Research for Sustainable Technologies

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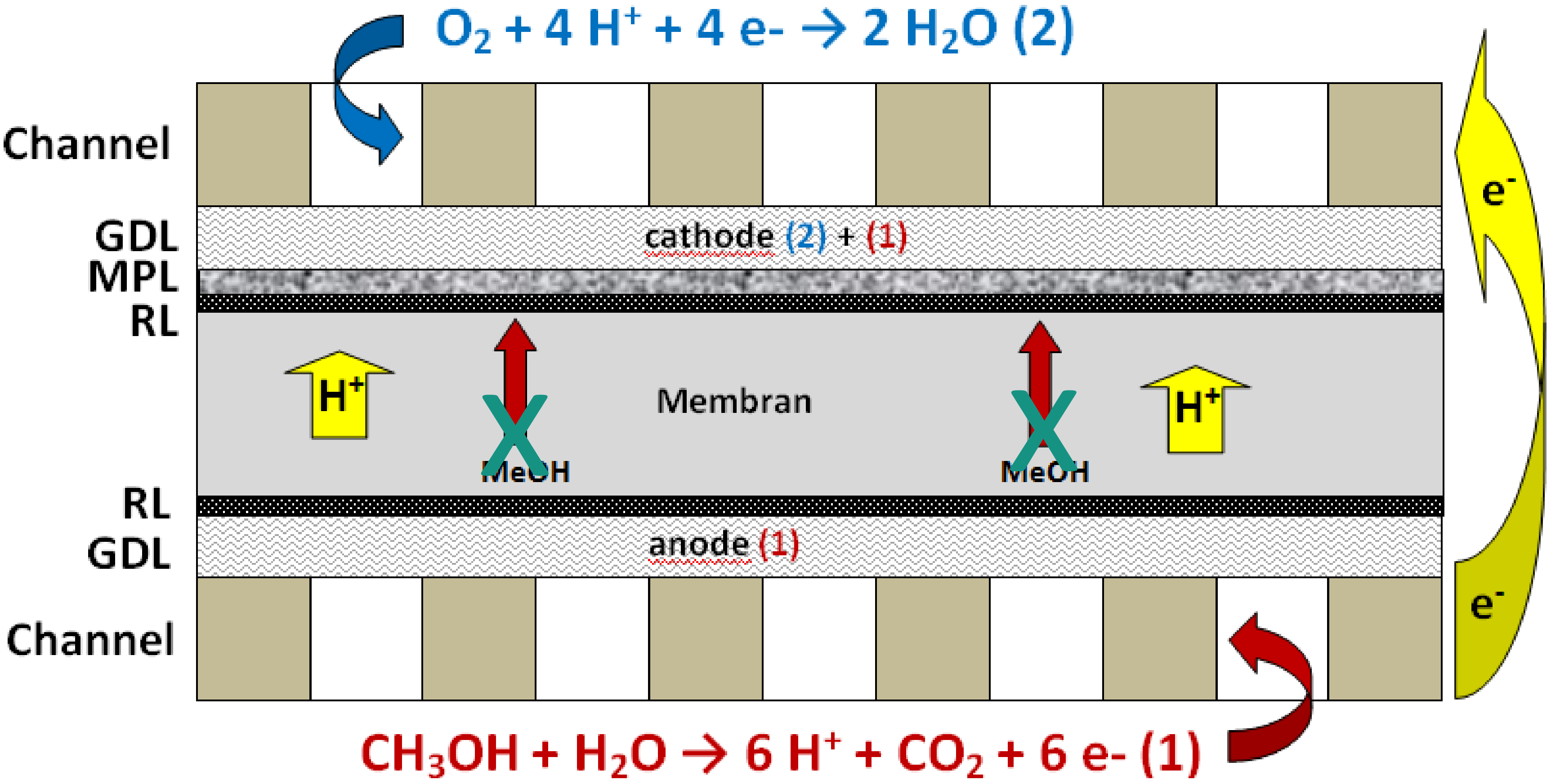
Simplified DMFC Model with COMSOL

COMSOL
CONFERENCE
2015 GRENOBLE

Materials
Chemical Engineering
Biotechnology

Principle of Direct Methanol Fuel Cell



Boundary condition for simplified DMFC model: no MeOH transport through PEM membrane

Geometry

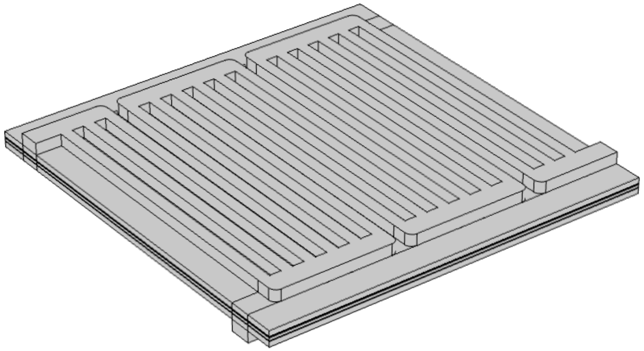
- **WP8 + extrude** opposite direction: H_ch + H_GDLc + H_MPLc + H_RLc+ H_M + H_Rla + H_GDLa

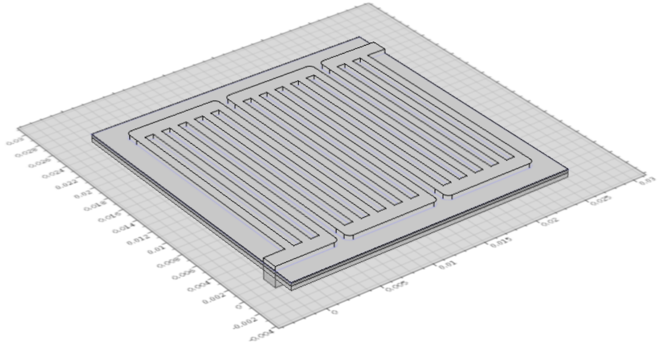
- **WP8**: channel cathode

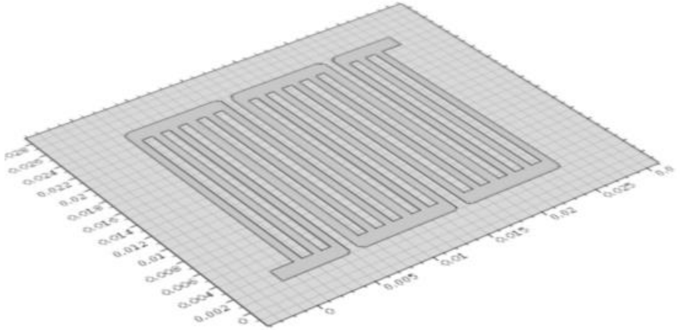
- **WP7 + extrude**: GDL cathode
- **WP6 + extrude**: MPL cathode
- **WP5 + extrude**: RL cathode
- **WP4 + extrude**: Membrane
- **WP3 + extrude**: RL anode
- **WP2 + extrude**: GDL anode

- **WP1 + extrude**: H_ch + H_GDLa + H_Rla + H_M + H_RLc + H_GDLc + H_MPLc

- **WP1**: channel anode

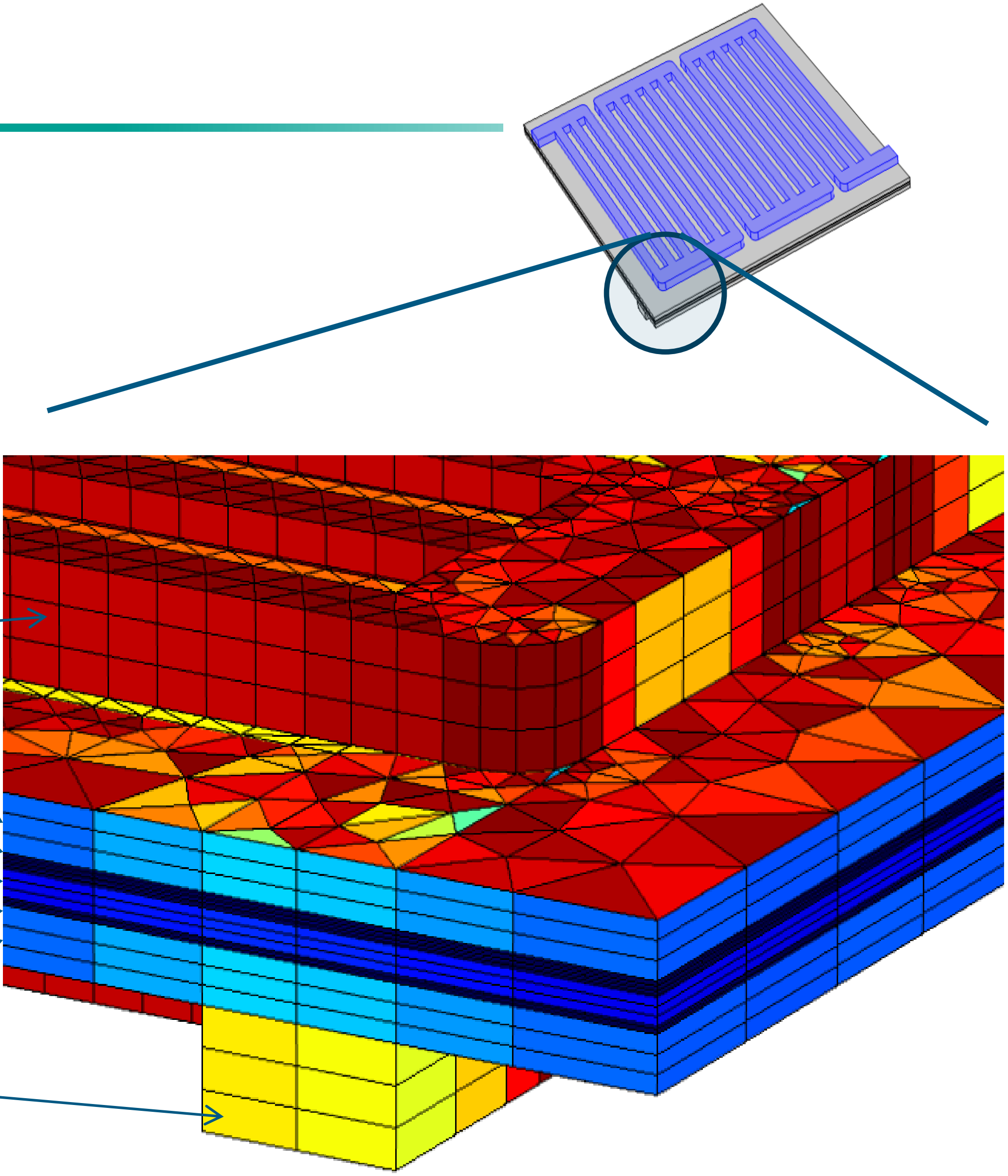






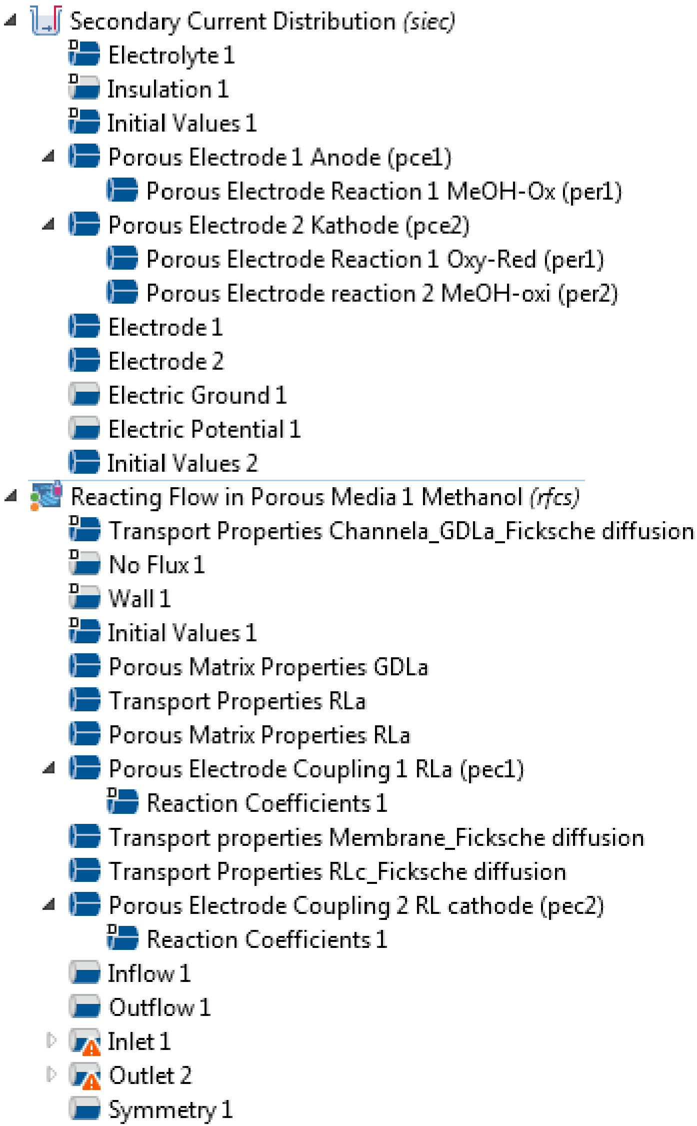
Mesh

- **Size:** fine
- **Free Triangular**
- **Swept:** generates **hexahedrons**
  - **Ditribution: 3** elements
- **Complete mesh** consists of
  - **253020** domain elements
  - **172658** boundary elements
  - **32654** edge elements.

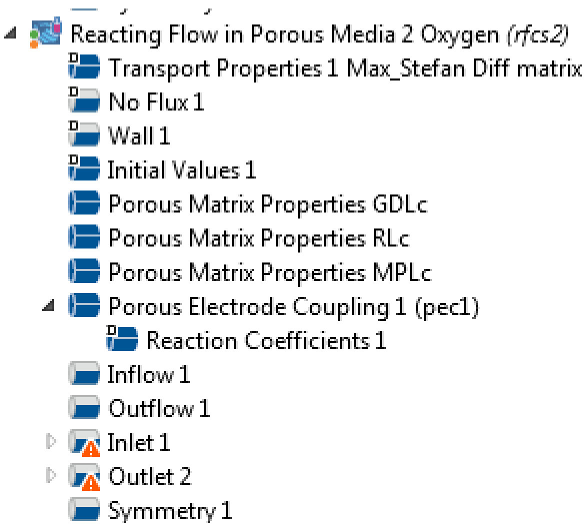


- Air Channel cathode
- Gas Diffusion Layer GDLc
- Micro Porous layer MPLc
- Reaction Layer RLc
- Membrane
- Reaction Layer RLa
- Gas diffusion Layer GDLa
- MeOH Channel inlet

Physics

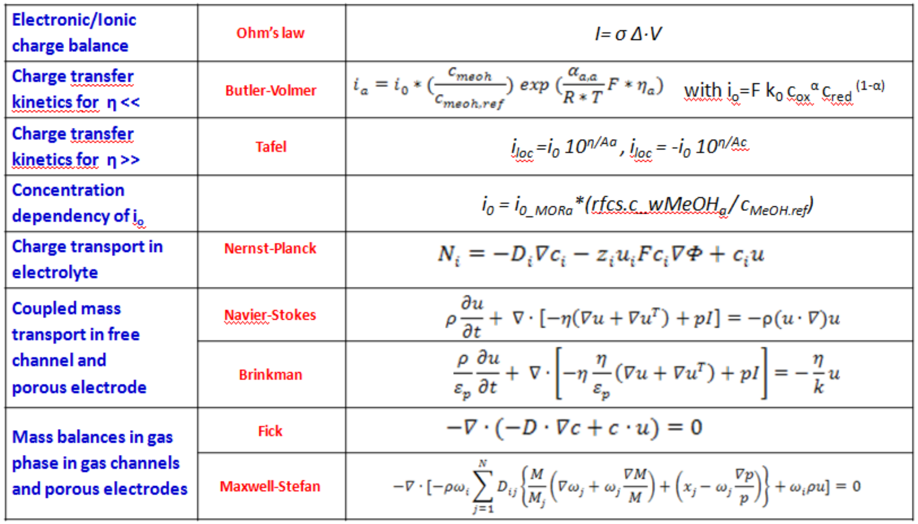


- Secondary Current Distribution *(siec)*
  - Electrolyte 1
  - Insulation 1
  - Initial Values 1
  - Porous Electrode 1 Anode (pce1)
    - Porous Electrode Reaction 1 MeOH-Ox (per1)
  - Porous Electrode 2 Kathode (pce2)
    - Porous Electrode Reaction 1 Oxy-Red (per1)
    - Porous Electrode reaction 2 MeOH-oxi (per2)
  - Electrode 1
  - Electrode 2
  - Electric Ground 1
  - Electric Potential 1
  - Initial Values 2
- Reacting Flow in Porous Media 1 Methanol *(rfcs)*
  - Transport Properties Channela_GDLa_Ficksche diffusion
  - No Flux 1
  - Wall 1
  - Initial Values 1
  - Porous Matrix Properties GDLa
  - Transport Properties RLa
  - Porous Matrix Properties RLa
  - Porous Electrode Coupling 1 RLa (pec1)
    - Reaction Coefficients 1
  - Transport properties Membrane_Ficksche diffusion
  - Transport Properties RLc_Ficksche diffusion
  - Porous Electrode Coupling 2 RL cathode (pec2)
    - Reaction Coefficients 1
  - Inflow 1
  - Outflow 1
  - Inlet 1
  - Outlet 2
  - Symmetry 1



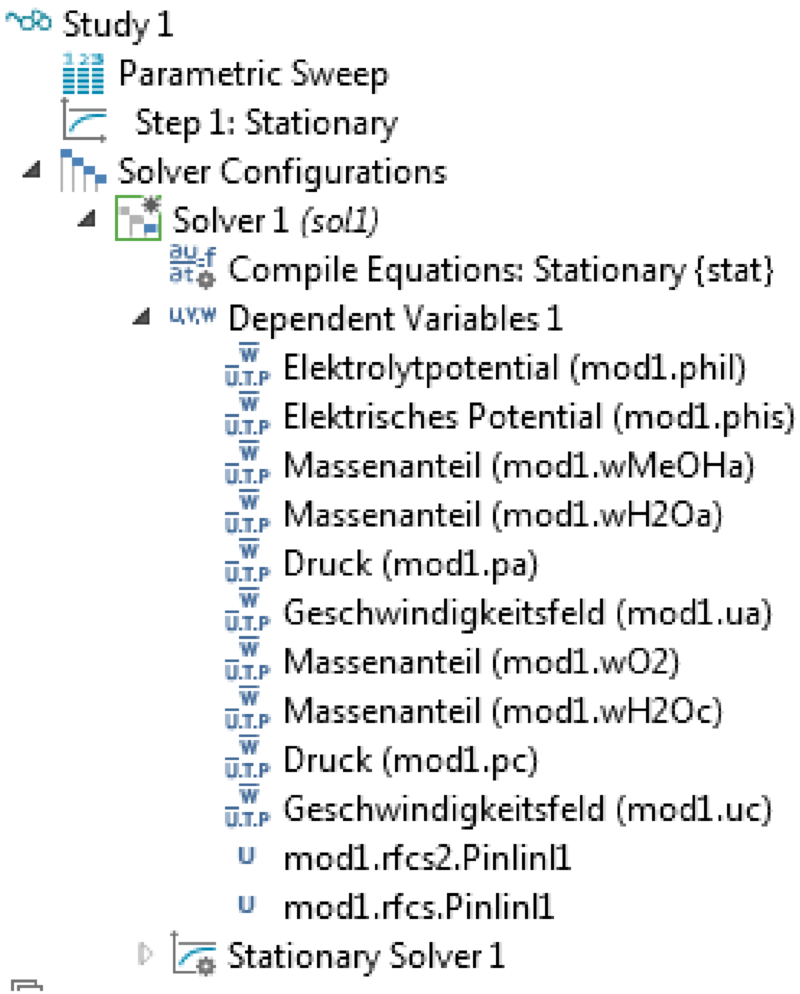
- Reacting Flow in Porous Media 2 Oxygen *(rfcs2)*
  - Transport Properties 1 Max_Stefan Diff matrix
  - No Flux 1
  - Wall 1
  - Initial Values 1
  - Porous Matrix Properties GDLc
  - Porous Matrix Properties RLc
  - Porous Matrix Properties MPLc
  - Porous Electrode Coupling 1 (pec1)
    - Reaction Coefficients 1
  - Inflow 1
  - Outflow 1
  - Inlet 1
  - Outlet 2
  - Symmetry 1

$c = concentration\ (mol\ m^{-3})$
$D = diffusion\ coefficient\ (m^2\ s^{-1})$
$F = Faraday\ constant\ (C\ mol^{-1})$
$i_a = anodic\ current\ density\ (A\ m^{-2})$
$i_0 = exchange\ current\ density\ (A\ m^{-2})$
$I = current\ (A)$
$N_i = charge\ transport\ in\ electrolyte\ (mol\ m^{-2}\ s^{-1})$
$p = pressure\ (Pa)$
$u = velocity\ (m\ s^{-1})$
$V = potential\ (V)$
$z = number\ of\ electron\ (-)$
$\alpha = symetrie\ factor\ (-)$
$\eta = dynamic\ viscosity\ (Pa \cdot s)$
$\eta_a = anodic\ overpotential\ (V)$
$\varepsilon_p = porosity\ (-)$
$\kappa = permeability\ (m^2)$
$\Phi = potential\ in\ electrolyte\ (V)$
$\rho = density\ (kg\ m^{-3})$
$\sigma = conductivity\ (S\ m^{-1})$
$II = Tensor$



Electronic/Ionic charge balance	**Ohm's law**	$I = \sigma\, \Delta \cdot V$
Charge transfer kinetics for η <<	**Butler-Volmer**	$i_a = i_0 * (\frac{c_{meoh}}{c_{meoh,ref}})\ exp\ (\frac{\alpha_{a,a}}{R*T} F * \eta_a)$ with $i_o = F\ k_0\ c_{ox}{}^{\alpha}\ c_{red}{}^{(1-\alpha)}$
Charge transfer kinetics for η >>	**Tafel**	$i_{loc} = i_0\ 10^{\eta/Aa}$, $i_{loc} = -i_0\ 10^{\eta/Ac}$
Concentration dependency of i_o		$i_0 = i_{0\_MORa} * (rfcs.c\_wMeOH_a / c_{MeOH.ref})$
Charge transport in electrolyte	**Nernst-Planck**	$N_i = -D_i \nabla c_i - z_i u_i F c_i \nabla \Phi + c_i u$
Coupled mass transport in free channel and porous electrode	**Navier-Stokes**	$\rho \frac{\partial u}{\partial t} + \nabla \cdot [-\eta(\nabla u + \nabla u^T) + pI] = -\rho(u \cdot \nabla)u$
	Brinkman	$\frac{\rho}{\varepsilon_p} \frac{\partial u}{\partial t} + \nabla \cdot \left[-\eta \frac{\eta}{\varepsilon_p}(\nabla u + \nabla u^T) + pI\right] = -\frac{\eta}{k} u$
Mass balances in gas phase in gas channels and porous electrodes	**Fick**	$-\nabla \cdot (-D \cdot \nabla c + c \cdot u) = 0$
	Maxwell-Stefan	$-\nabla \cdot [-\rho\omega_i \sum_{j=1}^{N} D_{ij} \left\{\frac{M}{M_j}\left(\nabla \omega_j + \omega_j \frac{\nabla M}{M}\right) + \left(x_j - \omega_j \frac{\nabla p}{p}\right)\right\} + \omega_i \rho u] = 0$

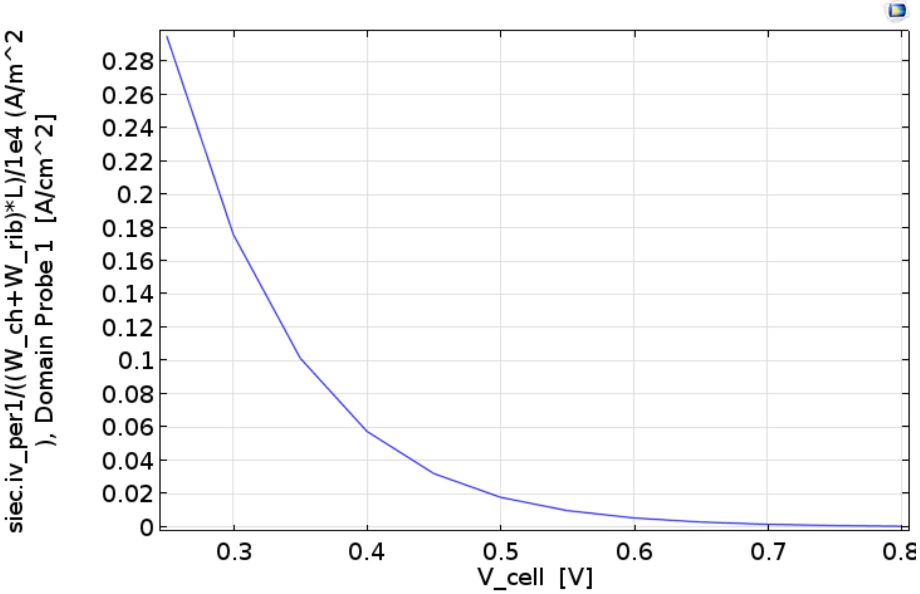
Study



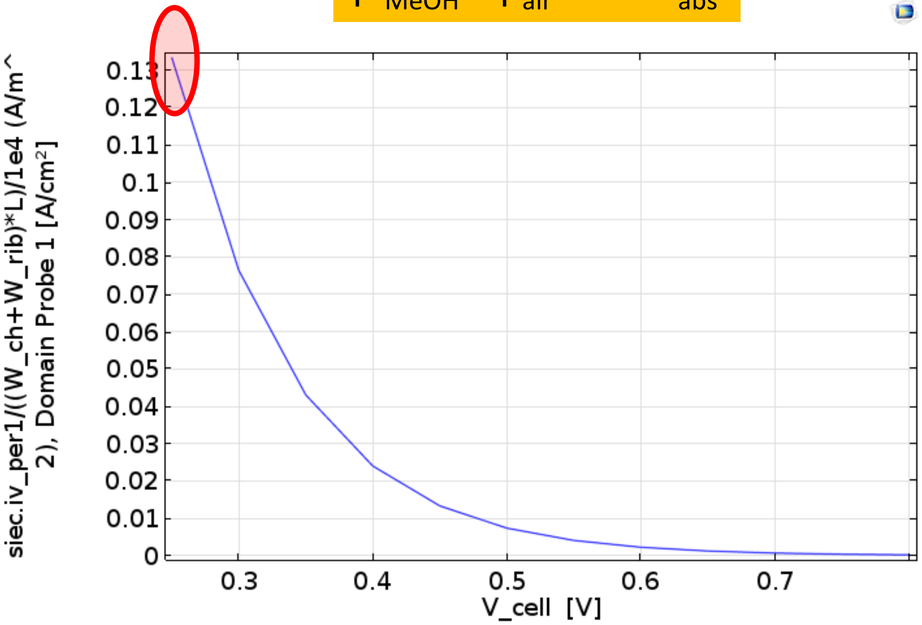
- Study 1
  - Parametric Sweep
  - Step 1: Stationary
  - Solver Configurations
    - Solver 1 *(sol1)*
      - Compile Equations: Stationary {stat}
      - Dependent Variables 1
        - Elektrolytpotential (mod1.phil)
        - Elektrisches Potential (mod1.phis)
        - Massenanteil (mod1.wMeOHa)
        - Massenanteil (mod1.wH2Oa)
        - Druck (mod1.pa)
        - Geschwindigkeitsfeld (mod1.ua)
        - Massenanteil (mod1.wO2)
        - Massenanteil (mod1.wH2Oc)
        - Druck (mod1.pc)
        - Geschwindigkeitsfeld (mod1.uc)
        - mod1.rfcs2.Pinlinl1
        - mod1.rfcs.Pinlinl1
      - Stationary Solver 1

Results: U_I characteristic in function of O_2 mass fraction

c_{MeOH}= 10 wt%
c_{O2} = 90 wt%
T = 80°C
$p_{MeOH} = p_{air}$ = 1 bar_{abs}

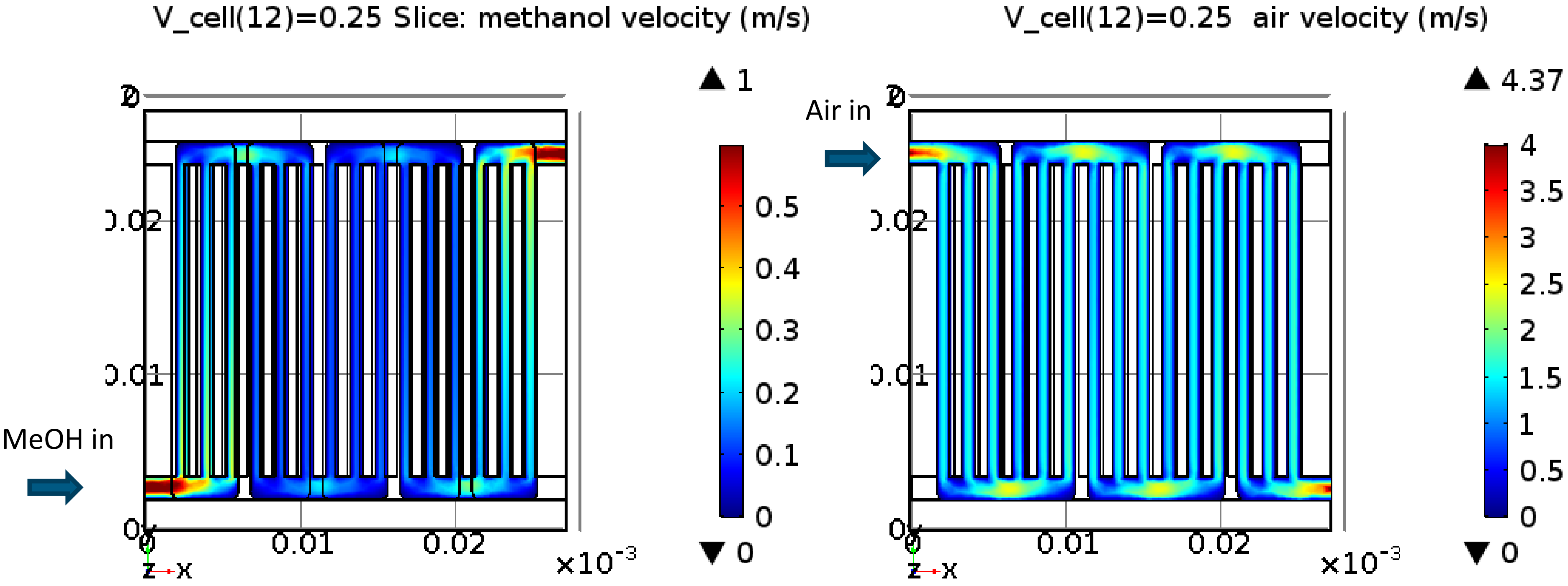


c_{MeOH}= 10 wt%
c_{O2} = 22,8 wt%
T = 80°C
$p_{MeOH} = p_{air}$ = 1 bar_{abs}



- **Fuel cell performance in air is half of that calculated in pure oxygen; this correlates well with experimental results.**

Results: MeOH and Air velocity profile @ 0,25 V

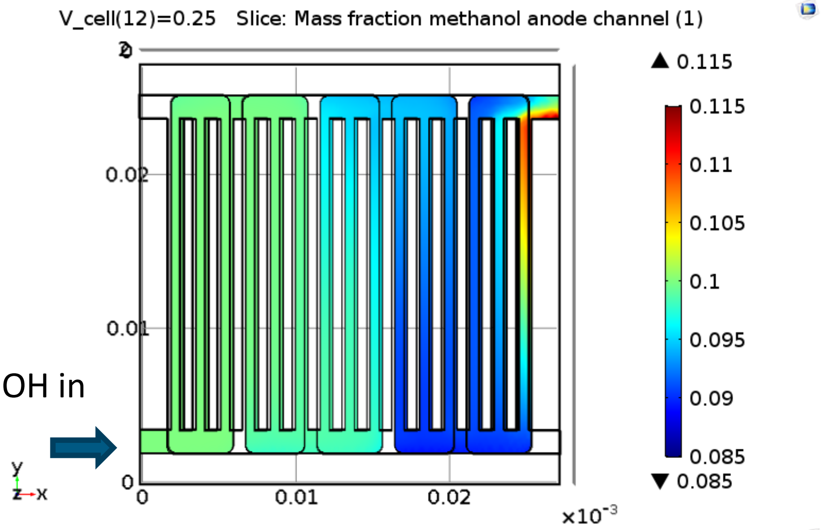


V_cell(12)=0.25 Slice: methanol velocity (m/s)

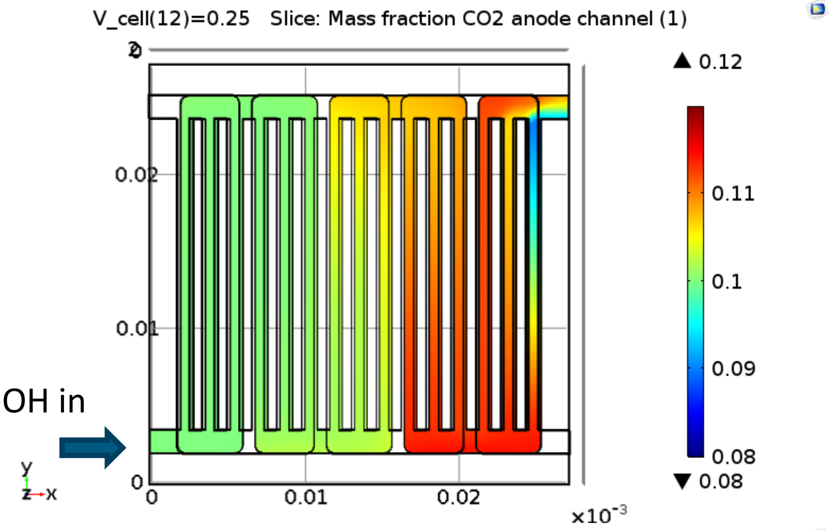
V_cell(12)=0.25 air velocity (m/s)

- **Fluids velocity/Flow fields geometry should be adapted/optimized for better fuel repartition**

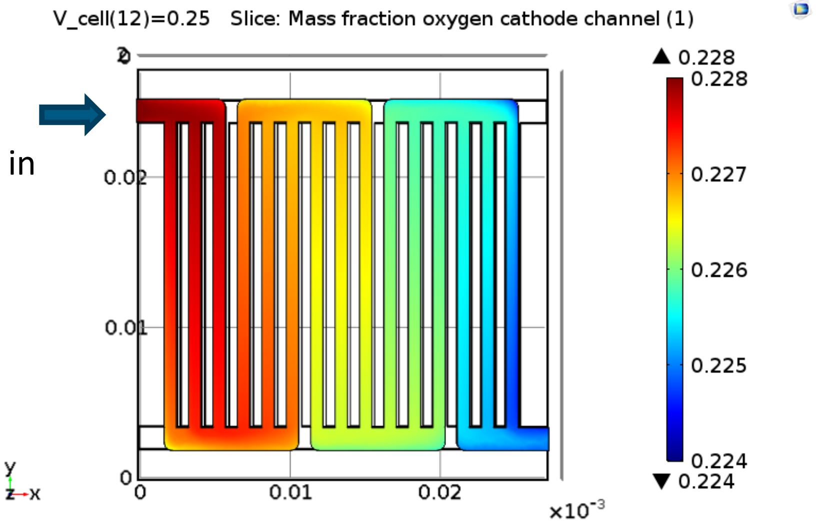
Results: Mass fraction distribution of reactants & products @ 0,25 V



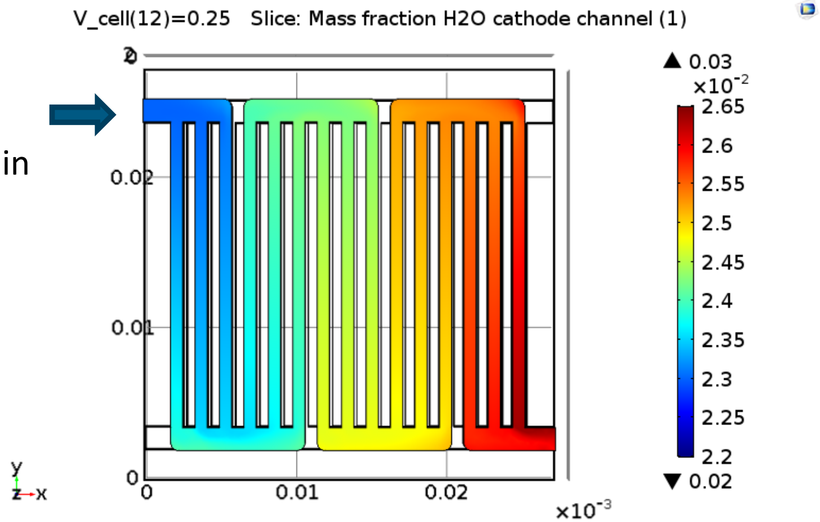
MeOH in



MeOH in



Air in



Air in

- ➢ **No relevant mass transport limitation and water flooding in flow fields channels**

Conclusions & acknowlegements

➢ First simplified DMFC model with Comsol **without** MeOH crossover through PEM membrane has been successfully developed.

➢ Next step: model extension **with** MeOH crossover & electro-osmotic drag implementation, as well as model validation.

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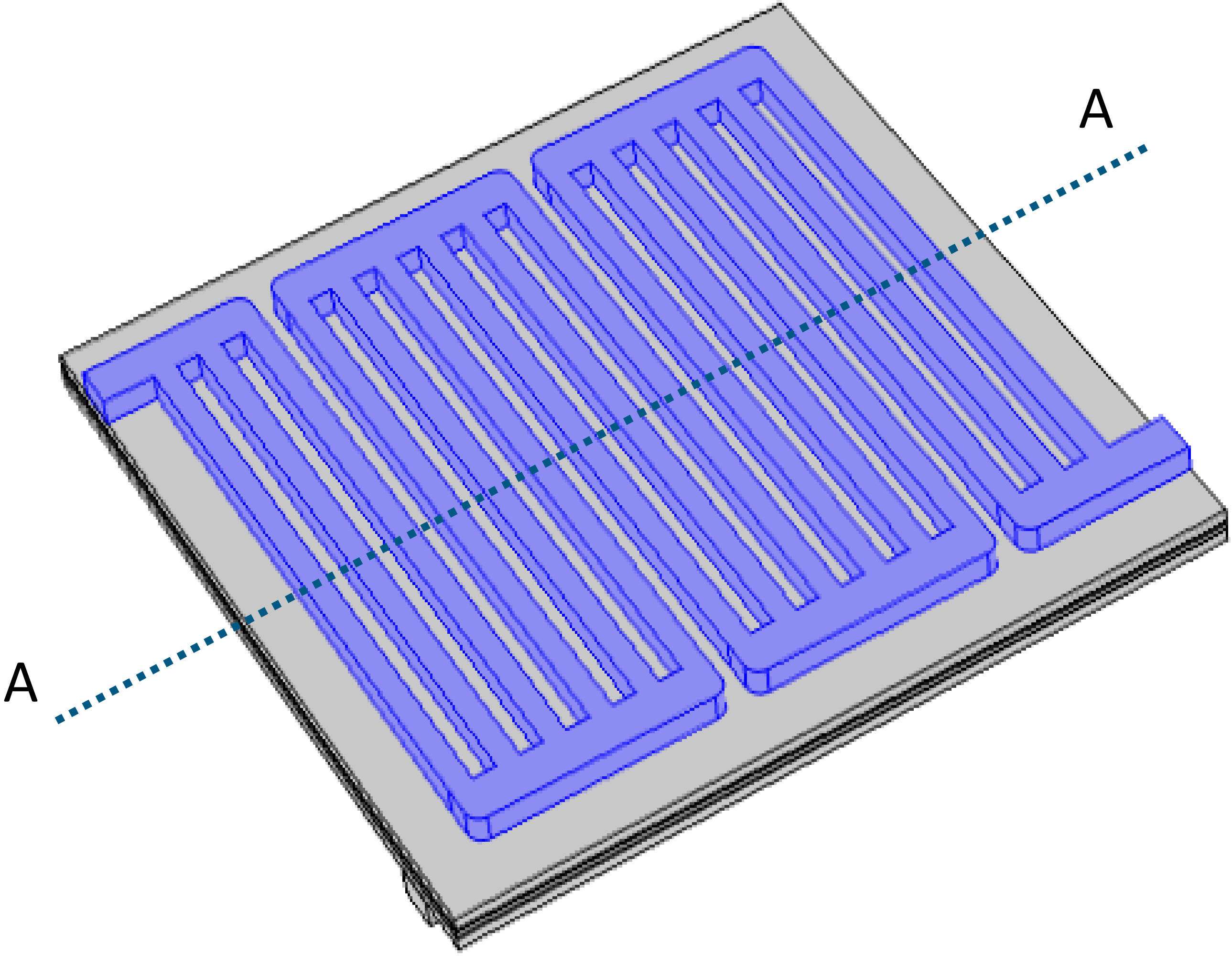
Thanks for your kind attention!

Direct Methanol Fuel Cell: Geometrie



Parameters

L 0.023[m] Cell length
H_ch 0.8e-3[m] Channel height
W_ch 0.8e-3[m] Channel width
W_rib 0.8e-3[m] Rib width
H_gdl 380e-6[m] GDL width
H_electrode 50e-6[m] Porous electrode thickness
H_membrane 100e-6[m] Membrane thickness
eps_gdl 0.4 GDL porosity
kappa_gdl 1.18e-11[m^2] GDL permeability
sigma_gdl 222[S/m] GDL electric conductivity
wMeOHa_in 0.1 Inlet MeOH mass fraction anode
wH2Oa_in 0.8 Inlet H2O mass fraction (cathode)
wO2_in 0.228 Inlet oxygen mass fraction cathode
wH2Oc_in 0.023 Inlet H2O massfraction cathode
U_in_anode 0.228[m/s] Inlet flow velocity 10 ml min-1 anode
U_in_cathode 1[m/s] Inlet flow velocity 25 ml min-1 cathode
mu_anode 1.19e-5[Pa*s] viscocity medium anode
mu_cathode 2.46e-5[Pa*s] viscocity medium cathode
MH2 0.002[kg/mol] Hydrogen molar mass
MN2 0.028[kg/mol] Nitrogen molar mass
MH2O 0.018[kg/mol] Water molar mass
MO2 0.032[kg/mol] Oxygen molar mass
MMeOH 0.032[kg/mol] Methanol molar mass
MCO2 0.044[kg/mol] CO2 molar mass
D_MeOH_H2O 9.15e-5*(T/307.1[K])^1.75[m^2/s] MeOH-H2O Binary diffusion coefficient
D_N2_H2O 2.56e-5*(T/307.15[K])^1.75[m^2/s] N2-H2O Binary diffusion coefficient
D_O2_N2 2.2e-5*(T/293.2[K])^1.75[m^2/s] O2-N2 binary diffusion coefficient
D_O2_H2O 2.82e-5*(T/308.1[K])^1.75[m^2/s] O2-H2O binary diffusion coefficient
D_CO2_MeOH 4.75e-9*(T/293[K])^3.6[m^2/s] CO2_MeOH binary diffusion coefficient [MJW Frank]
D_CO2_H2O 1.97e-9*(T/298[K])^6.5[m^2/s] CO2_H2O binary diffusion coefficient [MJW Frank]
T 80+273.15[K] Cell temperature
p_ref 101e3[Pa] Reference pressure
V_cell 0.8 Cell voltage
cO2_ref 40.88[mol/m^3] Oxygen reference concentration
cMeOH_ref 100[mol/m^3] Methanol reference concentratiion
eps_l 0.3
eps_cl 1-eps_l-eps_gdl Open volume fraction for gas diffusion in porous electrodes
kappa_cl kappa_gdl/5 Permeability (porous electrode)
i0_MORa 94.5[A/m^2] Exchange current density methanol oxydation anode Standard 94,5 A/m² Ren et al
i0_MORc 0[A/cm^2] Current exchange density methanol oxidation cathode
alpha_a 0.239
E0_ref 0.8[V]

Parameters

eps_GDLc 0.4
eps_MPLc 0.2
eps_RLc 1-eps_GDLc-eps_MPLc
eps_m 0.413
eps_GDLa 0.4
eps_RLa 1-eps_l-eps_GDLa
kappa_RLc kappa_GDLc/5
kappa_MPLc kappa_GDLc/5 vorsicht! kappa MPL= 1.6 e-15 m^2 in [A.Z. Weber JES 152 (2005) A682]
kappa_GDLc 1.18e-11[m^2]
kappa_GDLa 1.18e-11[m^2]
kappa_RLa kappa_GDLa/5
sigma_GDLc 222[S/m]
sigma_GDLa 222[S/m]
sigma_MPL 226[S/m]
sigma_m 12.3[S/m] Membrane conductivity [Ren et al. J. Electrochem. Soc. 147 (2)2 (2000)] exp(1268*(1/298-1/T))
L_1 0.023[m] Cell length
H_ch_1 0.8e-3[m] Channel height
W_ch_1 0.8e-3[m] Channel width
W_Tch 1.5e-3[m] Width transversal channel
W_rib_1 0.8e-3[m] Rib width
H_GDLa 380e-6[m] GDL width
H_RLa 50e-6[m] reaction layer anode thickness
H_M 183e-6[m] Membrane thickness Nafion117, 7 mil
H_RLc 50e-6[m] reaction layer cathode thickness
H_MPLc 50e-6[m] mpl cathode thickness
H_GDLc 380e-6[m] Gas diffusion layer cathode thickness
MEA_length 0.027[m] MEA dimension
MEA_width 0.027[m] MEA dimension
kappa_m 1.8e-1[cm^2] saturated membrane N112 permeability [A.Z. Weber, JES 152 (2005) A681]
Df_MeOH_GDLa 3.e-4[cm^2*s^-1] Methanol Diffusion Coefficient in GDL
Df_MeOH_RL 2.8e-5[cm^2*s^-1] MeOH Diffusion coefficient in reaction layer (K. Scott; JPS65 (1997) 165] Temperatur depency exp[2436(1/353-1/T)
Df_MeOH_mem 4.9e-6[cm^2*s^-1] MeOH Diffusion Coefficient in Nafion117 @ 60°C [K. Scott; JPS65 (1997) 165] Temperatur depency exp[2436(1/333-1/T)
Df_H2O_mem 7.3e-6[cm^2*s^-1] Water Diffusion Coefficient in Nafion117 [K. Scott; JPS65 (1997) 165] Temperatur depency exp[2436(1/353-1/T)
R 8.314[J*mol^-1*K^-1] Gaskonstante
d_hyd 4*(W_ch*H_ch)/(2*(W_ch+H_ch)) Charakterische Channel Länge für Reynodszahl als hydraulischer Durchmesser
nu_a 1.004e-6[m^2/s] Kinematic viscosity of water at 20°C
Re_a (d_hyd*U_in_anode)/nu_a Reynolds number anode
nu_c 13.3e-6[m^2/s] Kinematic viscosity of air at 20°C
Re_c (d_hyd*U_in_cathode)/nu_c Reynolds number cathode