CISTEM

Construction of Improved HT-PEM MEAs and Stacks for Long Term Stable Modular CHP Units

Three-dimensional mathematical model of the high temperature PEM fuel cell stack

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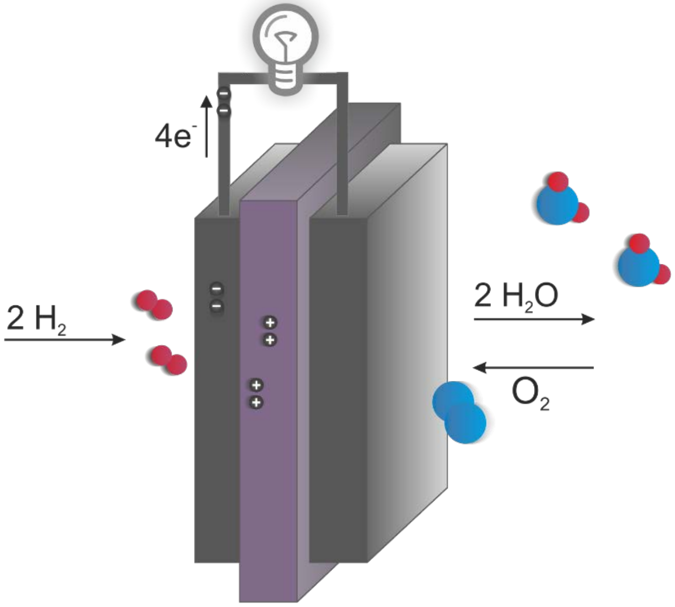
High Temperature PEM Fuel Cell

- Fuel cell (FC): direct conversion of chemical energy of fuel (H_2) to electricity
- PEM FC: Polymer Electrolyte Membrane Fuel Cell
  - Electrolyte: ion selective membrane – PBI doped by H_3PO_4
  - Electrodes: Pt/C
  - Temperature:160 °C
  - Main reactions:

$2\,H_2 \leftrightarrow 4\,H^+ + 4\,e^-$ (HOR)

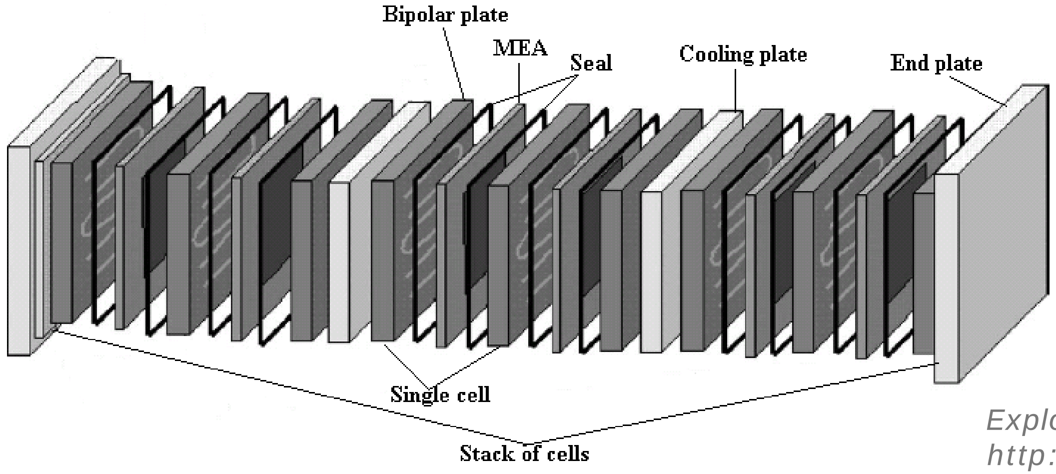
$O_2 + 4\,H^+ + 4\,e^- \leftrightarrow 2\,H_2O$ (ORR)



- Main advantages of HT PEM FC
  - Higher rate of electrode reactions
  - More effective utilization of waste heat
  - Lower sensitivity to catalyst poisons (CO)
  - Simpler water management

Fuel cell stack

- Plate-and-frame set-up
  - Reduction of the investment cost
  - Flexible process intensification/scale-up
- Potential obstacles of large-scale systems
  - Local inhomogeneity of the media, charge and heat distribution
- Consequences
  - Reduced process performance, efficiency and life-time



Exploded view of PEM fuel cell stack.
http://knowledge.electrochem.org

Mathematical modelling

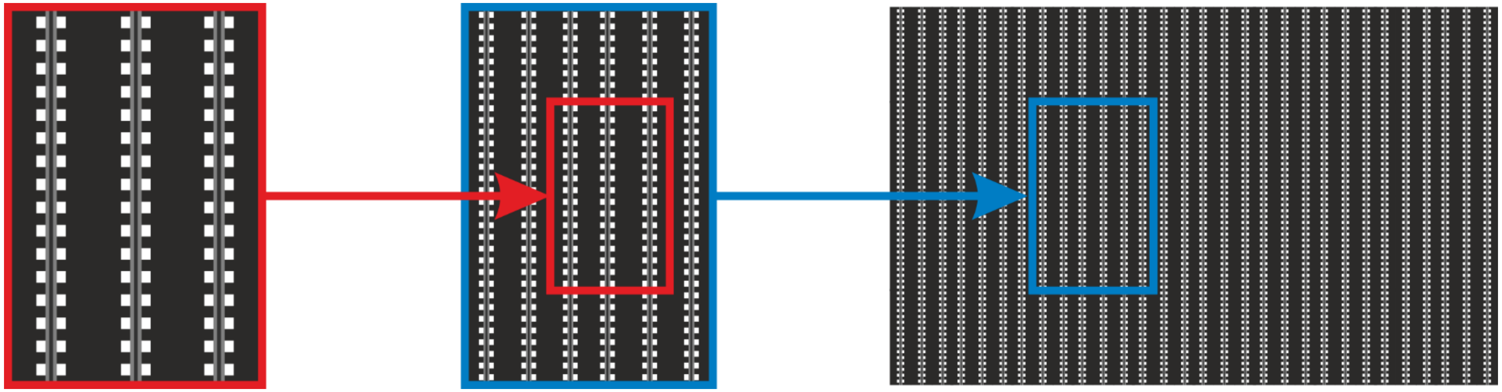
- Powerful tool in optimization of stack parameters
  - System geometry and construction
  - Operational parameters
  - Important saving in time and costs

- Main obstacles
  - High number of phase interfaces, often stiff behavior
  - Extreme increase in the computational power demands and computational time

- **Aim of the work**
  - Development of alternative model approach - acceptable hardware computational demands
  - 3D model of HT PEM FC stack

Macrohomogeneous approach

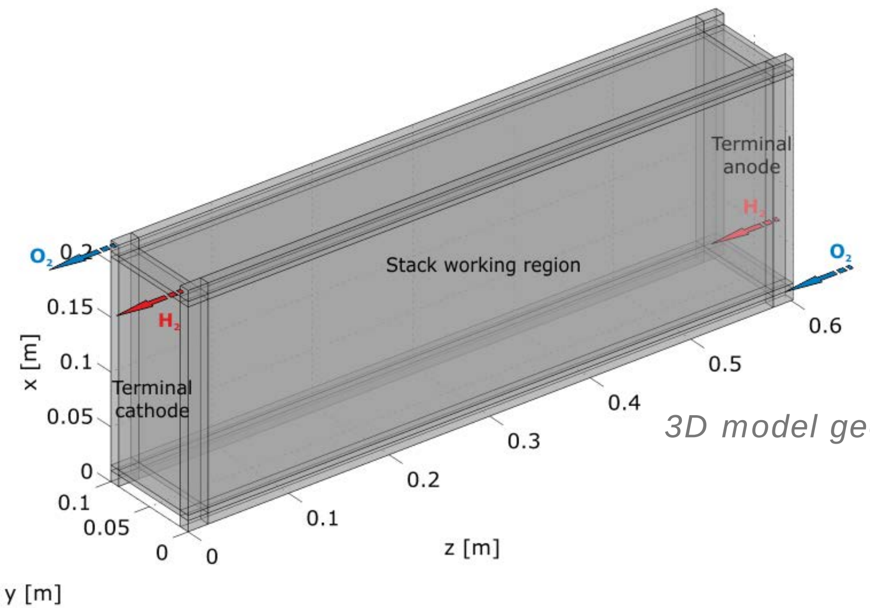
- **Basic idea and assumptions**
  - High number of the cells – system appears continuous from macroscopic point of view
  - Multiple layers/interfaces substituted by several overlapping continuums
  - Uniform radial distribution of physical quantity in each system layer



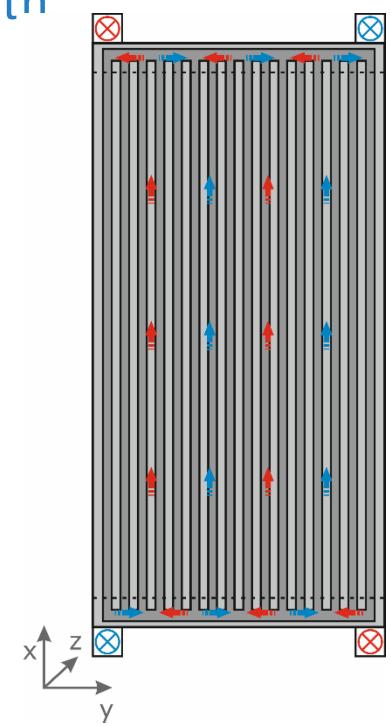
- **Main advantages**
  - Significantly reduced computational demands
  - Allows description of complex industrial size units – local distribution of physical quantities

Model Geometry

- Three-dimensional (3D) model
  - x-coordinate: parallel to membranes – stack height
  - y-coordinate: parallel to membranes – stack depth
  - z-coordinate: normal to membranes – stack width
- Flow-field with parallel straight channels



3D model geometry



x-y cross-section through the stack

Assumptions and simplification

- Stationary and isothermal condition
- Ideal gasses
- Neglected species transport limitation in GDLs and CLs
- Constant overvoltage in CLs along z-coordinate
- Considered reactions (100 % faradaic efficiency):
  - Oxygen reduction reaction (ORR)
    $O_2 + 4\ H^+ + 4\ e^- \leftrightarrow 2\ H_2O$
  - Hydrogen oxidation reaction (HOR)
    $2\ H^+ + 2\ e^- \leftrightarrow H_2$
    - Assumed to be considerably faster in comparison to ORR ⇨ overvoltage on the anode neglected

Kinetic parameters for ORR

Butler-Volmer type kinetic equation

$$j_{ORR,V} = j^0_{ORR,V} \left\{ \left(\frac{y_{H_2O}\, p_c}{p_{ref,H_2O}}\right)^2 \exp\left[\frac{(1-\beta_{ORR}) n_{ORR} F}{RT} \eta_{ORR}\right] - \left(\frac{y_{O_2}\, p_c}{p_{ref,O_2}}\right) \exp\left[-\frac{\beta_{ORR} n_{ORR} F}{RT} \eta_{ORR}\right] \right\}$$

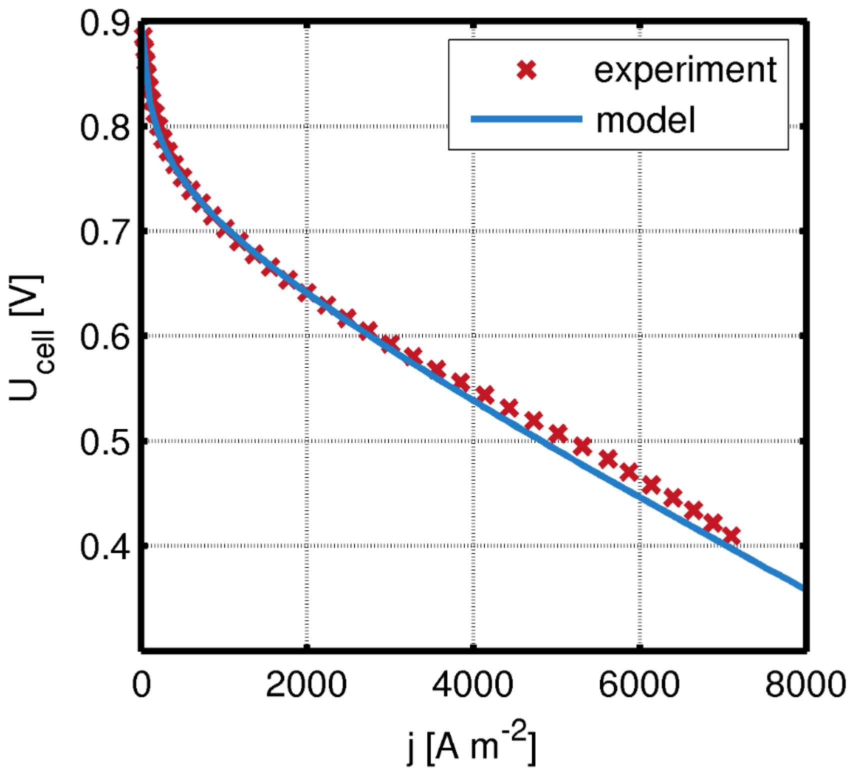
Kinetic parameters – from single cell experiment

- Experimental conditions:
  - MEA: Dapozol® G55, Batch no.: INH-13-002, ID: MEA-13-498
  - Dry gases
  - Active area 25 cm^2
  - Temperature 160 °C
  - j_{max} = 0.84 A cm^{-2} (fixed volumetric flow rate for this current load)
    - λ_{O2} = 2
    - λ_{H2} = 1.2

Kinetic parameters for ORR

- Exchange volumetric current
  $j^0_{ORR,V} = j^0_{ORR,A} a_{TPB} = 1.5 \cdot 10^6$ A m^{-3}
- Symmetry coefficient
  $\beta_{ORR} = 0.25$

- The differences for higher current load:
  - Transport limitations not considered
  - Resistance dependence on current load neglected



U-I curve – comparison of experimental data for single cell and model for 10 cells stack
Time – 49th day (after activation and before degradation)

Governing equations

- Mass balances

$$-\nabla \cdot (\mathbf{v}_{\mathrm{a}}\rho_{\mathrm{a}}) + S_{\mathrm{m,a}} = 0 \qquad -\nabla \cdot (\mathbf{v}_{\mathrm{c}}\rho_{\mathrm{c}}) + S_{m,c} = 0$$

$$\mathbf{v}_i = -\frac{\mathbf{P}}{\eta_i}\nabla^{\mathbf{T}} p_i$$

- Dependent variables:
  - pressure of anode gas stream p_{a}
  - pressure of cathode gas stream p_{c}
- Input parameters:
  - Permeability of flow field channels - Hagen-Poiseuille type equation
  - Viscosity - gas kinetic theory

Governing equations

- Material balances

$$-\nabla \cdot (\mathbf{J}_{O_2}) + S_{O_2} = 0$$

$$-\nabla \cdot (\mathbf{J}_{N_2}) + S_{N_2} = 0$$

$$y_w = 1 - y_{O_2} - y_{N_2}$$

$$\mathbf{J}_i = \frac{P_c}{RT}\left(-\mathbf{D}_c \nabla^T y_i + \mathbf{v}_c y_i\right)$$

- Dependent variables:
  - O_2 molar fraction y_{O_2}
  - N_2 molar fraction y_{N_2}
  - water vapour molar fraction y_w
- Input parameters:
  - Diffusion coefficient - gas kinetic theory

Governing equations

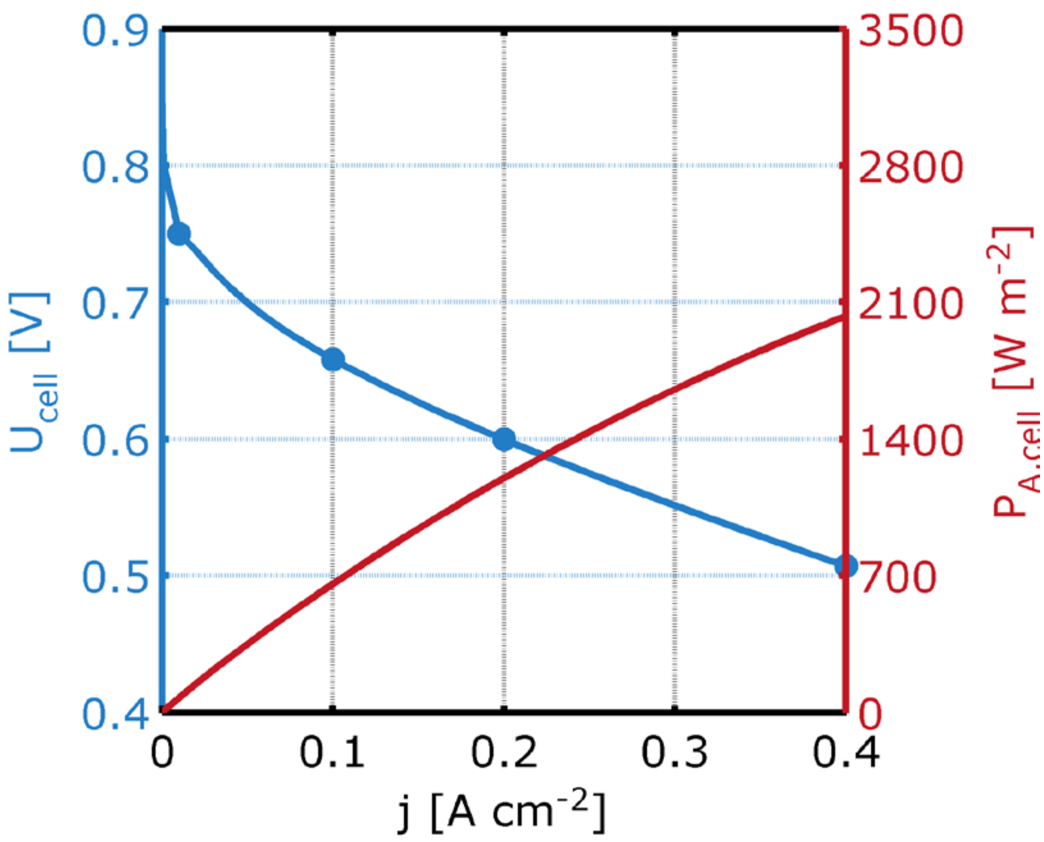
- Charge balance

$$\nabla \cdot \mathbf{j} = 0 \qquad 0 = j_{\mathrm{ORR,V}} - \frac{j_z}{w_{\mathrm{cl}}}$$

- Dependent variables:
  - cell averaged potential ϕ
  - cell averaged overpotential η
- Assumptions:
  - HOR overvoltage contribution to total overvoltage is neglected
- Local current density:

$$\mathbf{j} = -\mathbf{G}_s \cdot \begin{pmatrix} \frac{\partial \phi}{\partial z} + \frac{N_{\mathrm{cell}}}{W_{\mathrm{cell}}}\{U_{\mathrm{OCV}} + \eta\} \\ \frac{\partial \phi}{\partial y} \\ \frac{\partial \phi}{\partial x} \end{pmatrix}$$

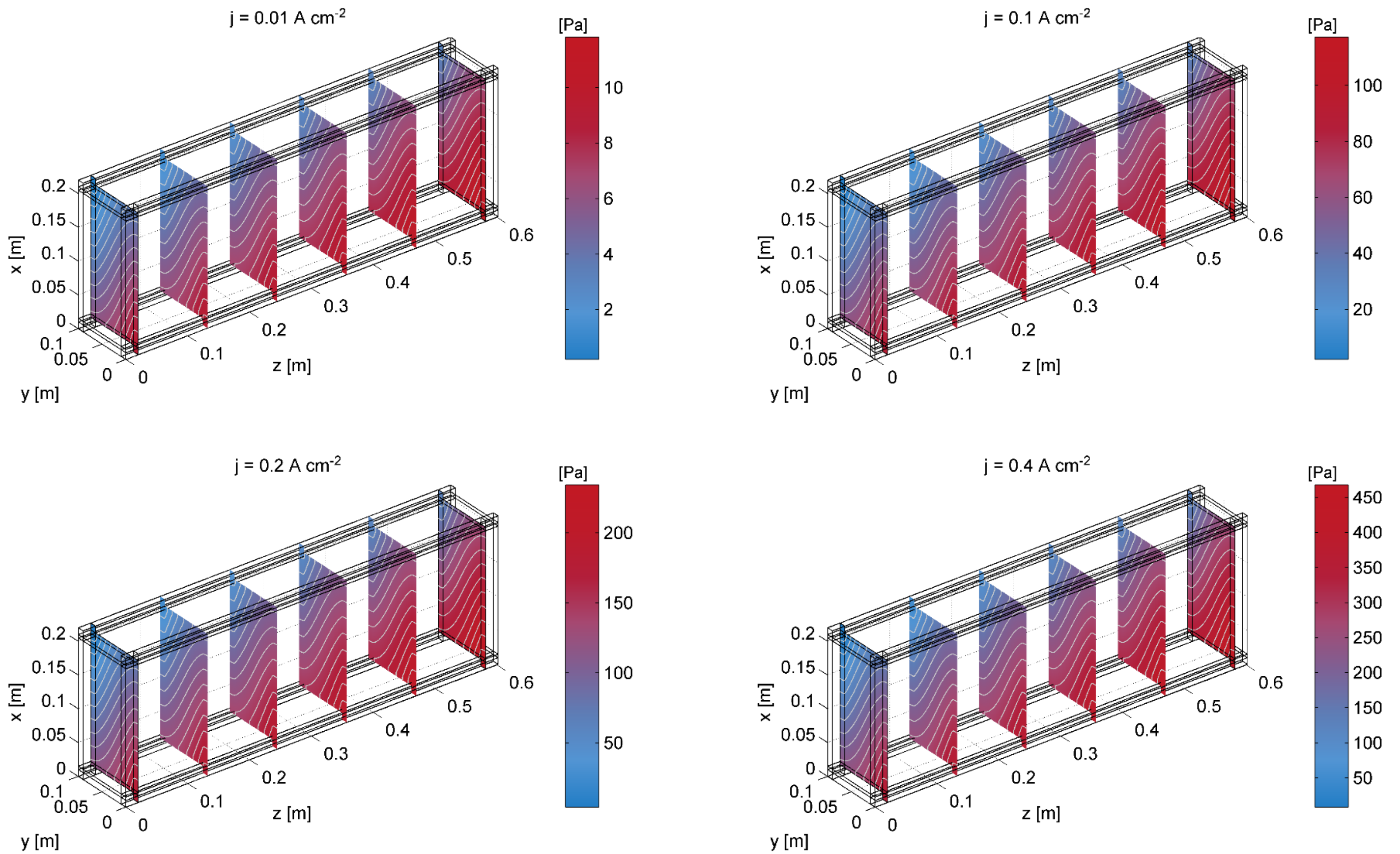
Load curve for stack



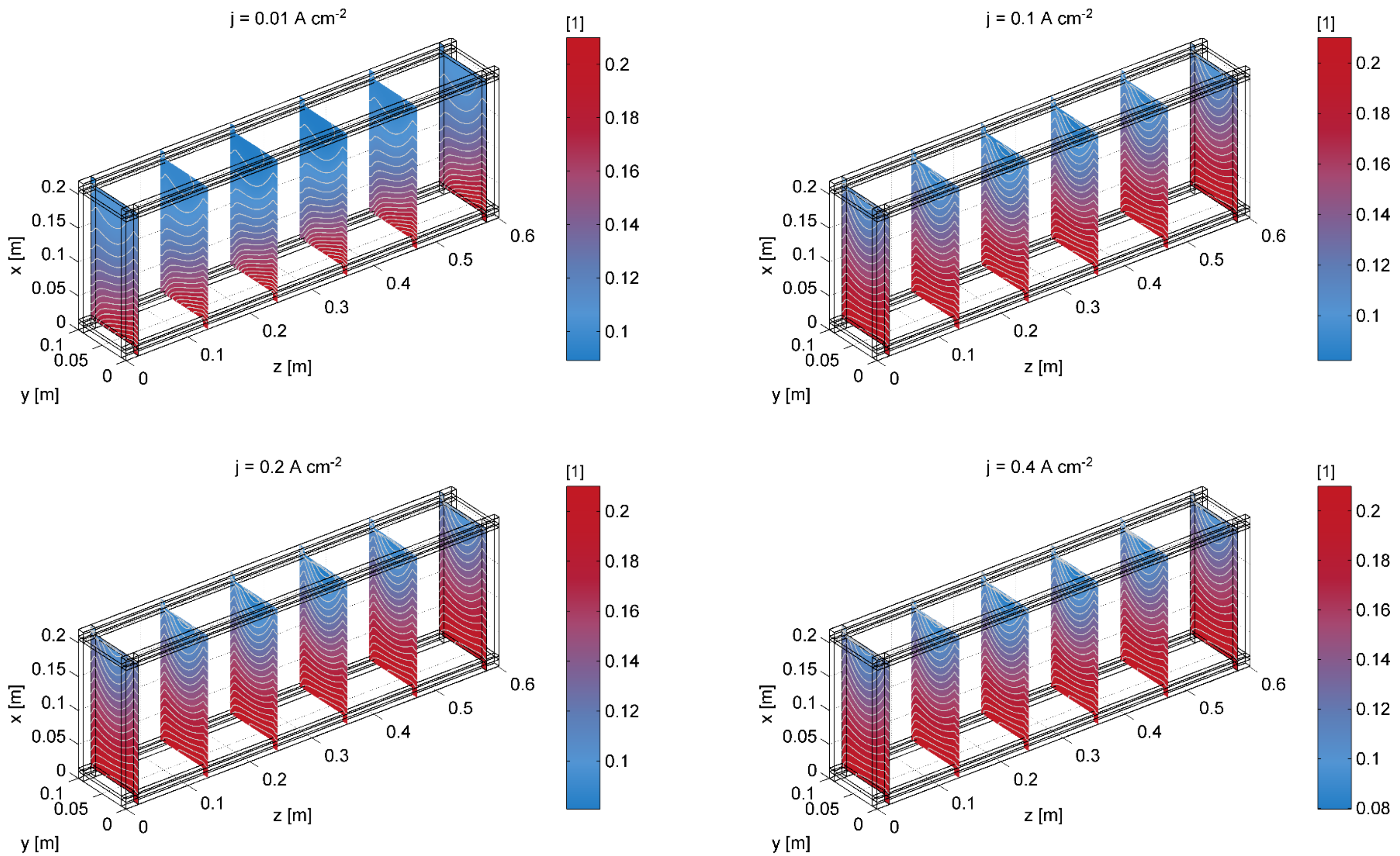
Input parameters

- 100 cells
- U_{OCV} = 0.9 V/cell
- T = 433 K
- P_{out} = 101 325 Pa
- $y^{in}_{H_2} = 1$
- $y^{in}_{O_2} = 0.21$
- $y^{in}_{N_2} = 0.79$
- $\lambda_{H_2} = 1.2$
- $\lambda_{O_2} = 2$

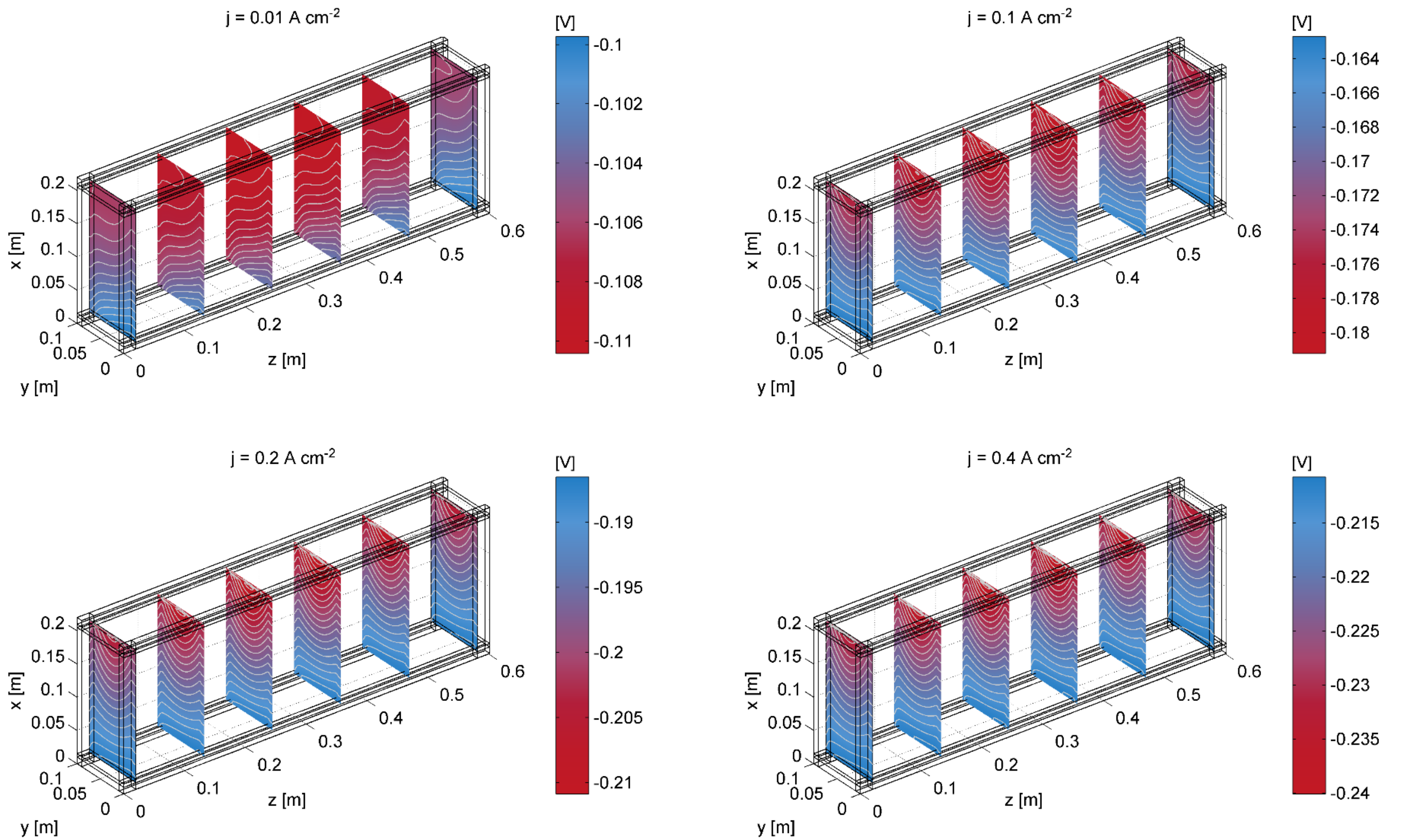
Pressure in cathode gas stream



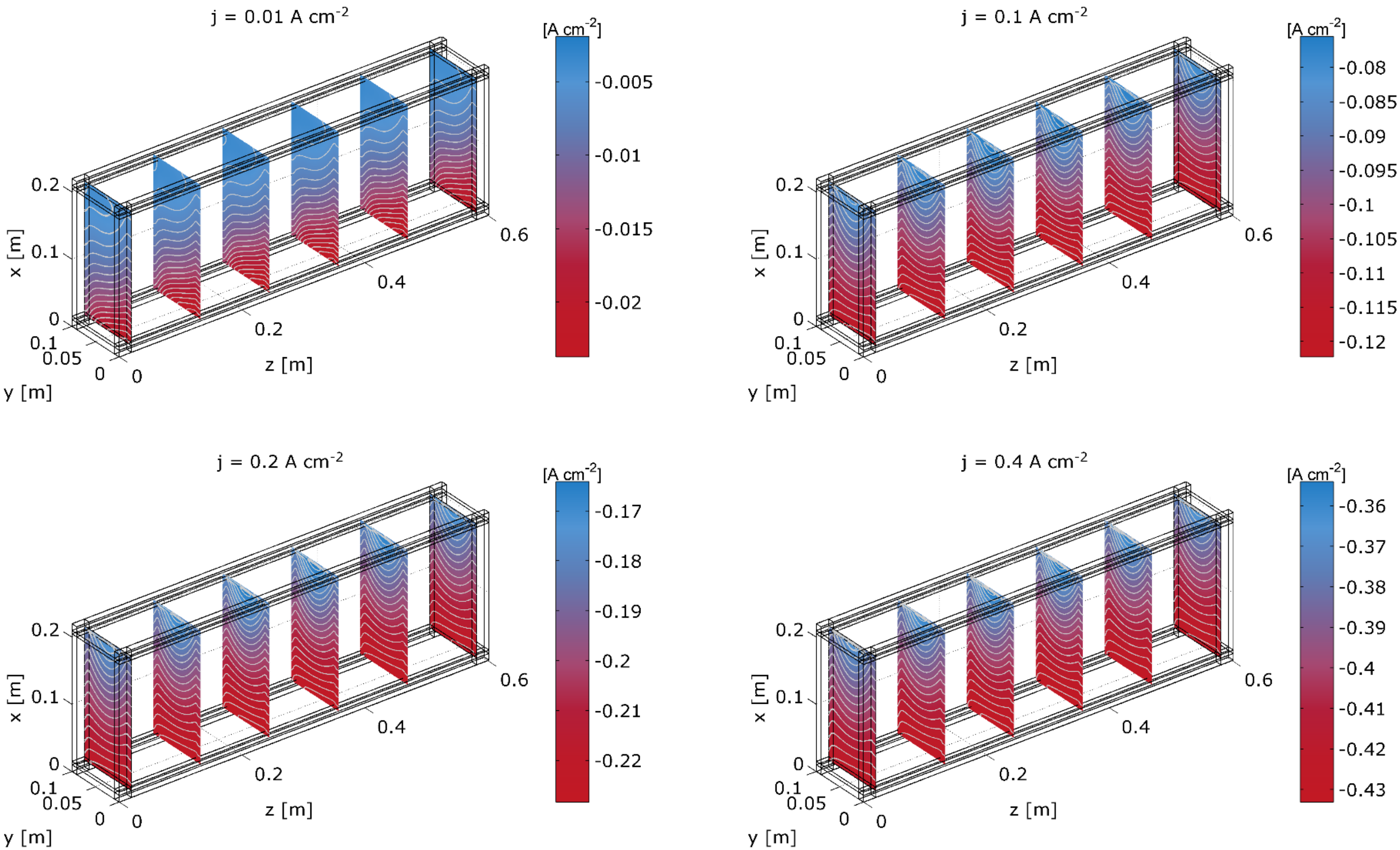
Molar fraction of oxygen



Cell averaged overpotential



Local current density in z-direction



Conclusion

- 3D model of HT PEM FC stack was successfully proposed and implemented in COMSOL Multiphysics®
- Enable visualization of local physical properties in the system
- Macrohomogeneous approach
  - Viable for modeling of FC stack
  - Physically (qualitatively) correct – the results correspond with expectations
  - Sufficiently low computational time
- Future prospects:
  - More types of flow-field geometry (optimization)
  - Dynamic model
  - Implementation of degradation reactions into the model

Thank you for your attention

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