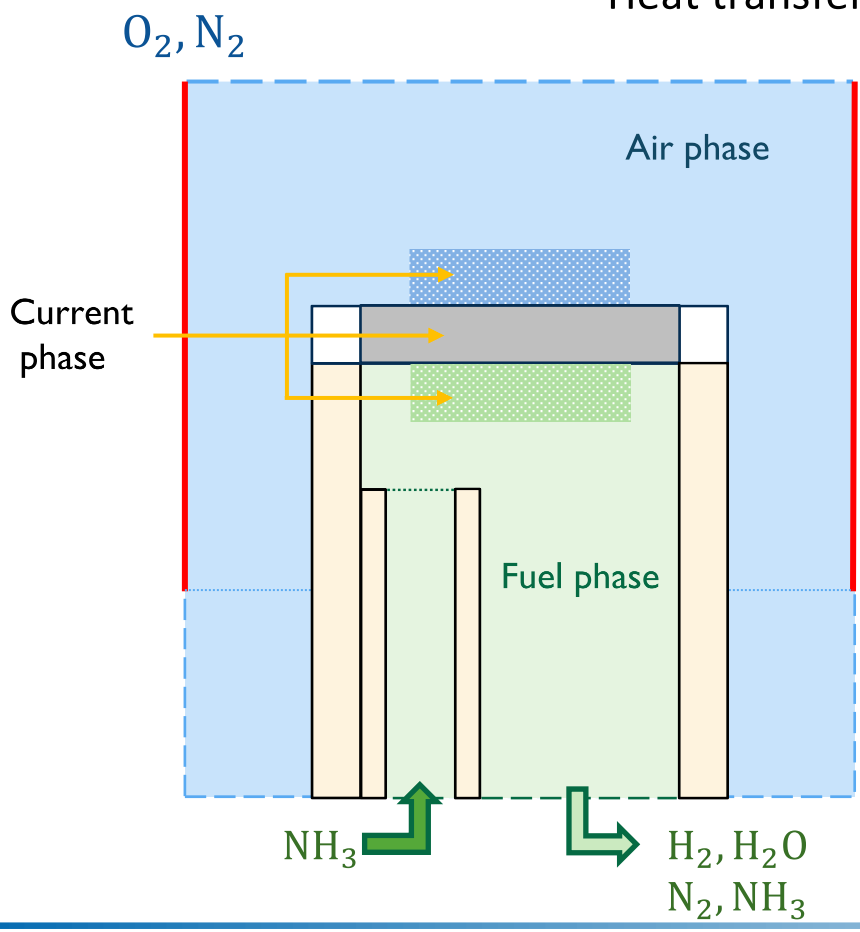
Maxwell-Stefan model

$$\begin{cases} \mathbf{j}_i = -\rho\omega_i \sum_k \tilde{D}_{ik,\text{eff}} \mathbf{d}_k, \\ \mathbf{d}_k = \nabla x_k + \frac{1}{p_{A,f}}((x_k - \omega_k)\nabla p_{A,f}). \end{cases}$$

METHODS

Simulation

- Electrochemistry
- Current
- Species transport
- **Fluid flow**
- Heat transfer



Free flow, fuel

$$\begin{cases} 0 = \nabla \cdot (-p_f \mathbf{I} + \mathbf{K}_f) & \text{in free flow regions,} \\ \mathbf{K}_f = \mu\left(\nabla \mathbf{u}_f + (\nabla \mathbf{u}_f)^\top\right) & \text{in free flow regions,} \\ \quad -\frac{2}{3}\mu(\nabla \cdot \mathbf{u}_f)\mathbf{I} & \\ \nabla \cdot (\rho \mathbf{u}_f) = 0 & \text{in free flow regions,} \\ \mathbf{u}_f = 0 & \text{on walls.} \end{cases}$$

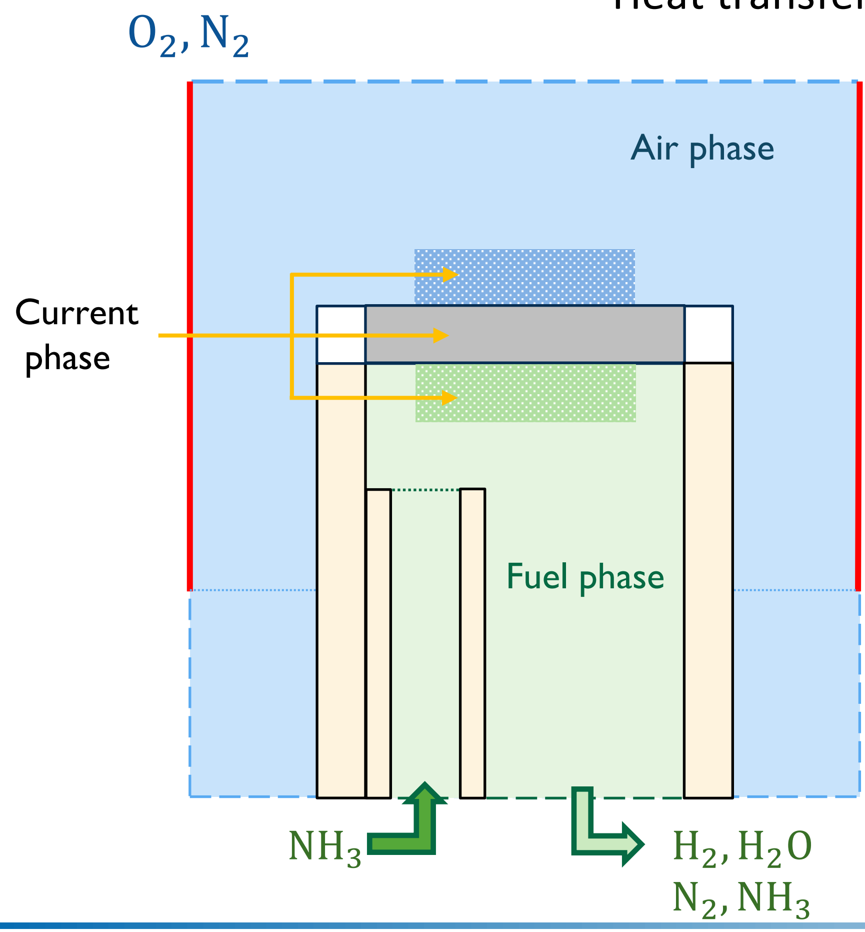
Porous media flow, fuel

$$\begin{cases} 0 = \nabla \cdot (-p_f \mathbf{I} + \mathbf{K}_f) & \text{in anode,} \\ \quad -\left(\frac{\mu}{\kappa} + \frac{S_{\text{mass}}}{\epsilon^2}\right)\mathbf{u}_f & \\ \mathbf{K}_f = \frac{\mu}{\epsilon}\left(\nabla \mathbf{u}_f + (\nabla \mathbf{u}_f)^\top\right) & \text{in anode,} \\ \quad -\frac{2}{3}\frac{\mu}{\epsilon}(\nabla \cdot \mathbf{u}_f)\mathbf{I} & \\ \nabla \cdot (\rho \mathbf{u}_f) = S_{\text{mass}} & \text{in anode,} \\ \mathbf{u}_f = 0 & \text{at top side.} \end{cases}$$

METHODS

Simulation

- Electrochemistry
- Current
- Species transport
- **Fluid flow**
- Heat transfer



Free flow, air

$$\begin{cases} 0 = \nabla \cdot (-p_a \mathbf{I} + \mathbf{K}_a) & \text{in free flow regions,} \\ \mathbf{K}_a = \mu\big(\nabla \mathbf{u}_a + (\nabla \mathbf{u}_a)^\top\big) & \text{in free flow regions,} \\ \quad - \frac{2}{3}\mu(\nabla \cdot \mathbf{u}_a)\mathbf{I} & \\ \nabla \cdot (\rho \mathbf{u}_a) = 0 & \text{in free flow regions,} \\ \mathbf{u}_a = 0 & \text{on walls.} \end{cases}$$

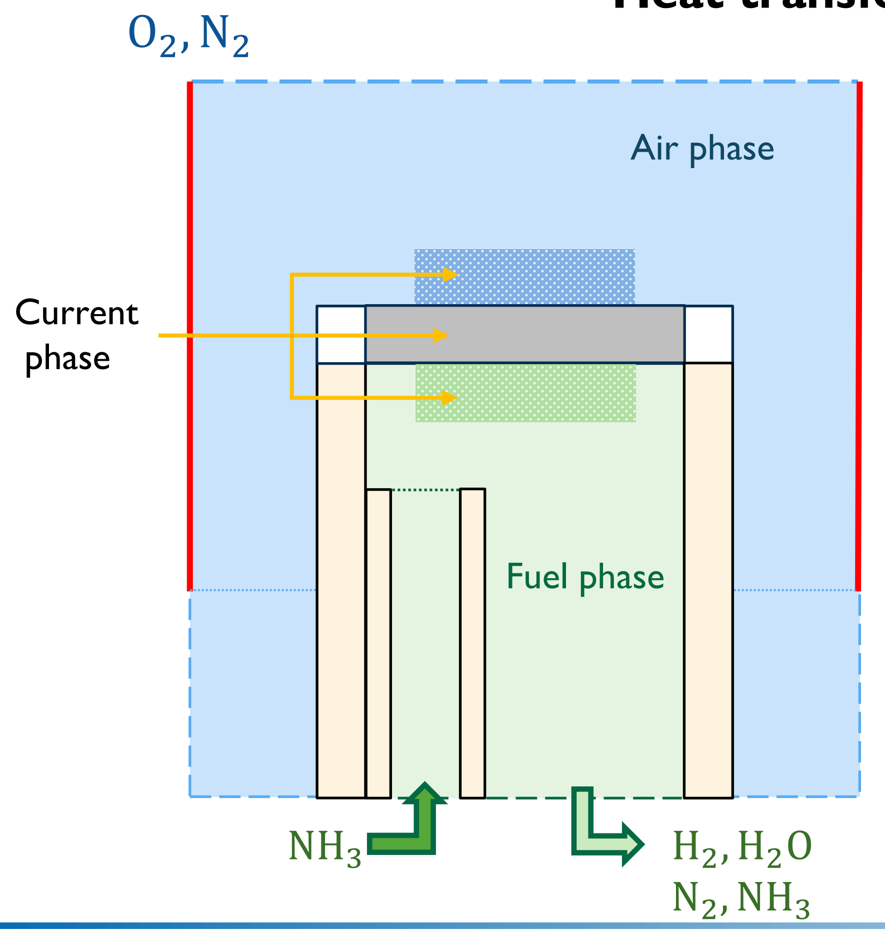
Porous media flow, air

$$\begin{cases} 0 = \nabla \cdot (-p_a \mathbf{I} + \mathbf{K}_a) & \text{in anode,} \\ \quad - \left(\frac{\mu}{\kappa} + \frac{S_{\text{mass}}}{\epsilon^2}\right)\mathbf{u}_a & \\ \mathbf{K}_a = \frac{\mu}{\epsilon}\big(\nabla \mathbf{u}_a + (\nabla \mathbf{u}_a)^\top\big) & \text{in anode,} \\ \quad - \frac{2}{3}\frac{\mu}{\epsilon}(\nabla \cdot \mathbf{u}_a)\mathbf{I} & \\ \nabla \cdot (\rho \mathbf{u}_a) = S_{\text{mass}} & \text{in anode,} \\ \mathbf{u}_a = 0 & \text{at bottom side.} \end{cases}$$

METHODS

Simulation

- Electrochemistry
- Current
- Species transport
- Fluid flow
- **Heat transfer**



Solids

$$\begin{cases} \nabla \cdot \mathbf{q} = S_{\text{heat}} & \text{in solids,} \\ \mathbf{q} = -k\nabla T & \text{in solids.} \end{cases}$$

Fluids

$$\begin{cases} \rho C_p \mathbf{u} \cdot \nabla T + \nabla \cdot \mathbf{q} = S_{\text{heat}} & \text{in free flow regions,} \\ \mathbf{q} = -k\nabla T & \text{in free flow regions,} \\ T = T_{\text{fnc}} & \text{on furnace walls} \end{cases}$$

Porous domains

$$\begin{cases} \rho^f C_p^f \mathbf{u} \cdot \nabla T + \nabla \cdot \mathbf{q} = S_{\text{heat}} & \text{in porous regions,} \\ \mathbf{q} = -k^{\text{eff}}\nabla T & \text{in porous regions.} \end{cases}$$

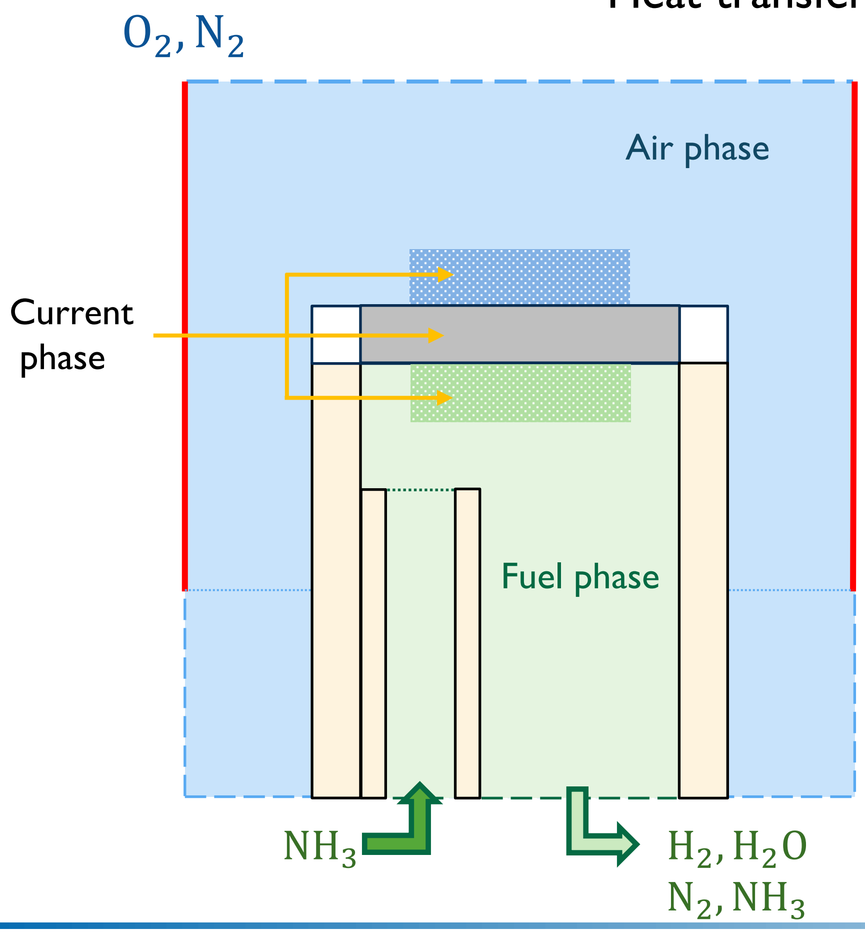
Boundary conditions

$$-\mathbf{n} \cdot \mathbf{q} = q_0 \quad \text{on remaining exterior walls.}$$

METHODS

Simulation

- **Electrochemistry**
- Current
- **Species transport**
- Fluid flow
- Heat transfer



Molar source/sink due to electrochemical reactions

$$R_i^{\mathrm{elec}} = -\frac{\nu_{i,m} i_v}{n_m F}.$$

Anode

$$R_{\mathrm{H_2O}} = R_{\mathrm{H_2O}}^{\mathrm{elec}} = \frac{i_v}{2F}, \qquad R_{\mathrm{H_2}} = R_{\mathrm{H_2}}^{\mathrm{elec}} = -\frac{i_v}{2F}.$$

Cathode

$$R_{\mathrm{O_2}} = R_{\mathrm{O_2}}^{\mathrm{elec}} = \frac{i_v}{4F}, \qquad R_{\mathrm{N_2}} = 0.$$

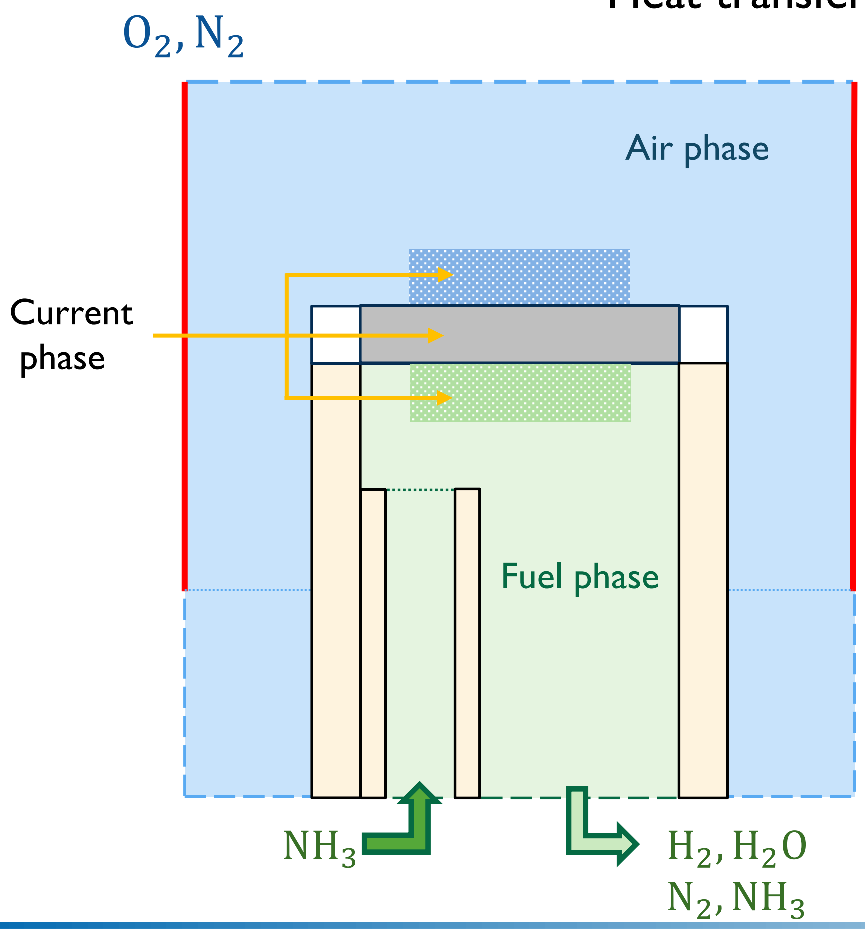
Mass source

$$S_i = M_i R_i - \omega_i S_{\mathrm{mass}}, \qquad S_{\mathrm{mass}} = \sum_i M_i R_i.$$

METHODS

Simulation

- **Chemistry**
- Current
- **Species transport**
- Fluid flow
- Heat transfer



Fuel phase

$$i = H_2,\ H_2O,\ NH_3,\ N_2$$

Ammonia cracking reaction

$$2\,NH_3 \longleftrightarrow N_2 + 3\,H_2 \quad \text{in anode}$$

Reaction rate

$$r_{NH_3} = \begin{cases} 4 \times 10^{15} \exp\left(\dfrac{-196200}{RT}\right) p_{NH_3} & \text{in anode,} \\ 0 & \text{elsewhere.} \end{cases}$$

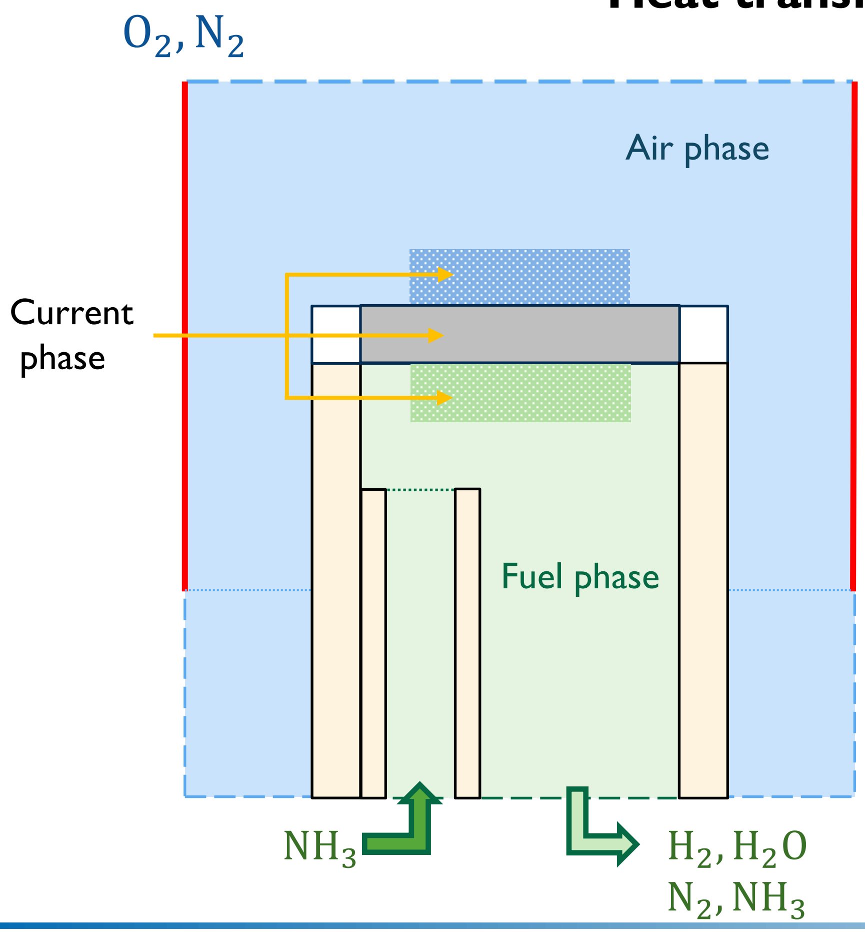
New sources and sinks

$$R_{NH_3} = -2\epsilon r_{NH_3}, \qquad R_{N_2} = \epsilon r_{NH_3},$$

$$R_{H_2} = 3\epsilon r_{NH_3} + R_{H_2}^{\text{elec}} = 3\epsilon r_{NH_3} - \frac{i_v}{2F}.$$

Simulation

- **Chemistry**
- Current
- Species transport
- Fluid flow
- **Heat transfer**



Heat sinks and sources

$$S_{\text{heat}}^{\text{crack}} = -r_{\text{NH}_3} \Delta H$$

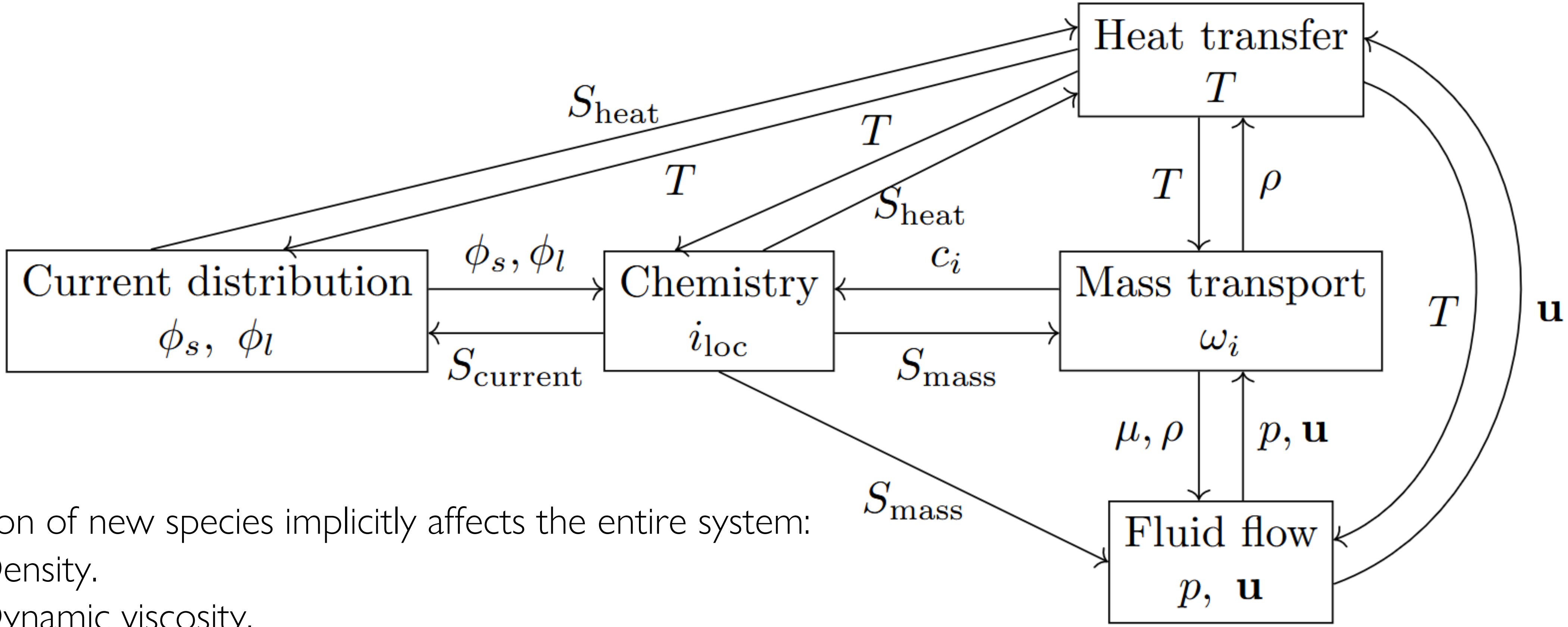
$$S_{\text{heat}}^{\text{Joule}} = Q_{\text{rev}} + Q_{\text{irrev}} = i_{\text{loc}}(E_{\text{eq}} - E_{\text{th}}) + i_{\text{loc}}\eta$$

Total source

$$S_{\text{heat}} = \begin{cases} S_{\text{heat}}^{\text{crack}} + S_{\text{heat}}^{\text{Joule}} & \text{in anode,} \\ S_{\text{heat}}^{\text{Joule}} & \text{in electrolyte \& cathode,} \\ 0 & \text{elsewhere.} \end{cases}$$

METHODS

Coupling strategy



Addition of new species implicitly affects the entire system:

- Density.
- Dynamic viscosity.
- Diffusion coefficients.
- Thermal properties.
- Mass sources for momentum equations.

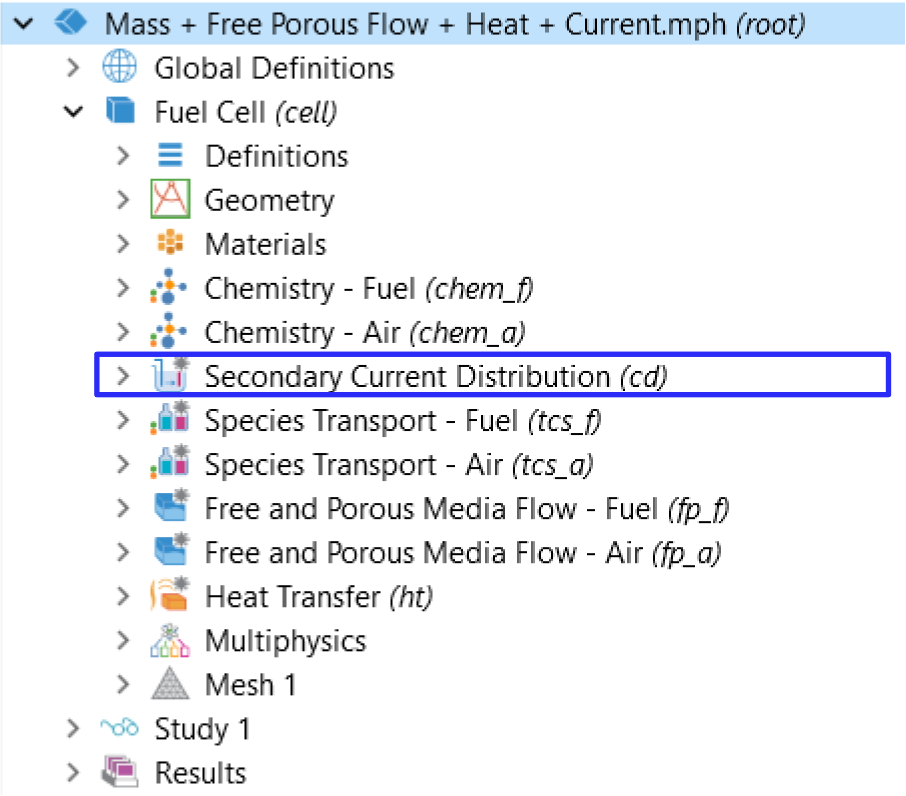
CONTENTS

METHODS

Implementation

COMSOL Multiphysics®

- Electrochemistry
- **Current**
- Species transport
- Fluid flow
- Heat transfer



Active domains

METHODS

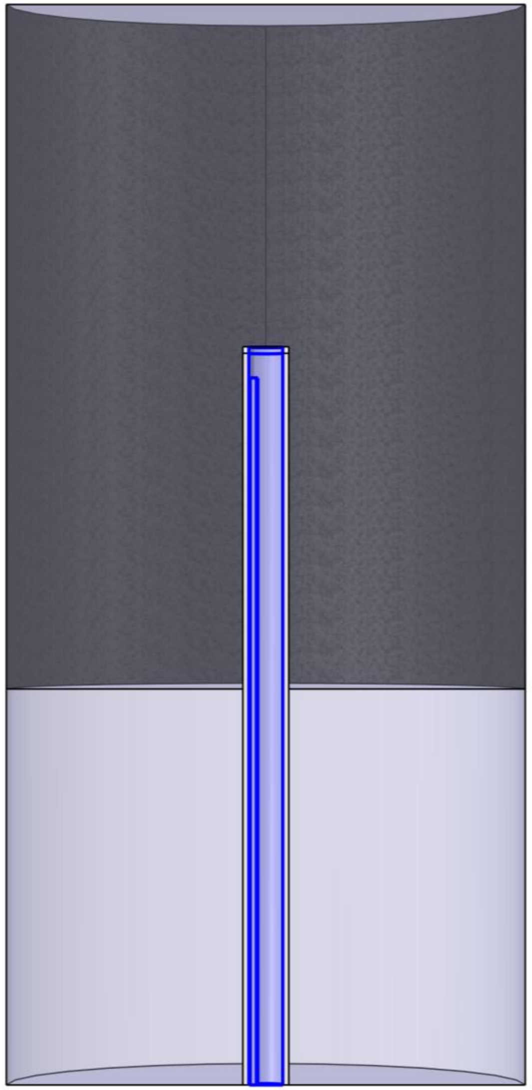
Implementation

COMSOL Multiphysics®

- Electrochemistry
- Current
- **Species transport**
- **Fluid flow**
- Heat transfer

Mass + Free Porous Flow + Heat + Current.mph *(root)*
- Global Definitions
- Fuel Cell *(cell)*
  - Definitions
  - Geometry
  - Materials
  - Chemistry - Fuel *(chem_f)*
  - Chemistry - Air *(chem_a)*
  - Secondary Current Distribution *(cd)*
  - Species Transport - Fuel *(tcs_f)*
  - Species Transport - Air *(tcs_a)*
  - Free and Porous Media Flow - Fuel *(fp_f)*
  - Free and Porous Media Flow - Air *(fp_a)*
  - Heat Transfer *(ht)*
  - Multiphysics
  - Mesh 1
- Study 1
- Results

Active domains



Coupling of cracking and electrochemical reactions

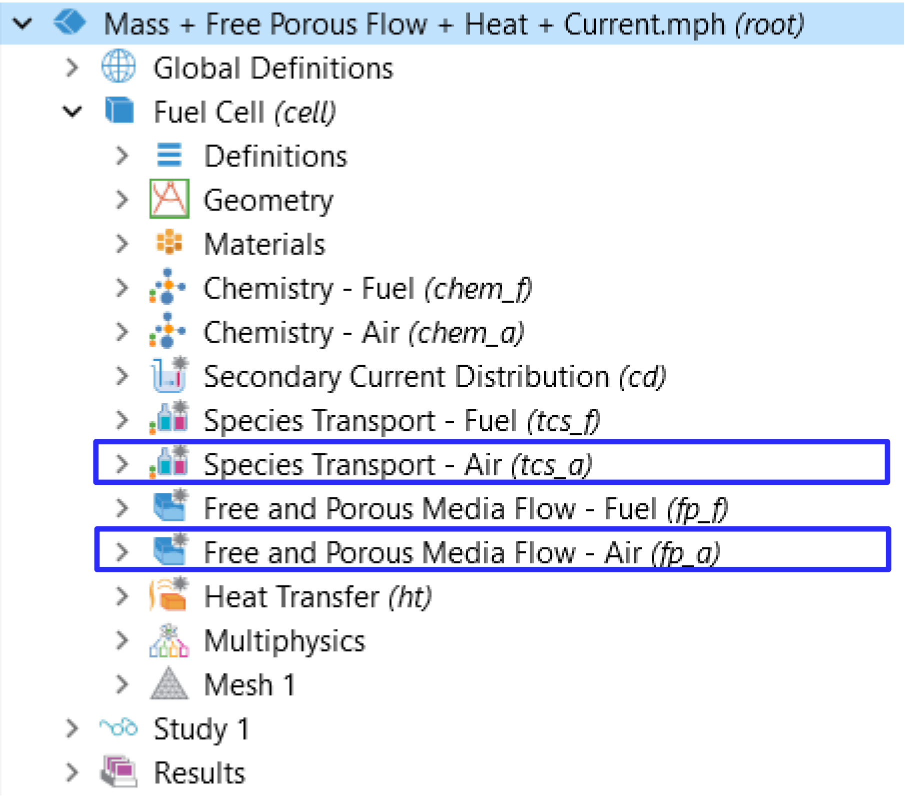
Species Transport - Fuel *(tcs_f)*
- Species Molar Masses 1
- Transport Properties 1
- Initial Values 1
- No Flux 1
- Porous Medium 1
- Porous Electrode Coupling 1
- Reaction Sources 1
- Inflow 1
- Outflow 1
- Symmetry 1
- Initial Values 2
- Equation View

METHODS

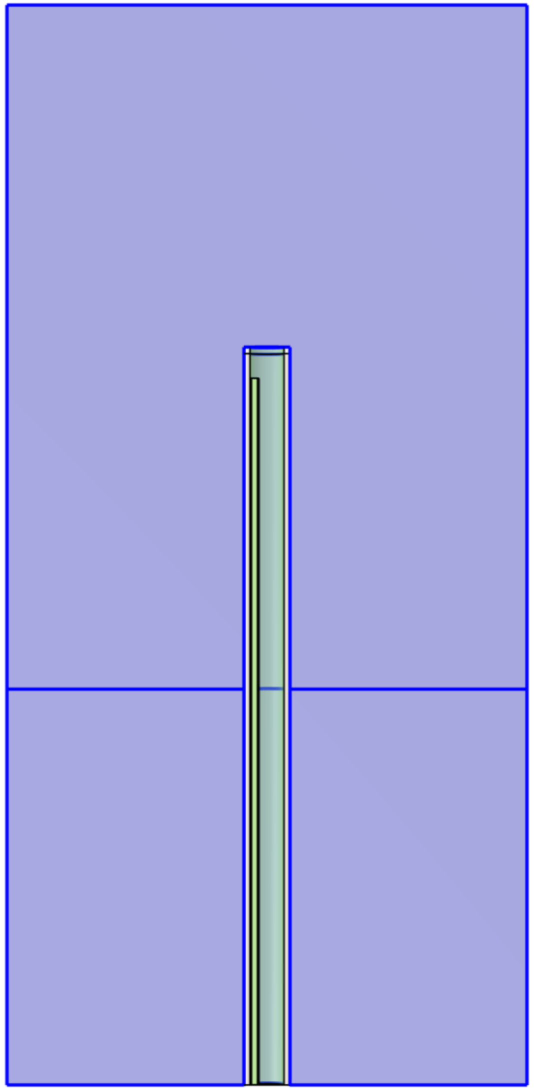
Implementation

COMSOL Multiphysics®

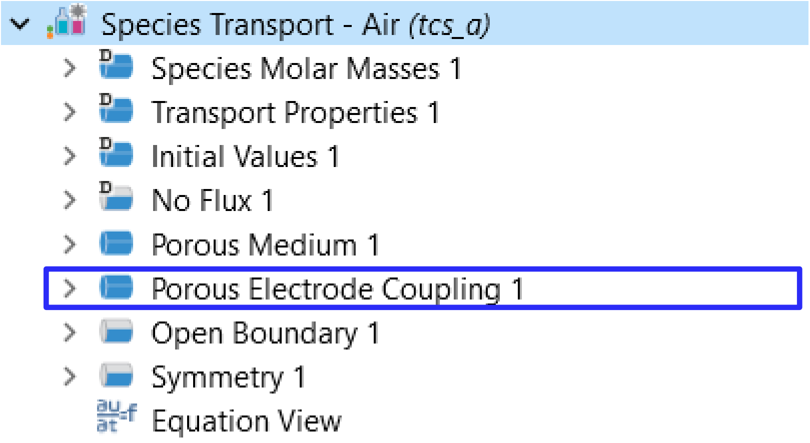
- Electrochemistry
- Current
- **Species transport**
- **Fluid flow**
- Heat transfer



Active domains



Only one reaction



METHODS

Implementation

- Electrochemistry
- Current
- Species transport
- Fluid flow
- **Heat transfer**

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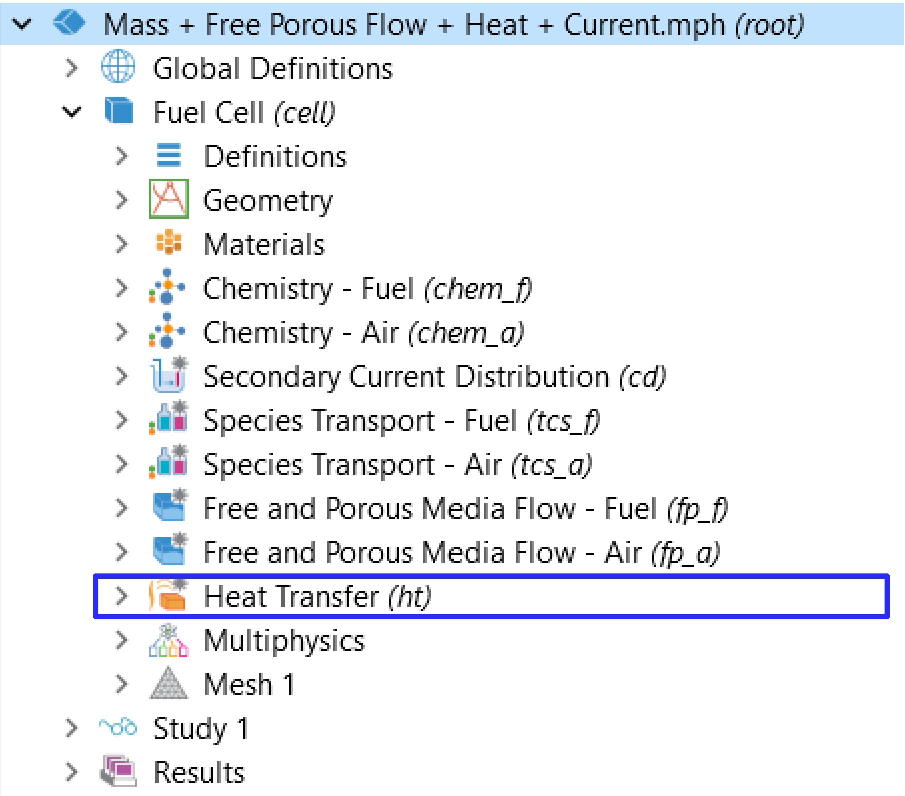
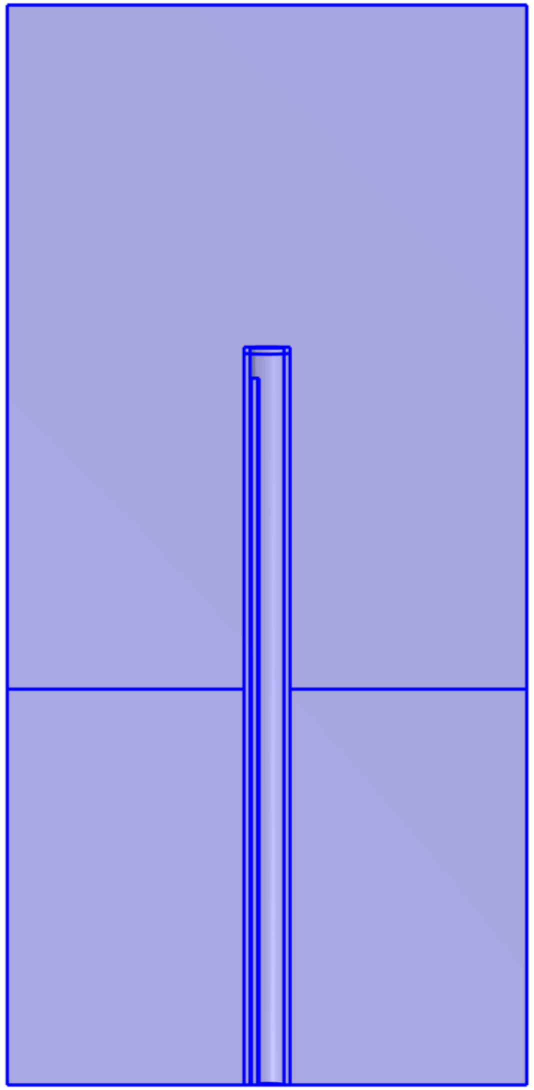
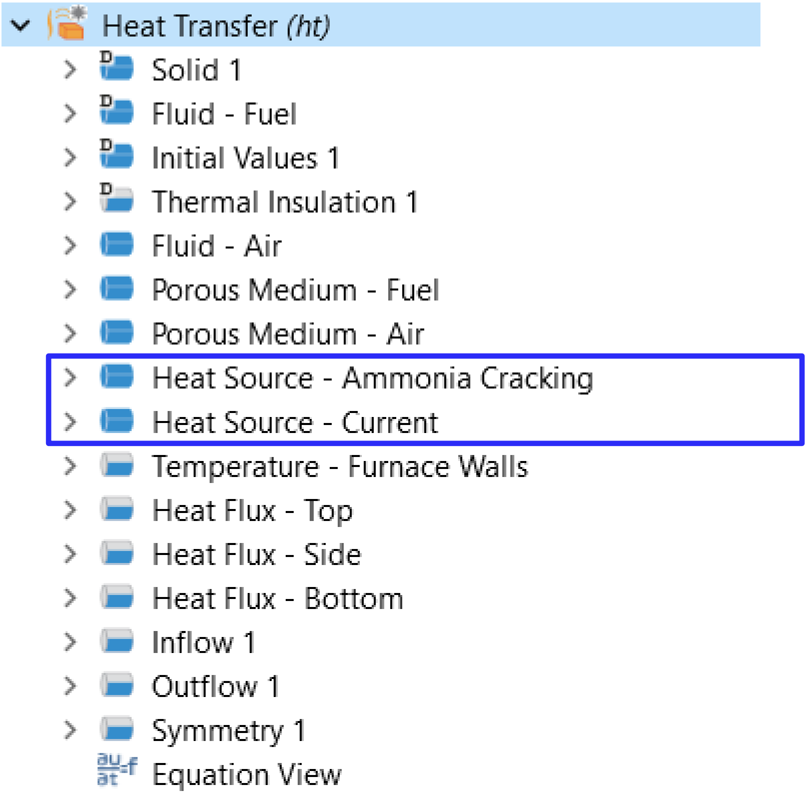


Active domains





METHODS

Implementation

- Electrochemistry
- Current
- Species transport
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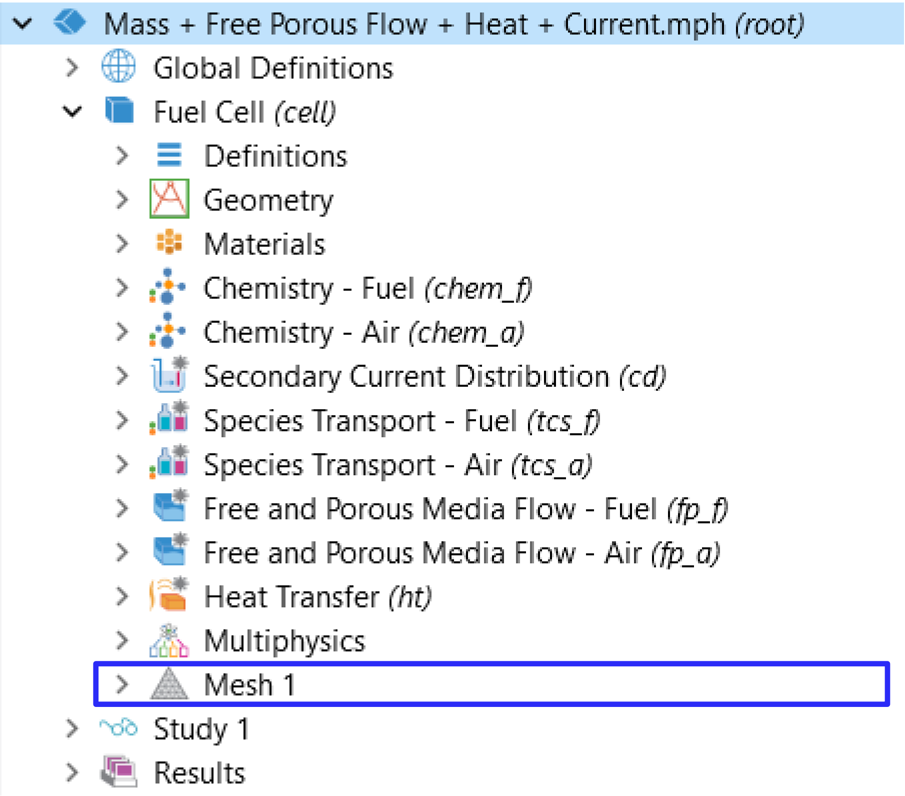

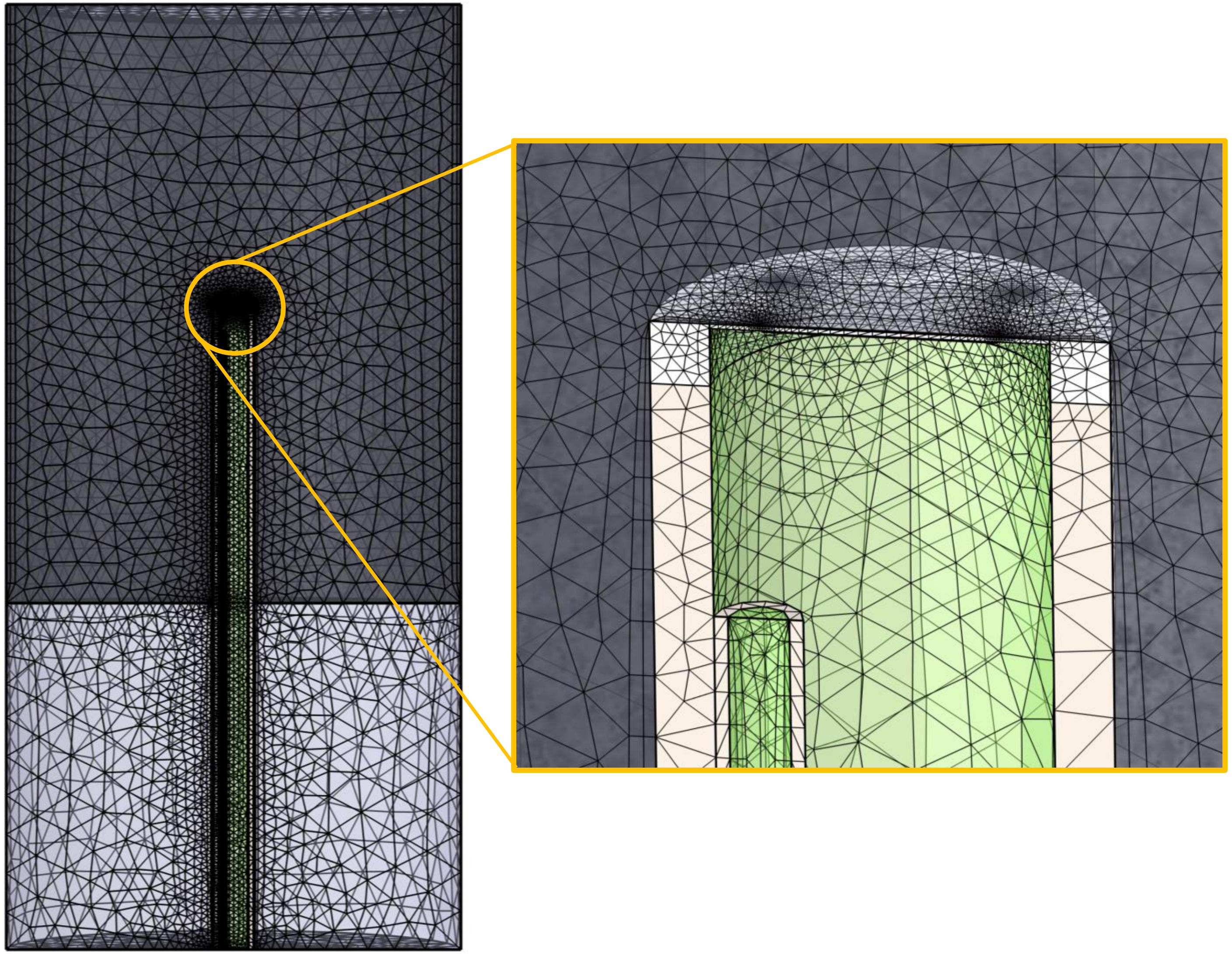

METHODS

Implementation

COMSOL Multiphysics®

- Electrochemistry
- Current
- Species transport
- Fluid flow
- Heat transfer

- Mass + Free Porous Flow + Heat + Current.mph *(root)*
  - Global Definitions
  - Fuel Cell *(cell)*
  - Study 1
    - Step 1: Current Distribution Initialization
    - Step 2: Fuel Species Initialization
    - Step 3: Heat Initialization
    - Step 4: Air Species Initialization
    - Step 5: Flow Initialization
    - Step 6: Full Model
    - Solver Configurations
  - Results

- Independent solution of physics to generate initial condition for coupled model.
- Parameter sweep with $T_{\mathrm{fnc}} = 750\ °\mathrm{C}, 700\ °\mathrm{C}, 650\ °\mathrm{C}$ and $V_{\mathrm{cell}} = 0.22\ \mathrm{V}, 0.32\ \mathrm{V}, \ldots, 1.02\ \mathrm{V}, 1.12\ \mathrm{V}$
- Solution of coupled model from furthest to nearest to equilibrium.

Study Extensions

☑ Auxiliary sweep

Sweep type: All combinations

Parameter nan	Parameter value list	Parameter unit
T_fnc (Tem|	750, 700, 650	degC
V_cell (Cell	range(0.22,0.1,1.12)	V

METHODS

Parameters

Parameter	Material			
	Anode	Electrolyte	Cathode	Tubes
$\sigma_{\text{ion}}\left(\frac{S}{\text{cm}}\right)$	$71 \cdot \exp\left(-\frac{62948}{RT}\right)$ [1]	$\approx 3.25 \cdot 10^{-2}$	10^{-2} [3]	N//A
$\sigma_{\text{ele}}\left(\frac{S}{\text{cm}}\right)$	$3.27 - 10.653 \cdot T$ [1]	N/A	≈ 43	N/A
$i_{0,\text{ref}}\left(\frac{\text{A}}{\text{cm}^2}\right)$	0.4 [3]	N/A	12 [3]	N/A

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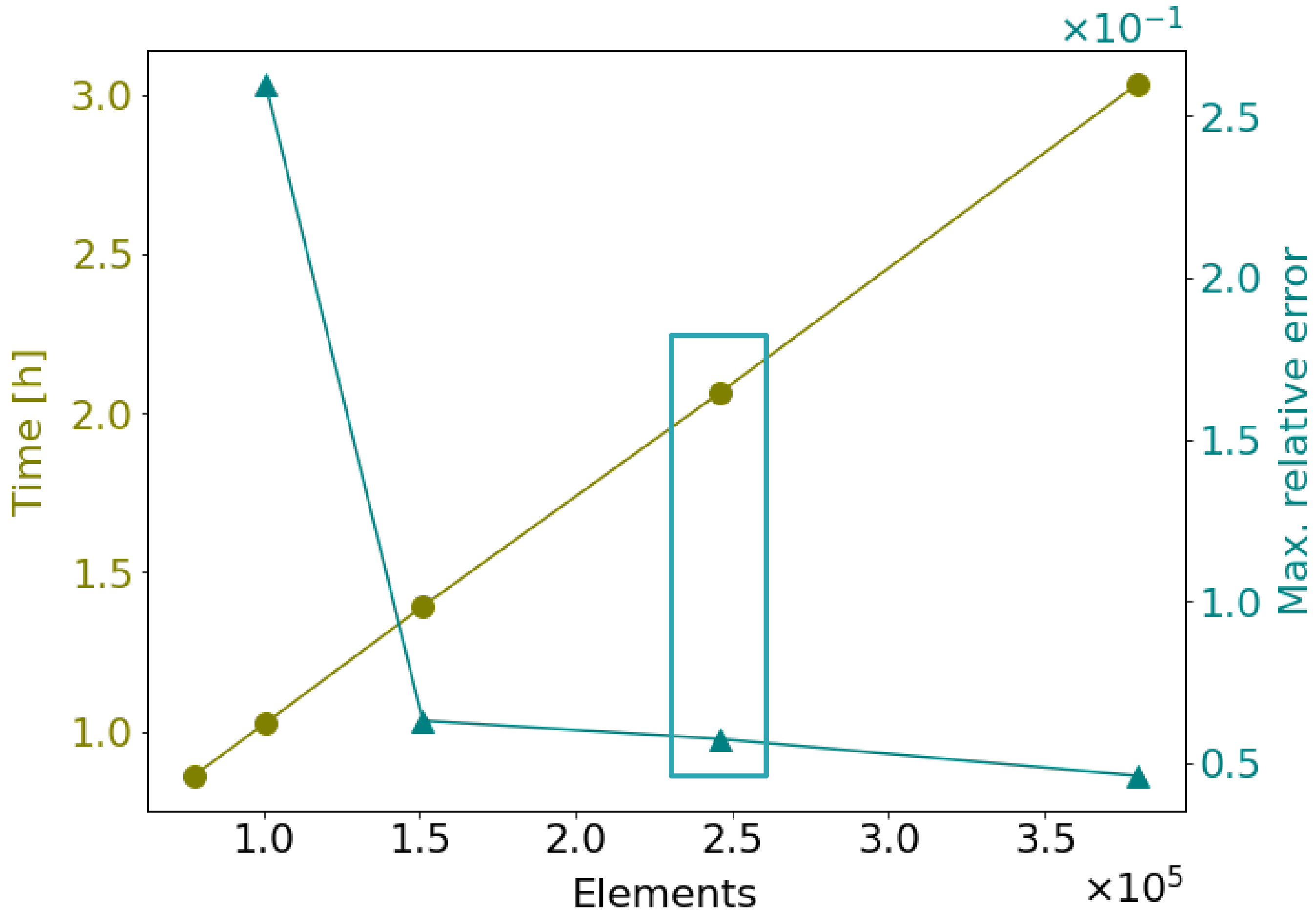
CONTENTS

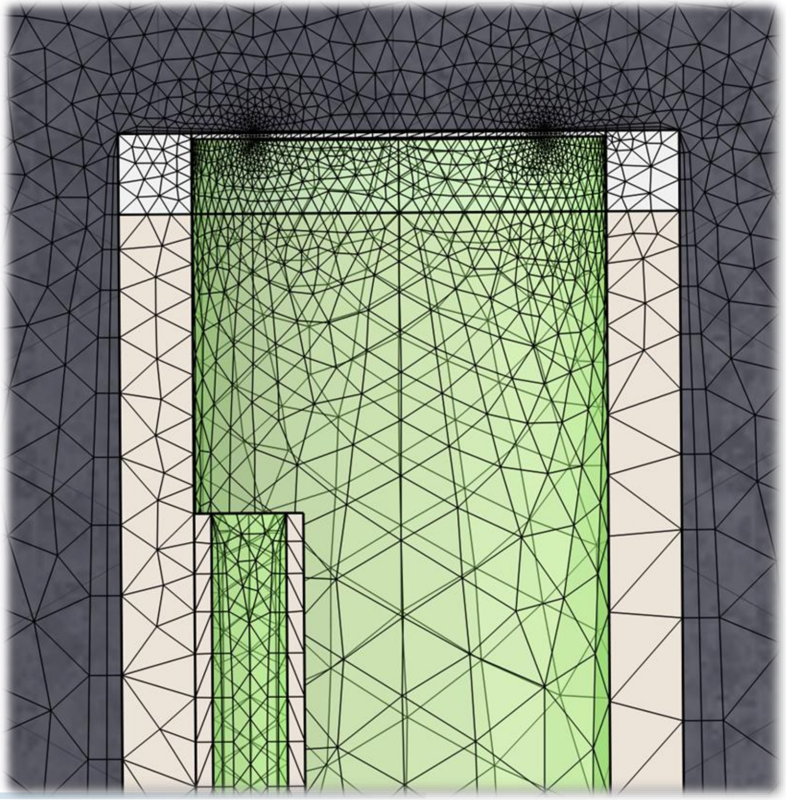
RESULTS

Mesh validation using NH_3



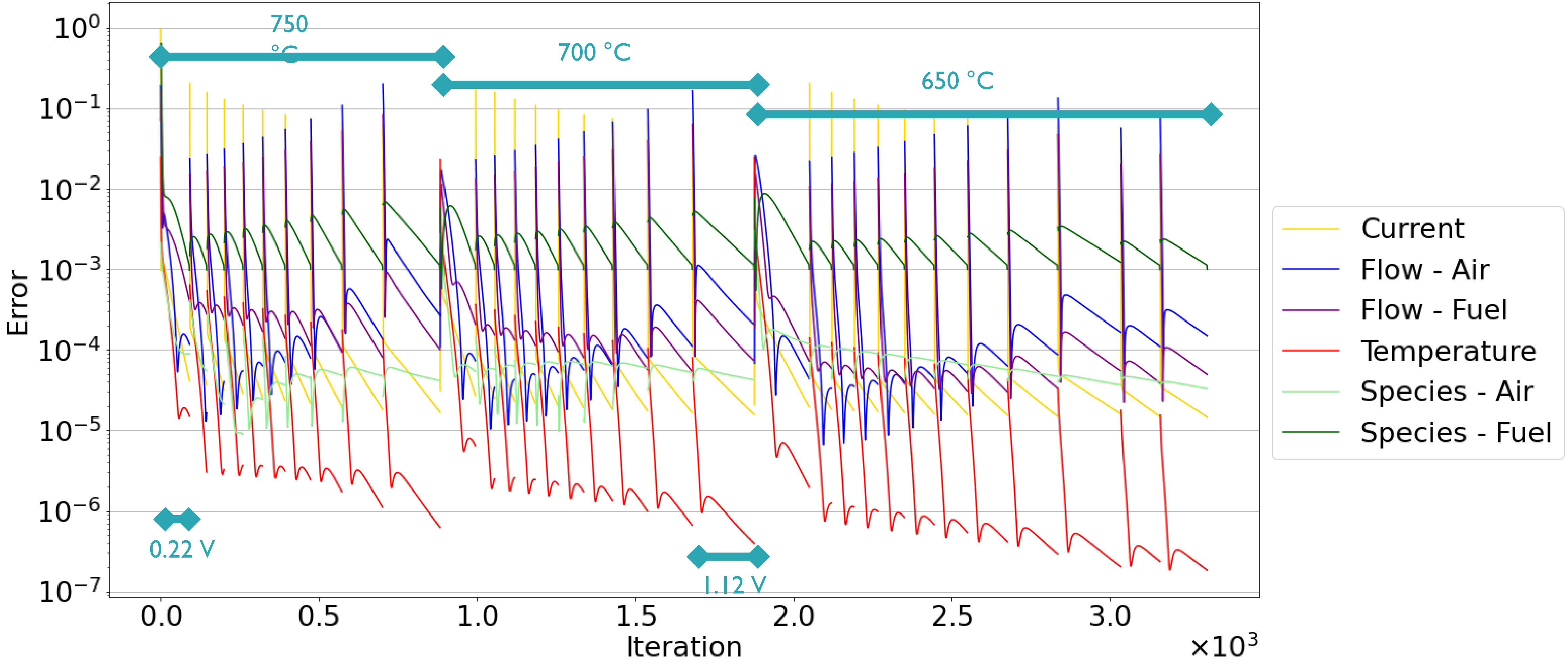
Final mesh

246,178 domain elements
31,303 boundary elements
2,167 edge elements



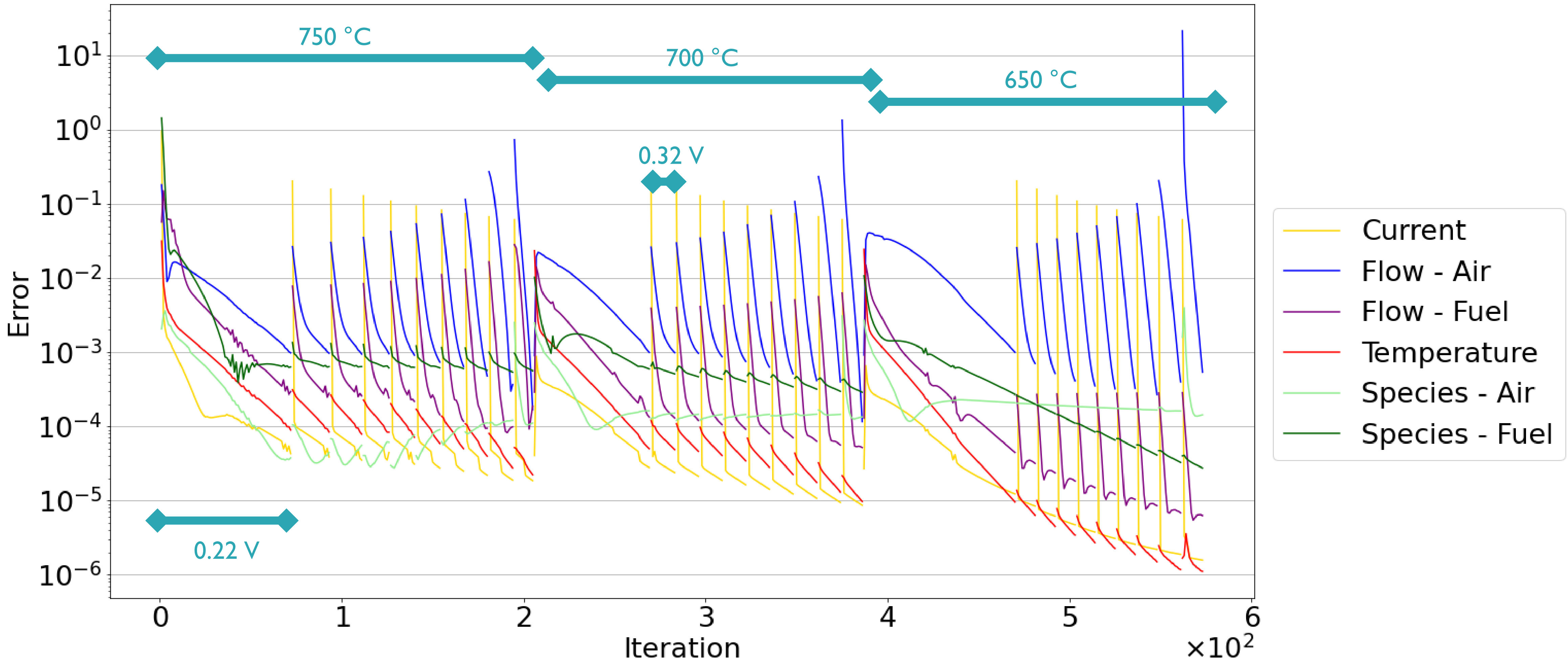
RESULTS

Convergence, H_2



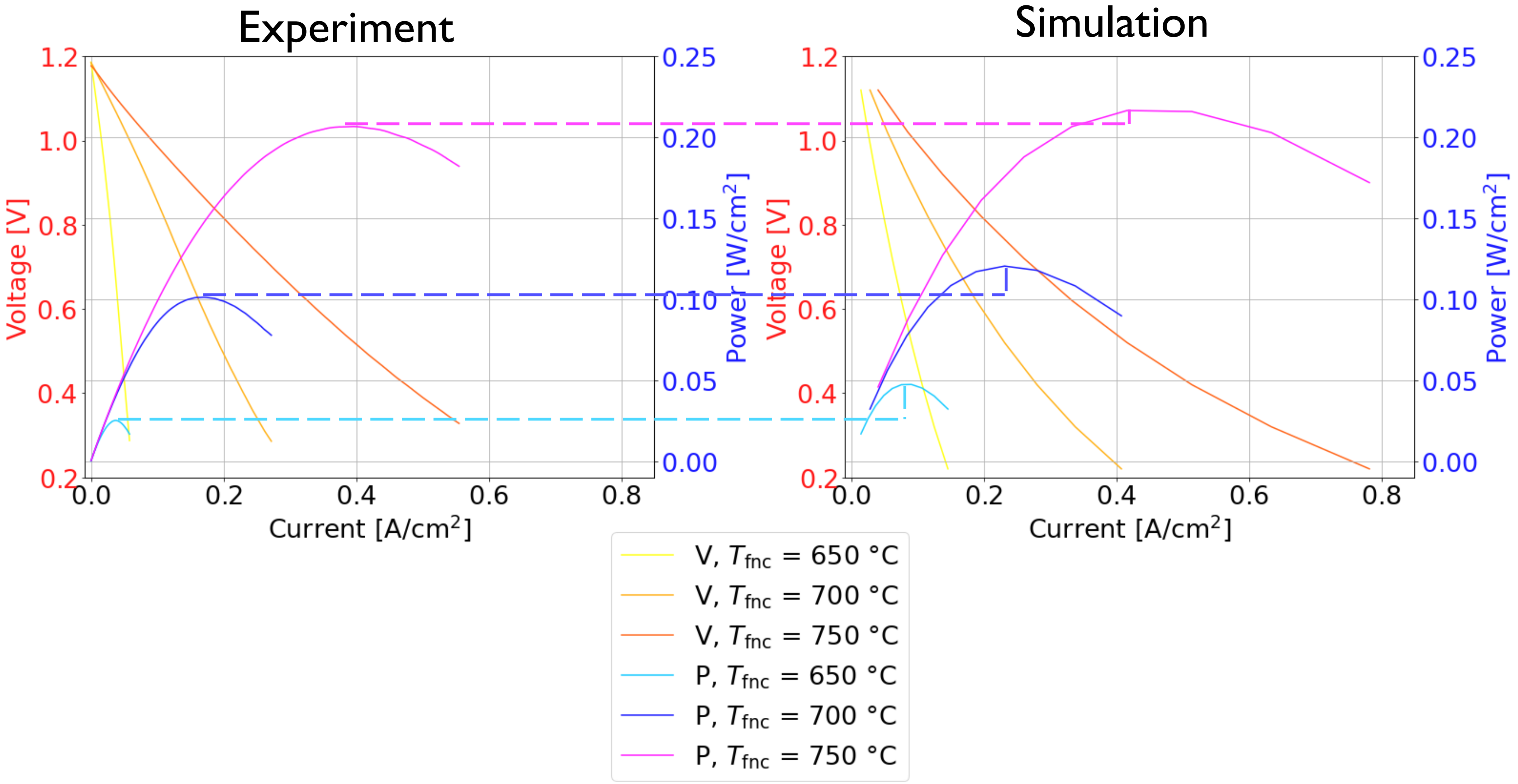
RESULTS

Convergence, NH_3



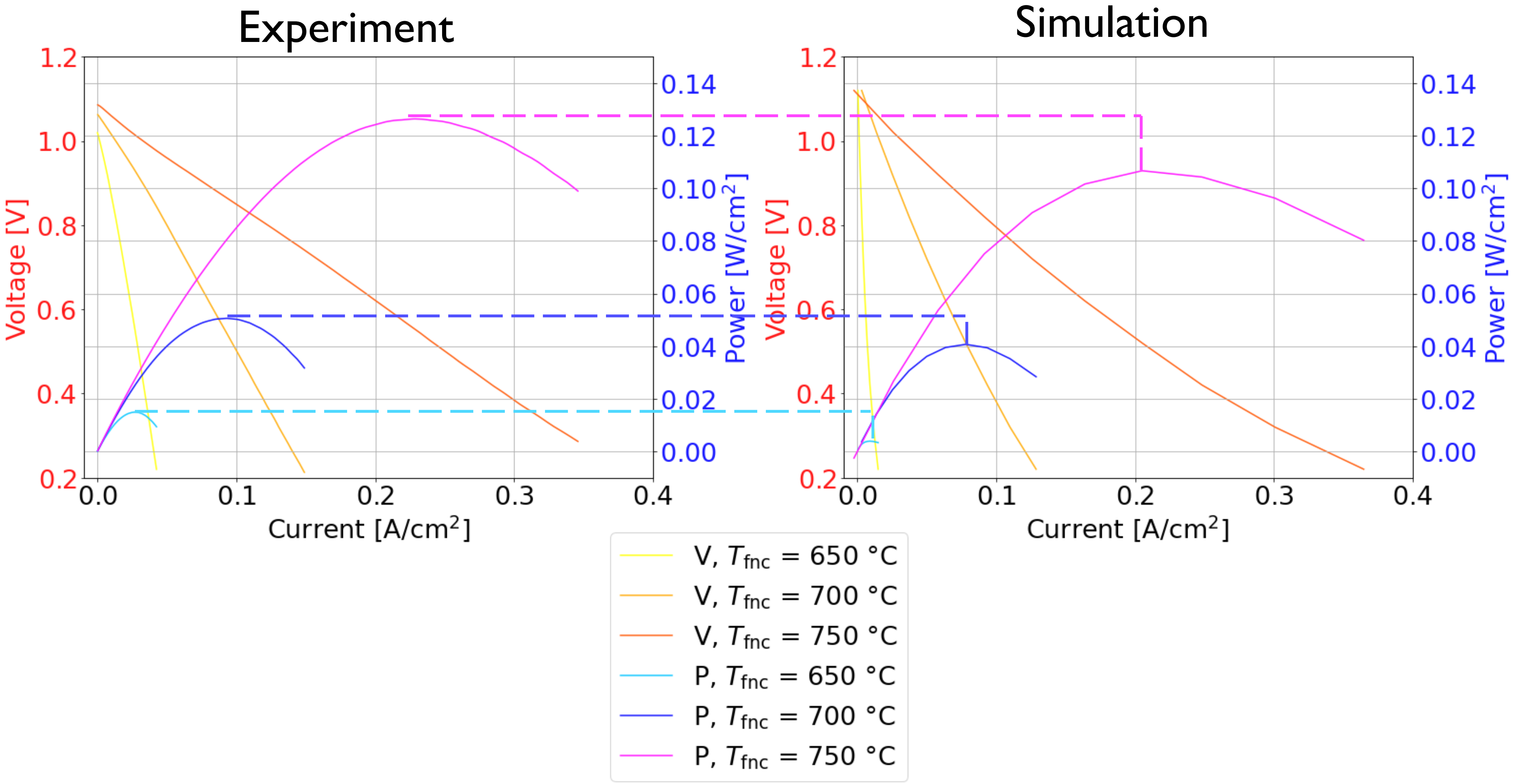
RESULTS

Power and polarization curves, H_2

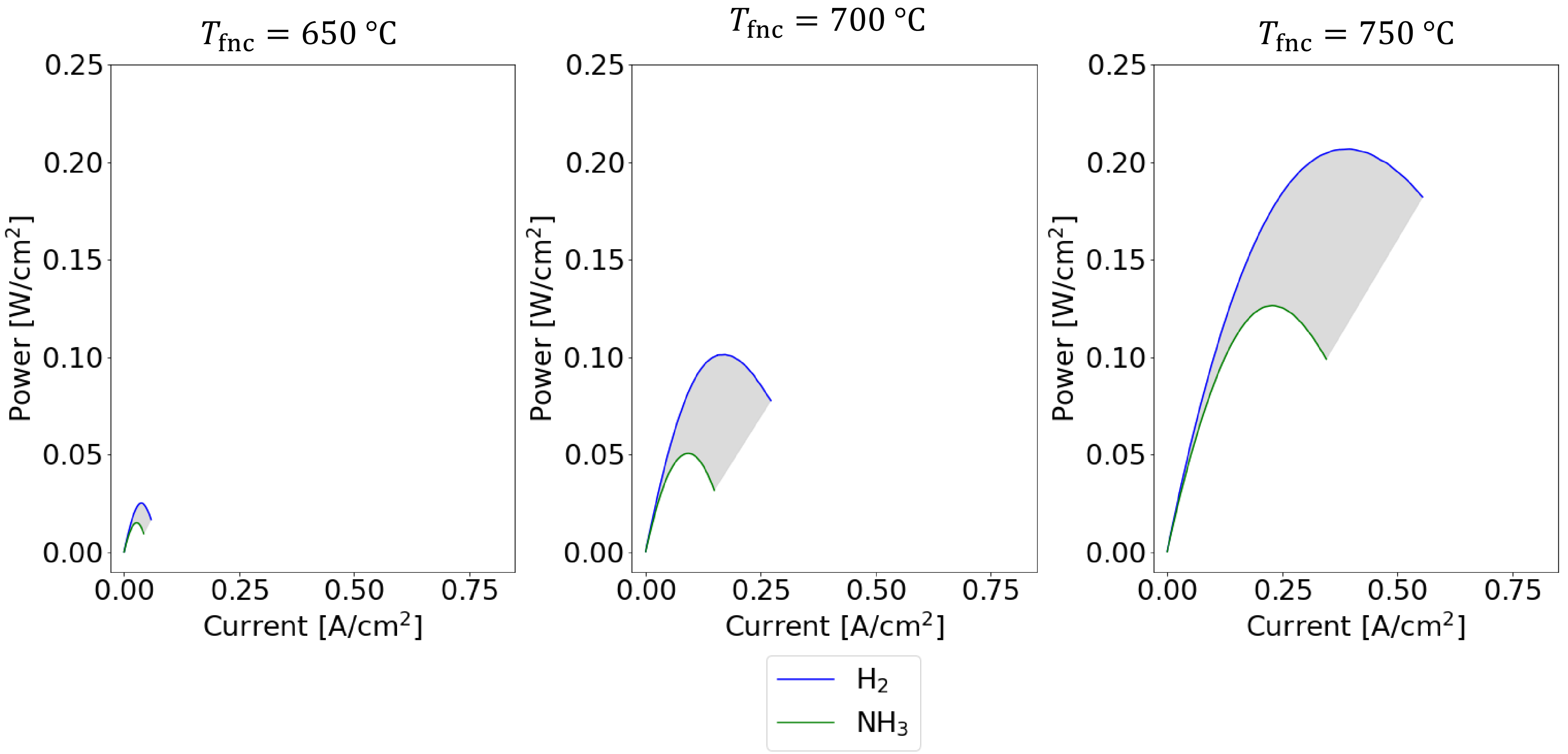


RESULTS

Power and polarization curves, NH_3

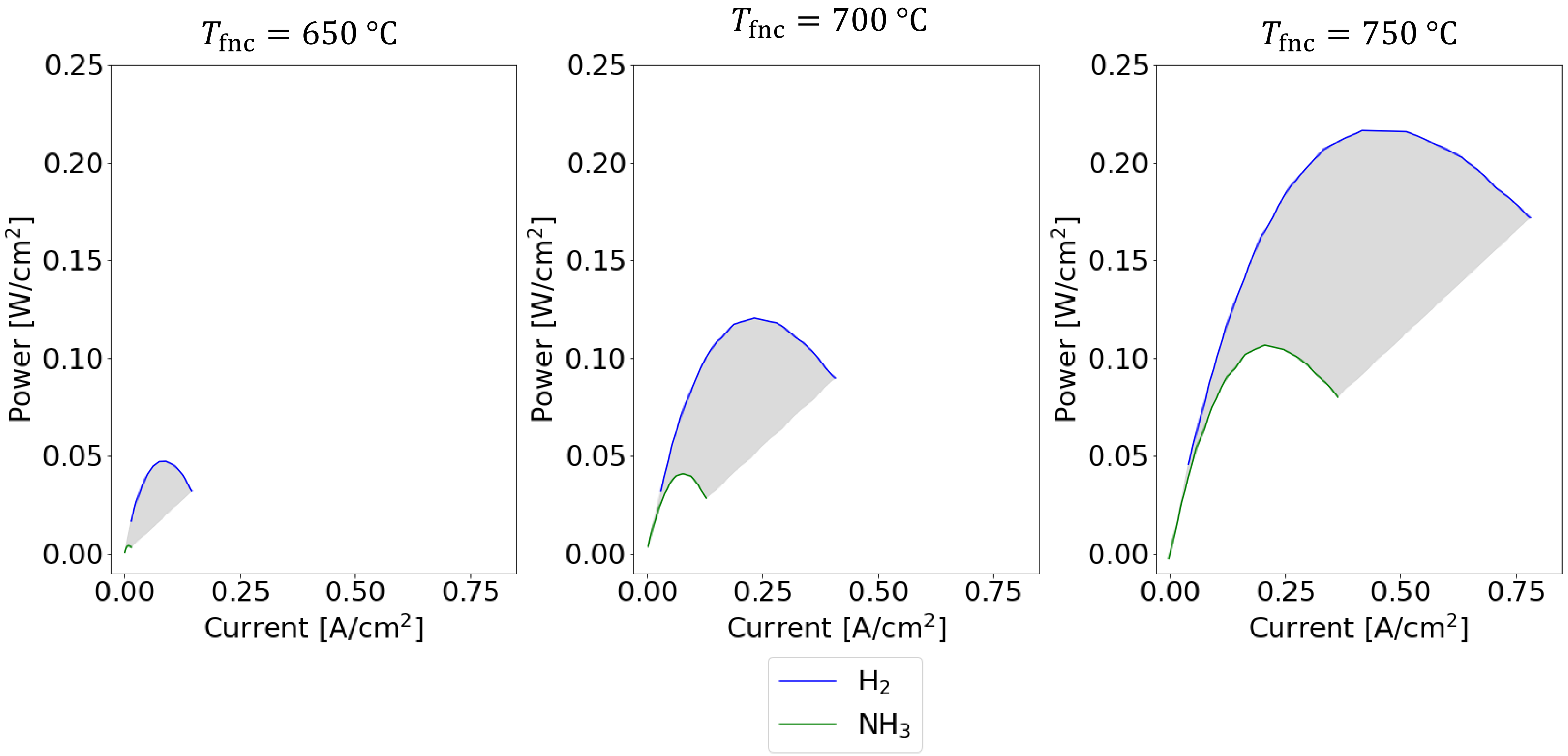


Power gap, experiment



RESULTS

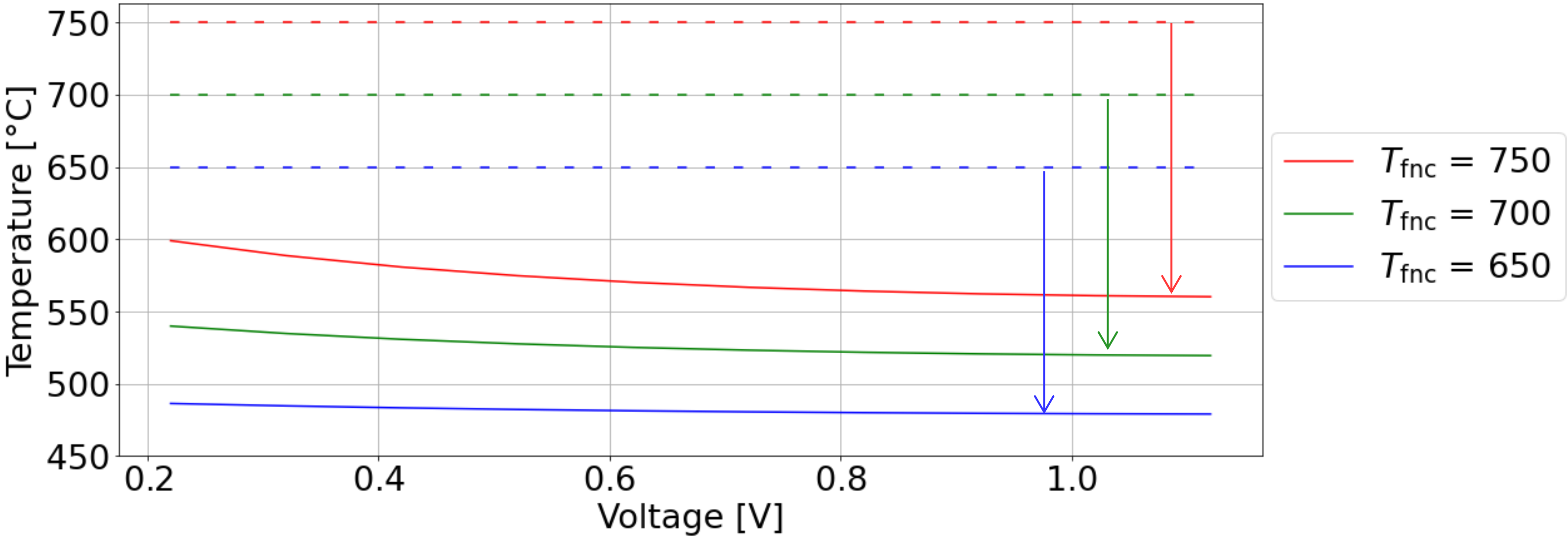
Power gap, simulation

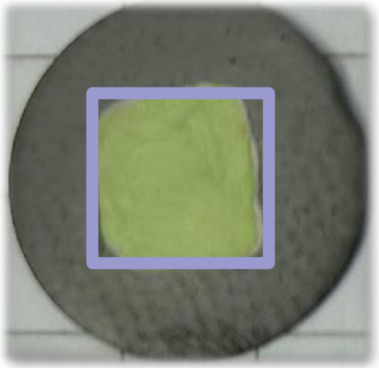


RESULTS

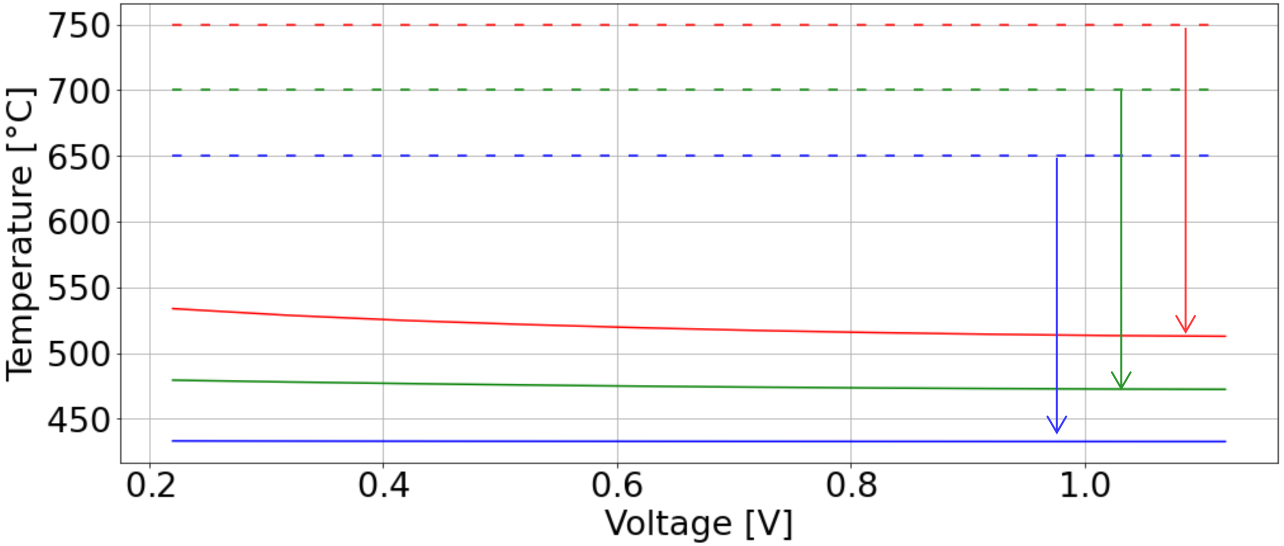
Average anode temperature, simulation

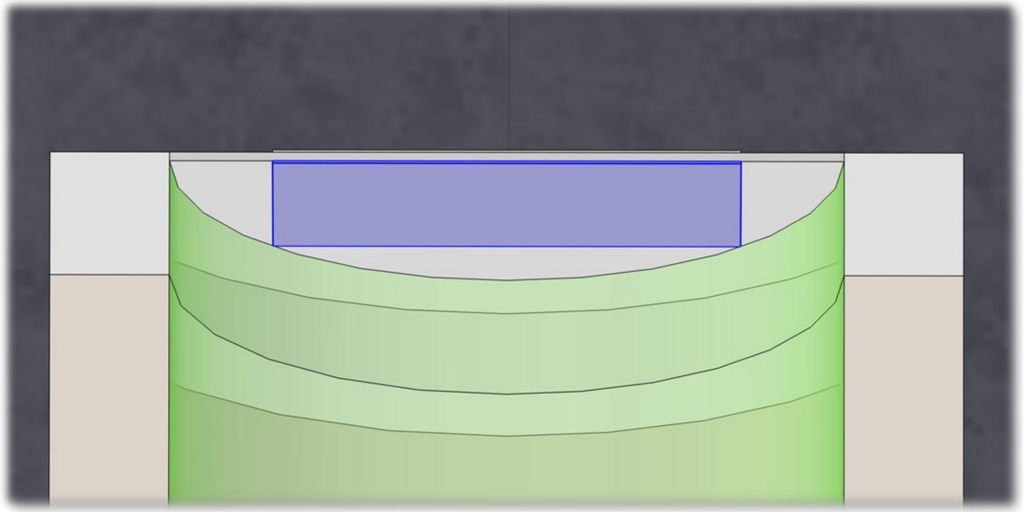
H_2



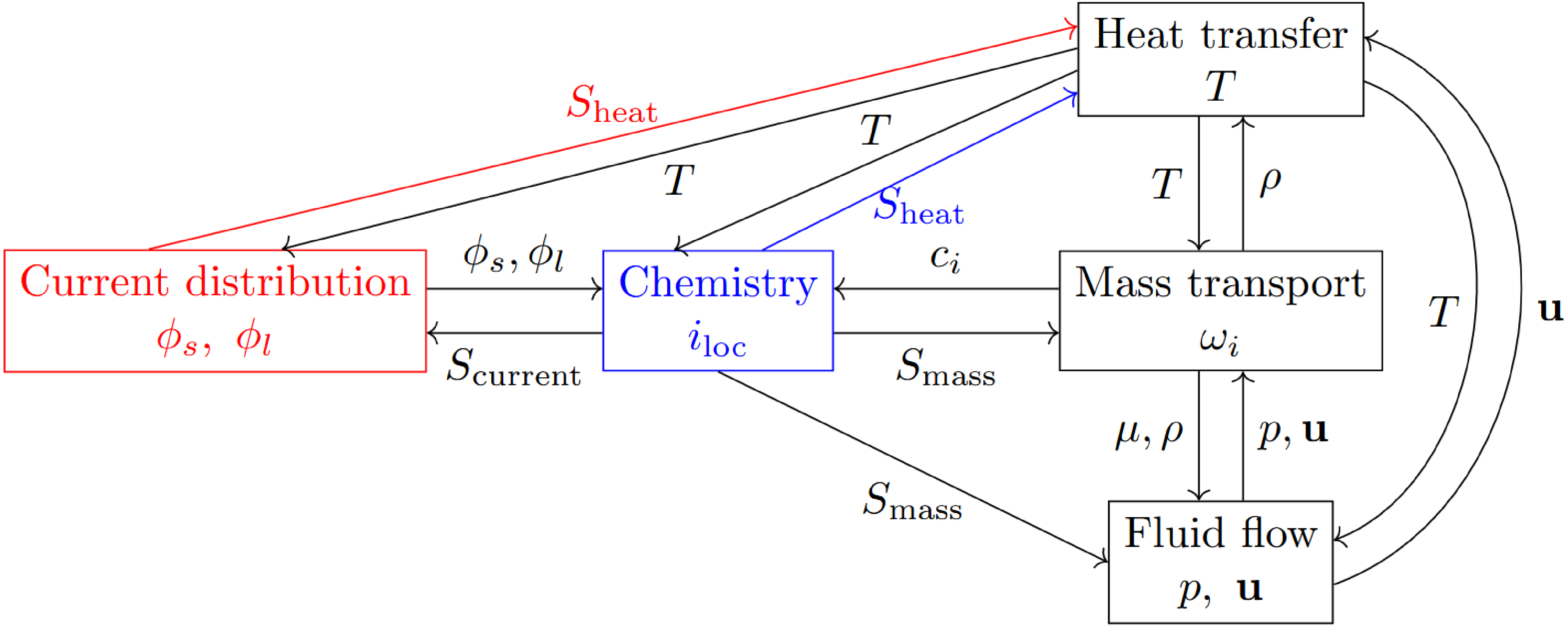


NH_3





Effect of heat sources at $T_{\mathrm{fnc}} = 750\ °\mathrm{C}$, $V_{\mathrm{cell}} = 0.22$ V, NH_3



RESULTS

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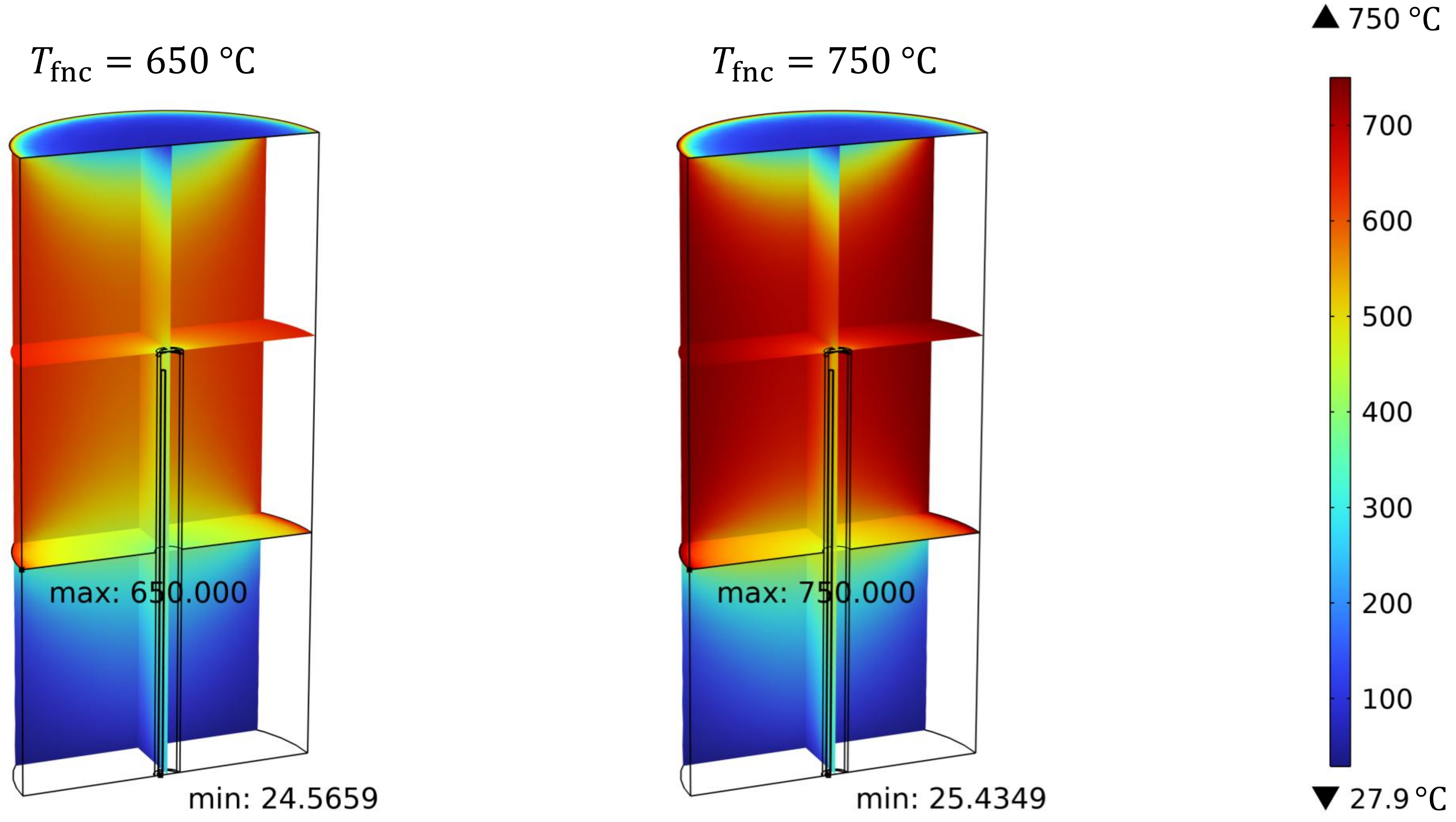
Effect of heat sources at $T_{fnc} = 750$ °C , $V_{cell} = 0.22$ V, NH_3

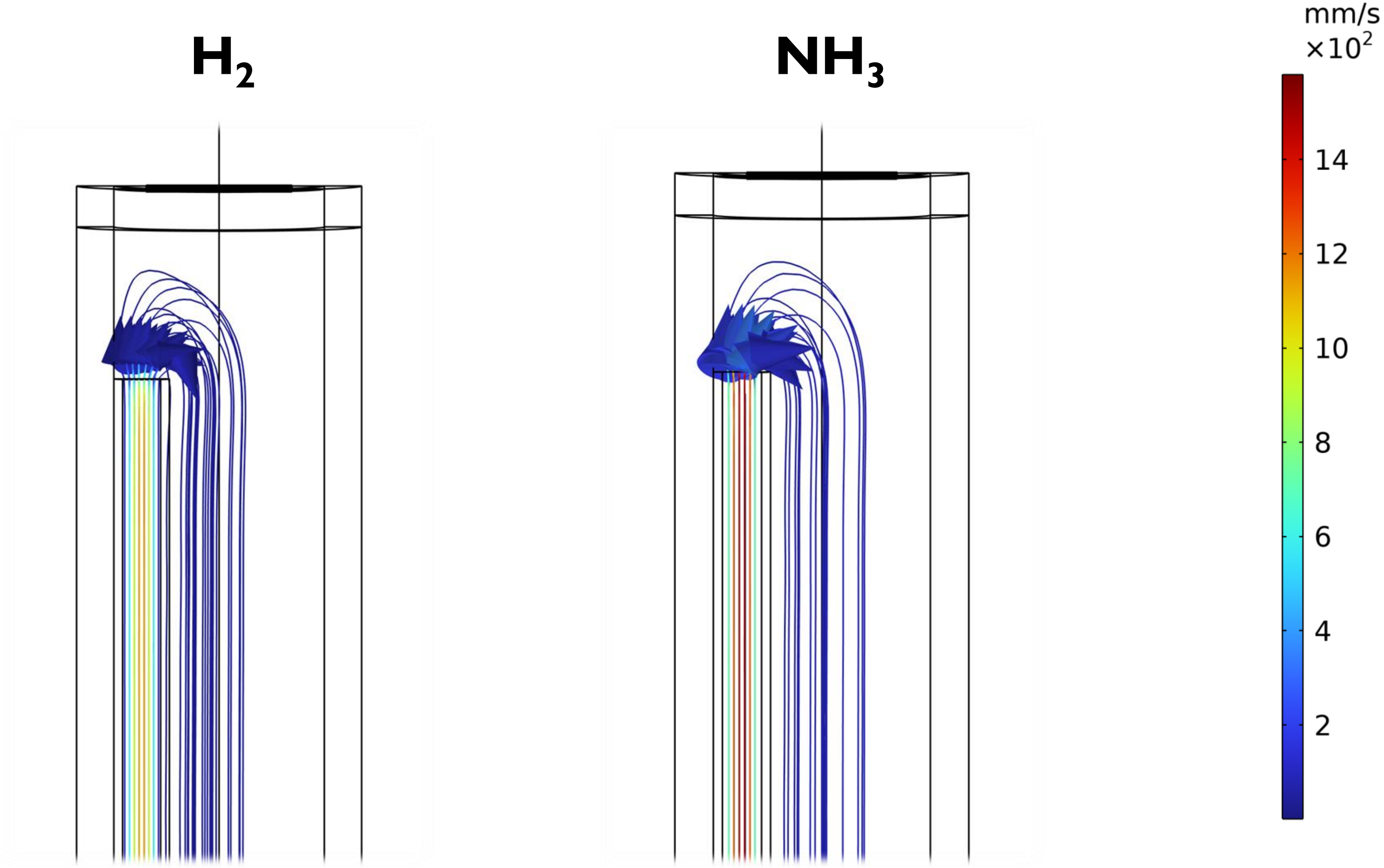
		Joule ✗	Joule ✓
Cracking	✗	$T_{and} \approx 561$ °C Total heat source ≈ 0 W/m³	$T_{and} \approx 601$ °C Total heat source ≈ $3.18 \cdot 10^7$ W/m³
Cracking	✓	$T_{and} \approx 514$ °C Total heat source ≈ $-3.38 \cdot 10^8$ W/m³	$T_{and} \approx 534$ °C Total heat source ≈ $-4.38 \cdot 10^8$ W/m³

Temperature, $V_{\mathrm{cell}} = 0.22\ \mathrm{V}$, NH_3



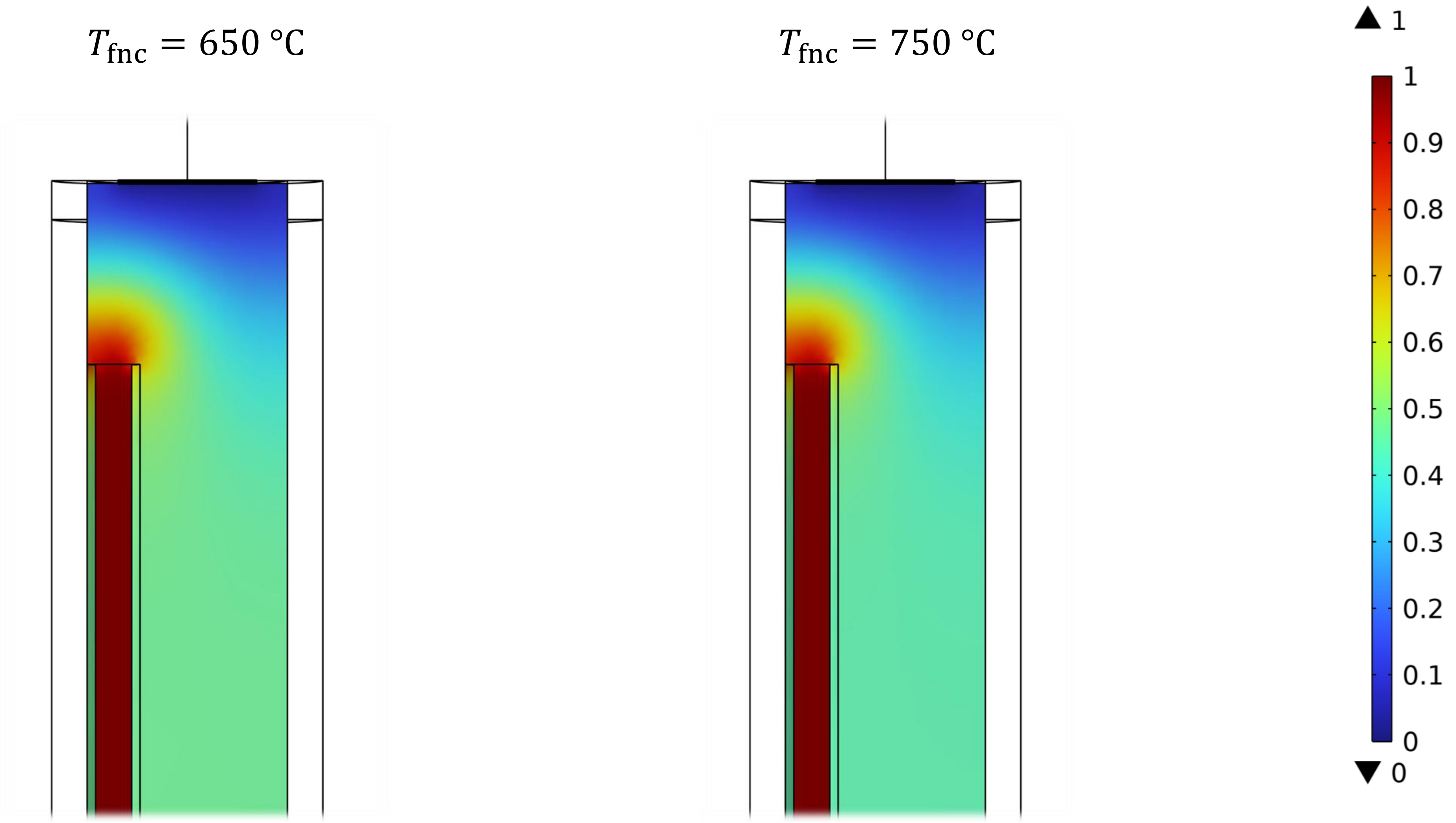
RESULTS

Velocity, $T_{\mathrm{fnc}} = 750\ °\mathrm{C}$, $V_{\mathrm{cell}} = 0.22\ \mathrm{V}$



RESULTS

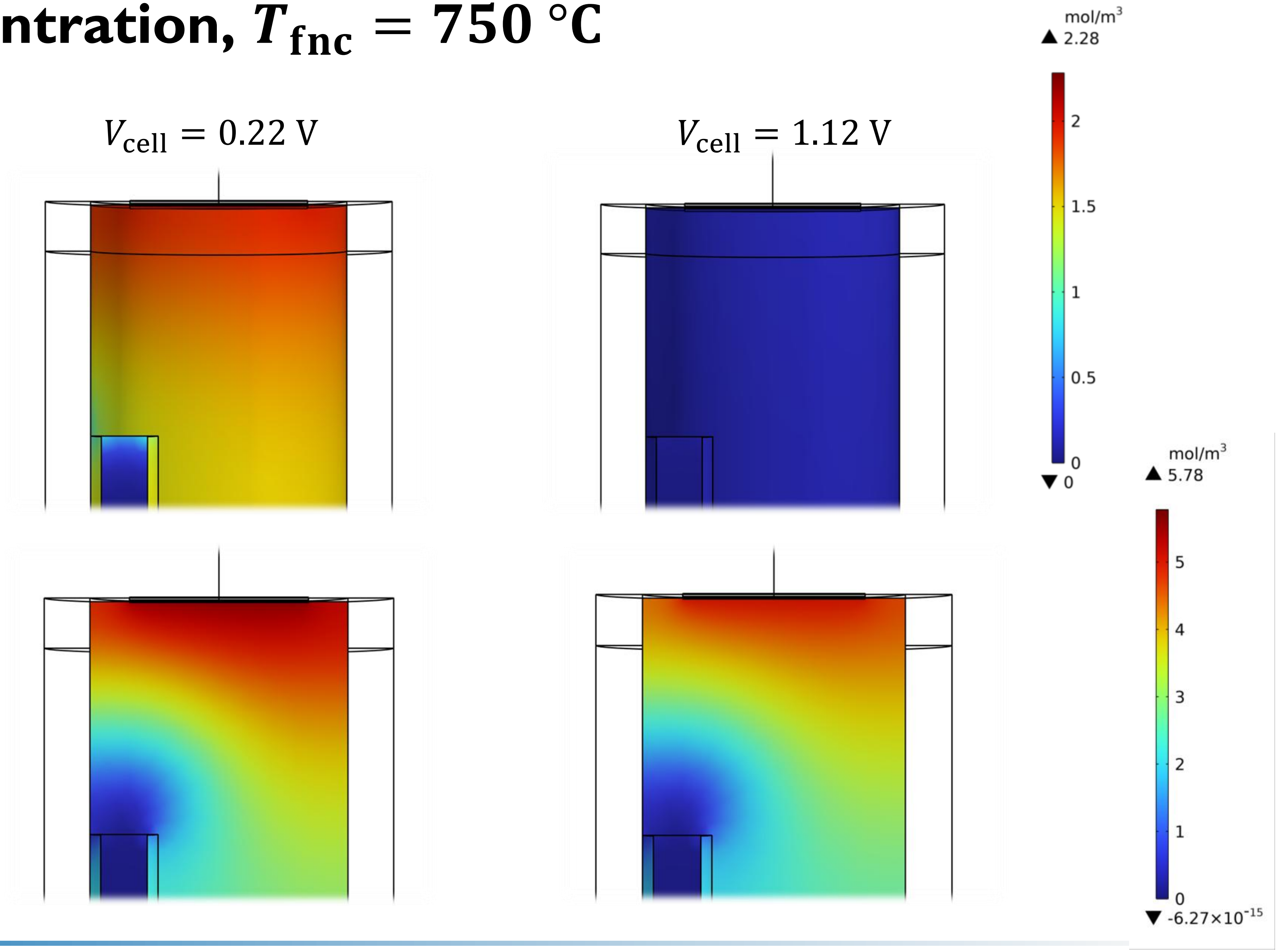
NH_3 molar fraction, $V_{cell} = 0.22$ V



H_2O concentration, $T_{\mathrm{fnc}} = 750\ °\mathrm{C}$

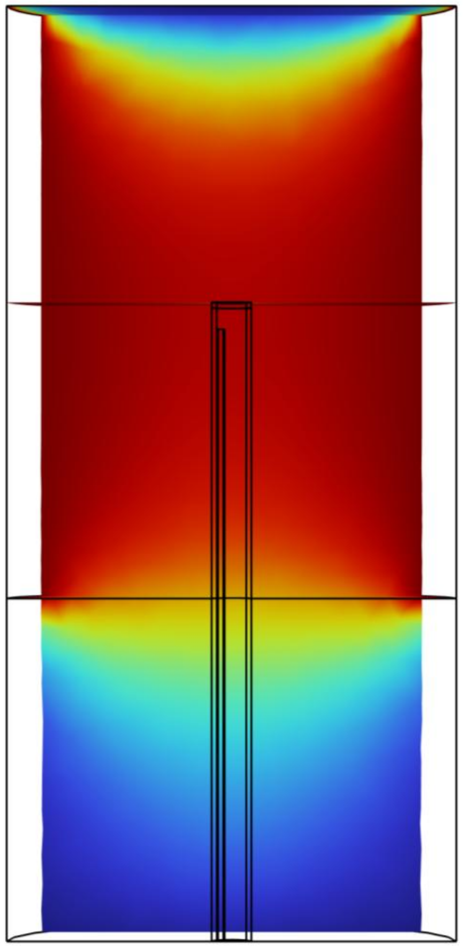
H_2

NH_3

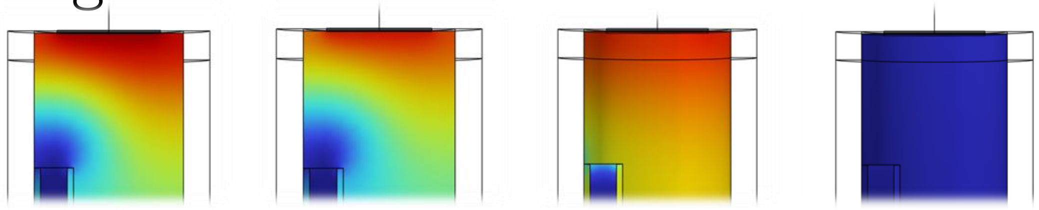


CONTENTS

Observations



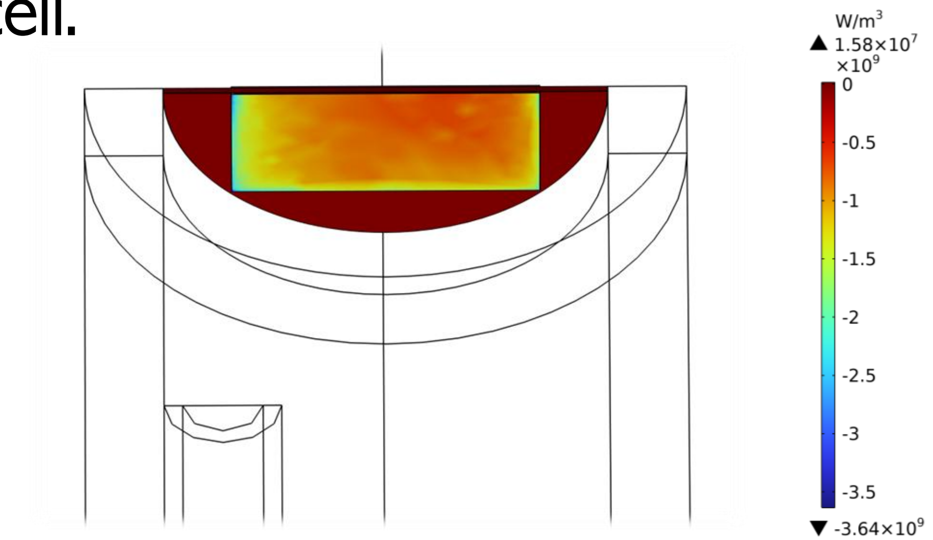
- Temperature in the air around the inlet is close to ambient, as expected.
- Temperature field reflects the gradient between the furnace and ambient temperature.
- The effect of polarization voltage on ammonia decomposition is negligible compared to the effect of temperature.
- Water generation appears to be less sensitive to polarization voltage if ammonia is used as fuel.



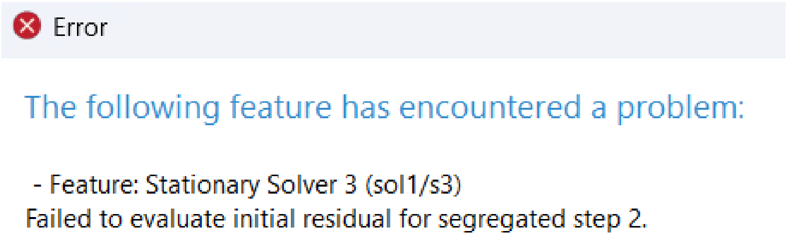
DISCUSSION

Observations

- Higher cracking reaction rate translates to a larger heat sink, resulting in lower anode temperature and thus slowing down the reaction.
- Higher overpotential results in a larger heat source.
- The two competing effects in the studied SOFC do not balance each other. The cooling effect of endothermic reactions is dominant, limiting the efficiency of the cell.

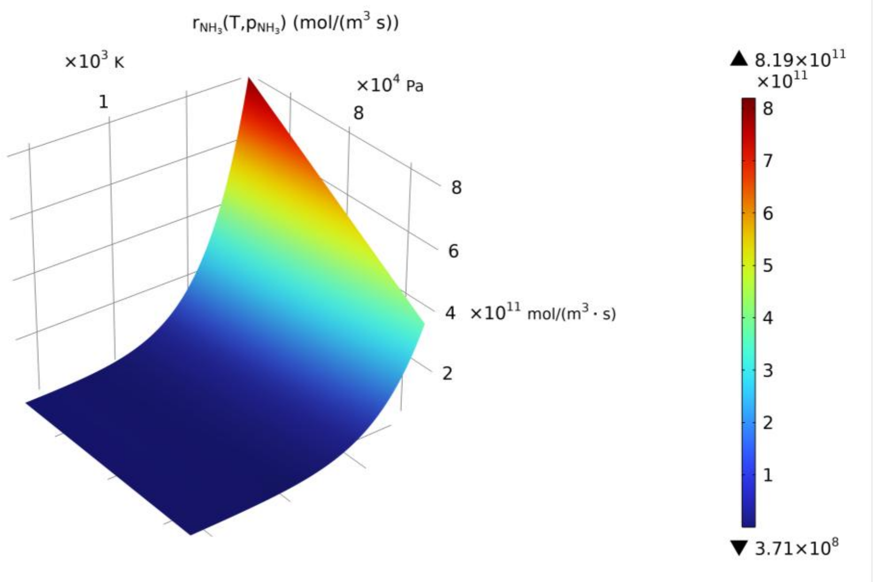


DISCUSSION
Challenges



- Model stability and convergence:
  - ❑ Solver will often arrive at diverging quantities.
  - ❑ Expressions with a denominator that can become zero should be avoided for this reason.
  - ❑ Initial conditions are also important.

- Missing parameters:
  - ❑ Some are difficult to measure, e.g. ionic conductivities and exchange currents.
  - ❑ Parameters that affect multiple physics interfaces should be prioritized, like $r_{\mathrm{NH_3}}$.



CONTENTS

CONCLUSIONS

Summary

- Hydrogen has better power output in the 650 °C ~ 750 °C temperature range.
- Simulated polarization curves reproduce experimental results without the need to adjust individual parameters.
- Competition between electrochemical and cracking reactions may be limiting to the efficiency.
- Multiphysics simulation lets us gauge the impact of each reaction individually, which is necessary for optimization and not possible experimentally.

Conclusion

The power loss on transition from H_2 to NH_3 as fuel could be attributed in part to ammonia cracking, as demonstrated by the simulations. However, this could be overcome by purposeful cell design.

OUTLOOK

With correct parameters multiphysics models can:

WHAT
- Visualize distribution of species
- Visualize distribution of electric currents
- Visualize distribution of temperature
- Identify location of e-chem activity and rate limiting processes

WHAT FOR
- Design stack geometry for optimum efficiency
- Minimize experimental effort in material design
- Generate data for AI-enhanced models
- Project useful life from thermal stresses upon heating/cooling
- Project performance for multi-fuel applications

ACKNOWLEDGMENT

This work was funded by the Millennium Institute on Green Ammonia as Energy Vector - MIGA (ICN2021_023) supported by the Millennium Scientific Initiative by the Agencia Nacional de Investigación y Desarrollo (ANID).