The Numerical Simulation of Fuel Cells of the PEMFC and SOFC type with the Finite Difference Element Method (FDEM)

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This research project was supported by the Fuel Cell Research Alliance Baden-Württemberg (FABZ), by the ZSW Ulm and by the University of Karlsruhe

Foreword

From May 2004 to February 2005 the Fuel Cell Research Alliance Baden-Württemberg (FABZ) granted to the Computer Center of the University of Karlsruhe the financial means to implement the PDEs (partial differential equations) for the PEMFCs and SOFCs into the FDEM program package. The PDEs for the PEMFCs should be delivered by the ZSW and for the SOFCs by the IWE. The special point was that such strongly nonlinear systems of PDEs, and in the case of SOFCs also on coupled domains, should be solved numerically whereas for the first time together with the solution should be computed a reliable error estimate, so that the engineer could trust the numerical solution. This allows to separate in the modeling process of FCs the model errors from the discretization errors. If there is no error estimate and there is a discrepancy between experiment and numerical results, one does not know if the difference comes from inaccuracies of the model or of the numerical solution method. Therefore an error estimate is a valuable new feature and an essential advantage. This is below confirmed by the results.

The first thing we all had to learn in this cooperation project was to speak to each other. This means that the technical engineers learned what the numerical engineers wanted and the numerical engineers learned what the technical engineers wanted. A special problem are always the boundary conditions and in the case of SOFCs also the coupling conditions between the solution for gas channel and for anode. Then the technical engineers could see from the numerical solution the quality of the used model for their FCs and they then got the hints how to improve the model. As they got together with the numerical solution an error estimate they had not to doubt the quality of the delivered numbers. Finally, we had for the PEMFC and for the SOFC a useable model. If the engineer has such a model, he can "play" in the computer with the many parameters that are included in such a model, can adapt them to new measurements and can, above all with the geometrical parameters, optimize his FC.

Because the financial means for this project were rather limited and the project time was very short for such a difficult problem, the project ended with the implementation of the PDEs and some smaller variations of parameters. Ultimately, this project was intended as a transitional task until in a larger project with industrial background the optimization of FCs on a broad basis should start. So the purpose to show that the PDEs of FCs of different types could be efficiently solved numerically on modern parallel supercomputers, with an error estimate for the generated solution, was fully attained. If industrial partners want to cooperate and use the invaluable experience of the project partners they should address the corresponding authors of this report.

This report is written by three different groups, the ZSW, the IWE and the RZ. To avoid lengthy coordinations, each group has written its part independently in its own preferred style. So this report consists of three parts: Part I by ZSW, Part II by IWE, Part III by RZ. Because of the independent writing the pages of the different parts are numbered by e.g. I.1, I.2 etc. or II.1, II.2 etc.

Above all in Part II and III there are many coloured figures. In the printed version they are in gray scale and much information is lost. Therefore we recommend to look at these figures at the screen of a computer in the on-line version of the paper. This is in

http://www.rz.uni-karlsruhe.de/rz/docs/FDEM/Literatur/fuelcells.pdf

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Part I: The Polymer-Electrolyte-Membrane Fuel Cell (PEMFC)

The aim at PEMFC operation and development is a nearly homogenous current density distribution and thus power distribution all over the electrochemical active cell area. In a real fuel cell the electrochemical reaction takes place inhomogeneous over the active cell area. The reaction runs best, where the best reaction conditions exist, expecially the highest educt concentrations and the best electrical conductivities for electron and proton conduction. Important mechanisms resulting in current density inhomogenities are material transport limitations, which appear especially in the gas diffusion layers (GDLs) of PEMFCs. Material transport limitations in the GDL result beside the transport resistance caused by the mass transport through the GDL thickness mainly from geometry effects as e.g. the alternation of gas channels and ribs of the flowfield structure. Therefore in order to study the behaviour of a fuel cell it is essential to consider multidimensional effects and simulate multidimensional models.

The model and the PDEs

Within this project a 2D-model of the cathode GDL under the channels and ribs was examined. The calculation region and the boundary conditions are shown in Fig. 1.



Fig. 1: Sketch: Calculation region and boundary conditions

The structural and geometry parameters according to Fig. 1 are given in Tab. 1.

The following model assumptions are made: constant concentration in the gas channel at given relative humidity; pure gas transport; phase changes aren't considered; infinitesimal thin reaction layer as boundary condition; constant cell voltage; isothermal cell.

parameter	symbol	unit	value	source
thickness of the GDL	$t_{\rm GDL}$	[m]	$190.0 \cdot 10^{-6}$	chosen
width of the channel	с	[m]	$1 \cdot 10^{-3}$	chosen
width of the rib	r	[m]	$1 \cdot 10^{-3}$	chosen

Tab. 1: Structural and geometry parameters

Within this project two models for the gas phase transport are compared: As first approach Fick's diffusion was used as gas transport mechanism, cause of it's simple model. Afterwards the so called Mean Transport Pore Model (MTPM) was used as gas phase transport mechanism, which considers molecular multicomponent diffusion according to Stefan Maxwell, pore diffusion according to Knudsen, convection according to Darcy and wall slip. The comparison of both models results should help to judge, whether the simple Fick's law is sufficient to model the gas transport in a porous PEMFC GDL or the more detailed MTPM has to be used.

Below the models governing equations and boundary conditions for the two transport mechanisms are listed.

Model with Fick's diffusion as transport mechanism

Governing equations

• transport equation:

$$\dot{n}_{o}^{x} = -\frac{\varepsilon(x)}{\tau} \frac{D_{o}}{\mathbf{R}T} \frac{\partial p_{o}}{\partial x} \tag{1}$$

$$\dot{n}_{o}^{y} = -\frac{\varepsilon(x)}{\tau} \frac{D_{o}}{\mathbf{R}T} \frac{\partial p_{o}}{\partial y}$$
 (2)

$$\dot{n}_{w}^{x} = -\frac{\varepsilon(x)}{\tau} \frac{D_{w}}{\mathbf{R}T} \frac{\partial p_{w}}{\partial x}$$
(3)

$$\dot{n}_{w}^{y} = -\frac{\varepsilon(x)}{\tau} \frac{D_{w}}{\mathbf{R}T} \frac{\partial p_{w}}{\partial y}$$

$$\tag{4}$$

• material balances:

$$\frac{\varepsilon(x)}{\mathbf{R}T}\frac{\partial p_o}{\partial t} = -\frac{\partial(\dot{n}_o^x)}{\partial x} - \frac{\partial(\dot{n}_o^y)}{\partial y}$$
(5)

$$\frac{\varepsilon(x)}{\mathbf{R}T}\frac{\partial p_w}{\partial t} = -\frac{\partial(\dot{n}_w^x)}{\partial x} - \frac{\partial(\dot{n}_w^y)}{\partial y} \tag{6}$$

One gets 6 PDEs for the dependent variables: \dot{n}_{o}^{x} , \dot{n}_{o}^{y} , \dot{n}_{w}^{x} , \dot{n}_{w}^{y} , p_{o} and p_{w} . In addition the current density i, which is used in Eq. 8 and in the boundary conditions Eqs. 16, 17, 47 and 48, is considered as a variable just at the boundary GDL-reaction layer.

The independent variables are x, y and t. The material balances are set in their general form. The calculations were done for the steady state case.

The dependent variables are listed in Tab. 2.

In PEMFCs the GDL is compressed under the ribs. In order to consider this effect and it's impact on the porosity a location dependent porosity is used:

$$\varepsilon(x) = 0.5 \varepsilon_0 \left(kf + 1 + (1 - kf) \frac{\exp\left[a\cos\left(\frac{2\pi}{c+r}x\right) + \frac{c}{r}\right] - \exp\left[-a\cos\left(\frac{2\pi}{c+r}x\right)\right]}{\exp\left[a\cos\left(\frac{2\pi}{c+r}x\right) + \frac{c}{r}\right] + \exp\left[-a\cos\left(\frac{2\pi}{c+r}x\right)\right]} \right)$$
(7)

The origin of the x coordinate is in the middle of the channel, as shown in Fig. 1.

The porosity via the x-location for the model's standard parameters is shown in Fig. 2.

The parameters needed for the governing equations are listed in Tab. 3.

parameter	symbol	unit
molar flux density of	n _o	$\mathrm{mol}\ \mathrm{m}^{-2}\ \mathrm{s}^{-1}$
oxygen in x-direction		
molar flux density of	\dot{n}_{o}^{y}	$\mathrm{mol}\ \mathrm{m}^{-2}\ \mathrm{s}^{-1}$
oxygen in y-direction		
molar flux density	\dot{n}_w^x	$ m mol\ m^{-2}\ s^{-1}$
of water vapour in		
x-direction		
molar flux density	\dot{n}_w^y	$ m mol\ m^{-2}\ s^{-1}$
of water vapour in		
y-direction		
oxygen partial pressure	$\mathbf{p}_{\mathbf{o}}$	Pa
water vapour partial	$\mathbf{p}_{\mathbf{w}}$	Pa
pressure		
current density	i	$A m^{-2}$

Tab. 2: Dependent variables for Fick's law

Tab. 3: Parameters for the governing equations

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parameter	symbol	unit	value	source
Univ. gas constant	R	$[\text{kg m}^2 \text{ s}^{-2} \text{ mol}^{-1} \text{K}^{-1}]$	8.3145	
Faraday's constant	F	$[\mathrm{C} \ \mathrm{mol}^{-1}]$	$9.648531 \cdot 10^4$	
Temperature	Т	[K]	333	chosen
Diffusion coefficient O_2	Do	$[m^2 s^{-1}]$	$0.178 \cdot 10^{-4}$	[3]
in air				
Diffusion coefficient	D_{w}	$[m^2 s^{-1}]$	$0.22 \cdot 10^{-4}$	[3]
H_2O vapour in air				
Porosity of the GDL	ε_0	[-]	0.7	chosen
without compression				
Porosity of the GDL	$\varepsilon(\mathbf{x})$	[-]	calculated	Eq. 7
with compression				
Parameter for the	a	[-]	10(2-20)	chosen
porosity calculation				
Compression factor	kf	[-]	0.7	chosen
Tortuosity of the GDL	au	[-]	4	chosen



Fig. 2: location dependent porosity

Boundary conditions

For the calculation of the boundary conditions the current density i in $[A m^{-2}]$ at the reaction layer according to the Tafel equation is needed (see [2]):

$$i = f_v i_0 \left(\frac{p_o^D}{p_o^{ref}}\right)^{\gamma} \exp\left[\frac{\alpha n \mathbf{F} \left(U_0 - U_Z - \frac{d_{mem}}{\kappa_{mem}}i\right)}{\mathbf{R}T}\right]$$
(8)

 p_o^D is the value of the oxygen partial pressure at the reaction layer (Index D). In Eq. 8 the ohmic resistance of the membrane is already considered and it is assumed, that the membrane conductivity κ_{mem} stays constant, according to a homogenous membrane humidification.

In addition the water vapour saturation pressure p_w^S in [Pa] according to the Antoine equation is needed for the calculation of the boundary values:

$$\log(10^{-2} \cdot p_w^S) = A - \frac{B}{C + (T - 273.15)}$$
(9)

Eq. 9 is a numerical equation.

The boundary conditions are listed below:

• channel boundary (UC):

In the channel a constant pressure at air composition and given relative humidity φ is assumed:

$$p_w^{UC} = \varphi p_w^S \tag{10}$$

$$p_o^{UC} = (p^{ch} - p_w^{UC}) \cdot y_{o,a}^{UC}$$
(11)

• rib boundary (UR):

The rib is assumed as impermeable for the reaction gases:

$$\dot{n}_o^{y,UR} = 0 \tag{12}$$

$$\dot{n}_w^{y, UR} = 0 \tag{13}$$

• left (L) and right (R) boundary: Symmetry boundary condition:

$$\dot{n}_o^{x,L/R} = 0 \tag{14}$$

$$\dot{n}_w^{x,L/R} = 0 \tag{15}$$

 reaction layer boundary (D): Molar flux density according to Faraday's law in dependence of the current density in Eq. 8:

$$\dot{n}_o^{y,D} = \frac{1}{4\mathbf{F}}i\tag{16}$$

$$\dot{n}_w^{y,D} = -\frac{1}{2\mathbf{F}}i\tag{17}$$

The negative sign in Eq. 17 marks, that the oxygen and the water vapour have to be transported in opposite directions.

The parameter needed for the boundary conditions are listed in Tab. 4.

Tab. 4: Parameters for the boundary conditions						
parameter	symbol	unit	value	source		
Total pressure in the	p^{ch}	[Pa]	$1.013\cdot 10^5$	chosen		
channel						
Relative humidity in	φ	[-]	0.8	chosen		
the channel						
Mole fraction of O_2 in	$y_{o,a}^{UC}$	[-]	0.21			
air						
Exchange current den-	i ₀	$[A m_{Pt}^{-2}]$	$6.7 \cdot 10^{-5}$	[2]		
sity						
Transfer coefficient	α	[-]	0.2695	[2]		
Number of electrons	n	[-]	4			
involved in electrode						
reaction (Faraday)						
Reference pressure	p_o^{ref}	[Pa]	$1.013\cdot 10^5$	[2]		
Surface extension fac-	f_v	$[\mathrm{m}_{\mathrm{Pt}}^2 \; \mathrm{m}^{-2}]$	79	[2]		
tor at 0.15 $\mathrm{mg}_{\mathrm{Pt}} \mathrm{cm}^{-2}$						
Reaction order	γ	[-]	0.75	[2]		
Open circuit voltage	U ₀	[V]	1.0	chosen		
Cell voltage	Uz	[V]	0.6	chosen		
Membrane thickness	d_{mem}	[m]	$30.0 \cdot 10^{-6}$	chosen		
Membrane electric	$\kappa_{\rm mem}$	$[\mathrm{S} \mathrm{m}^{-1}]$	10.0	[6]		
conductivity						
Water vapour satura-	p_w^S	[Pa]	calculated	Eq. 9		
tion pressure						
	A	[-]	8.0732991	[6]		
Antoine parameters	В	[-]	1656.39	[6]		
	С	[—]	226.86	[6]		

Tab. 4: Parameters for the boundary conditions

Model with MTPM as transport mechanism

Governing equations

The MTPM is now applied for the transport equations ([1]). So the transport equations become implicit and the nitrogen partial pressure p_n and the total pressure p have to be considered as further variables.

• transport equations:

$$\frac{\dot{n}_{o}^{x}}{DKn_{o}} + \frac{p_{w}\dot{n}_{o}^{x} - p_{o}\dot{n}_{w}^{x}}{(D_{ow} \cdot p)} + \frac{p_{n}\dot{n}_{o}^{x} - p_{o}\dot{n}_{n}^{x}}{(D_{on} \cdot p)} = -\frac{1}{\mathbf{R}T}\frac{\partial p_{o}}{\partial x} + \frac{1}{\mathbf{R}Tp}p_{o}\frac{\partial p}{\partial x} - \left[\frac{B_{o}}{DKn_{o}} + \frac{B_{o}}{(D_{ow} \cdot p)}p_{w}\left(1 - \frac{B_{w}}{B_{o}}\right) + \frac{B_{o}}{(D_{on} \cdot p)}p_{n}\left(1 - \frac{B_{n}}{B_{o}}\right)\right]\frac{p_{o}}{\mathbf{R}Tp}\frac{\partial p}{\partial x}$$
(18)

$$\frac{\dot{n}_{o}^{y}}{DKn_{o}} + \frac{p_{w}\dot{n}_{o}^{y} - p_{o}\dot{n}_{w}^{y}}{(D_{ow} \cdot p)} + \frac{p_{n}\dot{n}_{o}^{y} - p_{o}\dot{n}_{n}^{y}}{(D_{on} \cdot p)} = -\frac{1}{\mathbf{R}T}\frac{\partial p_{o}}{\partial y} + \frac{1}{\mathbf{R}Tp}p_{o}\frac{\partial p}{\partial y} - \left[\frac{B_{o}}{DKn_{o}} + \frac{B_{o}}{(D_{ow} \cdot p)}p_{w}\left(1 - \frac{B_{w}}{B_{o}}\right) + \frac{B_{o}}{(D_{on} \cdot p)}p_{w}\left(1 - \frac{B_{o}}{B_{o}}\right)\right] + \frac{B_{o}}{(D_{on} \cdot p)}p_{n}\left(1 - \frac{B_{n}}{B_{o}}\right) = \frac{p_{o}}{\mathbf{R}Tp}\frac{\partial p}{\partial y}$$
(19)

$$\frac{\dot{n}_{w}^{x}}{DKn_{w}} + \frac{p_{o}\dot{n}_{w}^{x} - p_{w}\dot{n}_{o}^{x}}{(D_{wo} \cdot p)} + \frac{p_{n}\dot{n}_{w}^{x} - p_{w}\dot{n}_{n}^{x}}{(D_{wn} \cdot p)} = -\frac{1}{\mathbf{R}T}\frac{\partial p_{w}}{\partial x} + \frac{1}{\mathbf{R}Tp}p_{w}\frac{\partial p}{\partial x} - \left[\frac{B_{w}}{DKn_{w}} + \frac{B_{w}}{(D_{wo} \cdot p)}p_{o}\left(1 - \frac{B_{o}}{B_{w}}\right) + \frac{B_{w}}{(D_{wn} \cdot p)}p_{o}\left(1 - \frac{B_{o}}{B_{w}}\right)\right] + \frac{B_{w}}{(D_{wn} \cdot p)}p_{n}\left(1 - \frac{B_{n}}{B_{w}}\right) = \frac{p_{w}}{\mathbf{R}Tp}\frac{\partial p}{\partial x}$$
(20)

$$\frac{\dot{n}_{w}^{y}}{DKn_{w}} + \frac{p_{o}\dot{n}_{w}^{y} - p_{w}\dot{n}_{o}^{y}}{(D_{wo} \cdot p)} + \frac{p_{n}\dot{n}_{w}^{y} - p_{w}\dot{n}_{n}^{y}}{(D_{wn} \cdot p)} = -\frac{1}{\mathbf{R}T}\frac{\partial p_{w}}{\partial y} + \frac{1}{\mathbf{R}Tp}p_{w}\frac{\partial p}{\partial y} - \left[\frac{B_{w}}{DKn_{w}} + \frac{B_{w}}{(D_{wo} \cdot p)}p_{o}\left(1 - \frac{B_{o}}{B_{w}}\right) + \frac{B_{w}}{(D_{wn} \cdot p)}p_{n}\left(1 - \frac{B_{n}}{B_{w}}\right)\right]\frac{p_{w}}{\mathbf{R}Tp}\frac{\partial p}{\partial y}$$
(21)

$$\frac{\dot{n}_{n}^{x}}{DKn_{n}} + \frac{p_{o}\dot{n}_{n}^{x} - p_{n}\dot{n}_{o}^{x}}{(D_{no} \cdot p)} + \frac{p_{w}\dot{n}_{n}^{x} - p_{n}\dot{n}_{w}^{x}}{(D_{nw} \cdot p)} = -\frac{1}{\mathbf{R}T}\frac{\partial p_{n}}{\partial x} + \frac{1}{\mathbf{R}T}p_{n}\frac{\partial p}{\partial x} - \left[\frac{B_{n}}{DKn_{n}} + \frac{B_{n}}{(D_{no} \cdot p)}p_{o}\left(1 - \frac{B_{o}}{B_{n}}\right) + \frac{B_{n}}{(D_{nw} \cdot p)}p_{w}\left(1 - \frac{B_{w}}{B_{n}}\right)\right]\frac{p_{n}}{\mathbf{R}Tp}\frac{\partial p}{\partial x}$$
(22)

$$\frac{\dot{n}_{n}^{y}}{DKn_{n}} + \frac{p_{o}\dot{n}_{n}^{y} - p_{n}\dot{n}_{o}^{y}}{(D_{no} \cdot p)} + \frac{p_{w}\dot{n}_{n}^{y} - p_{n}\dot{n}_{w}^{y}}{(D_{nw} \cdot p)} = -\frac{1}{\mathbf{R}T}\frac{\partial p_{n}}{\partial y} + \frac{1}{\mathbf{R}Tp}p_{n}\frac{\partial p}{\partial y} - \left[\frac{B_{n}}{DKn_{n}} + \frac{B_{n}}{(D_{no} \cdot p)}p_{o}\left(1 - \frac{B_{o}}{B_{n}}\right) + \frac{B_{n}}{(D_{nw} \cdot p)}p_{w}\left(1 - \frac{B_{w}}{B_{n}}\right)\right]\frac{p_{n}}{\mathbf{R}Tp}\frac{\partial p}{\partial y}$$
(23)

• material balances:

$$\frac{\varepsilon(x)}{\mathbf{R}T}\frac{\partial p_o}{\partial t} = -\frac{\partial(\dot{n}_o^x)}{\partial x} - \frac{\partial(\dot{n}_o^y)}{\partial y}$$
(24)

$$\frac{\varepsilon(x)}{\mathbf{R}T}\frac{\partial p_w}{\partial t} = -\frac{\partial(\dot{n}_w^x)}{\partial x} - \frac{\partial(\dot{n}_w^y)}{\partial y}$$
(25)

$$\frac{\varepsilon(x)}{\mathbf{R}T}\frac{\partial p_n}{\partial t} = -\frac{\partial(\dot{n}_n^x)}{\partial x} - \frac{\partial(\dot{n}_n^g)}{\partial y}$$
(26)

• condition for the total pressure:

$$p = p_o + p_w + p_n \tag{27}$$

Finally one gets 9 PDE's and one algebraic equation for the dependent variables \dot{n}_{o}^{x} , \dot{n}_{o}^{y} , \dot{n}_{w}^{x} , \dot{n}_{w}^{y} , \dot{n}_{n}^{x} , \dot{n}_{w}^{y} , \dot{n}_{n}^{x} , \dot{n}_{o}^{y} , \dot{n}_{w}^{x} , \dot{n}_{w}^{y} , \dot{n}_{n}^{x} , \dot{n}_{o}^{y} , \dot{n}_{u}^{x} , \dot{n}_{w}^{y} , \dot{n}_{n}^{x} , \dot{n}_{u}^{y} , \dot{n}_{u}^{x} , \dot{n}_{u}^{x} , \dot{n}_{u}^{y} , \dot{n}_{u}^{x} , \dot{n}_{u}^{x} , \dot{n}_{u}^{y} , \dot{n}_{u}^{x} , \dot{n}_{u}^{y} , \dot{n}_{u}^{x}

Eq. 8 and in the boundary conditions Eqs. 16, 17, 47 and 48, is considered as a variable just at the boundary to the reaction layer.

The comparison of Eqs. 1 to 4 with Eqs. 18 to 23 shows, that the model with the MTPM as transport mechanism is more elaborate as the one with Fick's law.

The dependent variables for the MTPM are listed in Tab. 5

For the transport equations the following partially variable dependend parameters are needed. All new parameters within the MTPM are listed in Table 6.

The binary diffusion coefficients \mathcal{D}_{jk} in the continuum in $[m^2 s^{-1}]$ are ([5]):

$$\mathcal{D}_{jk} = \frac{0.01013 \ T^{1.75} \sqrt{1 \cdot 10^{-3} \frac{M_j + M_k}{M_j M_k}}}{p \left[V d_j^{\frac{1}{3}} + V d_k^{\frac{1}{3}} \right]} \qquad \qquad j,k = o, w, n$$
(28)

Eq. 28 is a numerical equation.

The binary diffusion coefficients in the porous medium D_{jk} in $[m^2 s^{-1}]$ are calculated from the binary diffusion coefficients in the continuum by multiplication with the structural parameter $\varepsilon(x)/\tau$:

$$D_{jk} = \frac{\varepsilon(x)}{\tau} \mathcal{D}_{jk} \qquad \qquad j, k = o, w, n \tag{29}$$

In the transport equations Eqs. 18 to 23 the following abbreviation is used:

$$(D_{jk} \cdot p) = \frac{\varepsilon(x)}{\tau} \frac{0.01013 \ T^{1.75} \sqrt{1 \cdot 10^{-3} \frac{M_j + M_k}{M_j M_k}}}{\left[V d_j^{\frac{1}{3}} + V d_k^{\frac{1}{3}} \right]} \qquad \qquad j,k = o, w, n \tag{30}$$

The effective permeabilities ${\rm B}_{\rm j}$ in $[{\rm m}^2 \; {\rm s}^{-1}]$ are according to [1]:

$$B_j = DKn_j \frac{\omega\nu_j + K_j}{1 + K_j} + \frac{\langle r^2 \rangle \frac{\varepsilon(x)}{\tau} p}{8\eta} \qquad \qquad j = o, w, n \tag{31}$$

In Eq. 31 the following variable dependent parameters are needed:

The square roots of the relative molecular weights of the gas components ν_{j} :

$$\nu_j = \sqrt{M_j / \sum_{k=1}^K \frac{p_k}{p} M_k} \qquad \qquad j = o, w, n \tag{32}$$

In Eq. 32 the summation is done with the components k = o,w,n.

The total viscosity η in [Pa s] is (see [6]):

$$\eta = \frac{\sum_{k=1}^{K} p_k \eta_k \sqrt{M_k}}{\sum_{k=1}^{K} p_k \sqrt{M_k}}$$
(33)

The Knudsen diffusion coefficients DKn_j in $[m^2 s^{-1}]$ are:

$$DKn_j = \frac{4}{3} \frac{\varepsilon(x)}{\tau} \langle r \rangle \sqrt{\frac{2\mathbf{R}T}{\pi M_j}} \qquad \qquad j = o, w, n \tag{34}$$

Tab. 5. Dependent va	nables for	the MITIM
parameter	symbol	unit
molar flux density of	n _o	$\mathrm{mol}\ \mathrm{m}^{-2}\ \mathrm{s}^{-1}$
oxygen in x-direction		
molar flux density of	n _o y	$mol m^{-2} s^{-1}$
oxygen in y-direction		
molar flux density	n ^x w	$\mathrm{mol}\ \mathrm{m}^{-2}\ \mathrm{s}^{-1}$
of water vapour in		
x-direction		
molar flux density	\dot{n}_w^y	$\mathrm{mol}\ \mathrm{m}^{-2}\ \mathrm{s}^{-1}$
of water vapour in		
y-direction		
molar flux density of	\dot{n}_n^x	$\mathrm{mol}\ \mathrm{m}^{-2}\ \mathrm{s}^{-1}$
nitrogen in x-direction		
molar flux density of	\dot{n}_n^y	$mol m^{-2} s^{-1}$
nitrogen in y-direction		
oxygen partial pressure	$\mathbf{p}_{\mathbf{o}}$	Pa
water vapour partial	$\mathbf{p}_{\mathbf{w}}$	Pa
pressure		
nitrogen partial pres-	$\mathbf{p}_{\mathbf{n}}$	Pa
sure		
total pressure	р	Pa
current density	i	$A m^{-2}$

Tab. 5: Dependent variables for the MTPM

The dimensionless Knudsen numbers K_j are achieved by dividing the mean free path lengths λ_j by the mean pore diameter 2 $\langle r \rangle$:

$$K_j = \frac{\lambda_j}{2\langle r \rangle} \qquad \qquad j = o, w, n \tag{35}$$

The mean free path lenghts λ_j in [m] are calculated according to the kinetic theory of gases:

$$\lambda_j = \eta_j \sqrt{\frac{3\mathbf{R}T}{p_j M_j p}} \qquad \qquad j = o, w, n \tag{36}$$

Boundary conditions

Below the boundary conditions for the MTPM are listed in short form. The current density i is calculated with Eq. 8; the water vapour saturation pressure $\mathbf{p}^{\rm S}_{\rm w}$ is calculated with Eq. 9.

• channel boundary (UC):

In the channel a constant pressure at air composition and given relative humidity φ is assumed:

$$p^{UC} = p^{ch} \tag{37}$$

$$p_w^{UC} = p^{ch}$$
(37)

$$p_w^{UC} = \varphi p_w^S$$
(38)

$$p_a^{UC} = (p^{ch} - p_w^{UC}) \cdot y_{a,a}^{UC}$$
(39)

$$p_o^{UC} = (p^{ch} - p_w^{UC}) \cdot y_{o,a}^{UC}$$
(39)

$$p_n^{UC} = (p^{cn} - p_w^{UC}) \cdot (1 - y_{o,a}^{UC})$$
(40)

• rib boundary (UR):

The rib is assumed as impermeable for the reaction gases:

$$\dot{n}_o^{y,UR} = 0 \tag{41}$$

$$\dot{n}_w^{y,OR} = 0 \tag{42}$$

$$\dot{n}_n^{y,UR} = 0 \tag{43}$$

• left (L) and right (R) boundary: Symmetry boundary condition:

$$\dot{n}_o^{x,L/R} = 0 \tag{44}$$

$$\dot{n}_{w}^{x,L/R} = 0$$
 (45)

$$\dot{n}_n^{x,L/R} = 0 \tag{46}$$

• reaction layer boundary (D):

Molar flux density according to Faraday's law in dependence of the current density from eq. 8 and gas tight membrane for the nitrogen flow:

$$\dot{n}_o^{y,D} = \frac{1}{4\mathbf{F}}i\tag{47}$$

$$\dot{n}_w^{y,D} = -\frac{1}{2\mathbf{F}}i\tag{48}$$

$$\dot{n}_n^{y,D} = 0 \tag{49}$$

The parameters for the MTPM boundary conditions are the same as listed for the Fick's law boundary conditions.

parameter	symbol	unit	value	source
Binary diffusion coeffi-	\mathcal{D}_{jk}, D_{jk}	$[m^2 s^{-1}]$	calculated	Eqs. 28, 29
cients				
Diffusion volume of O_2	Vd _o	numerical eq.	16.6	[5] Da 35
Diffusion volume of	Vd_{w}	numerical eq.	12.7	[5] Da 35
H ₂ O vapour				
Diffusion volume of N_2	Vd_n	numerical eq.	17.9	[5] Da 35
Effective permeabili-	B _j	$[m^2 s^{-1}]$	calculated	Eq. 31
ties				
Square roots of the	$ u_{ m j}$	[-]	calculated	Eq. 32
relative molecular				
weights				
Total viscosity	η	[Pa s]	calculated	Eq. 33
Dynamic viscosity of	$\eta_{ m o}$	$[Pa \ s]$	$22.53\cdot 10^{-6}$ at 60 $^{\circ}\mathrm{C}$	[5] Db 71
O_2				
Dynamic viscosity of	$\eta_{ m w}$	$[Pa \ s]$	$12.27\cdot 10^{-6}$ at 100 $^{\circ}\mathrm{C}$	[5] Db 8
H_2O vapour				
Dynamic viscosity of	$\eta_{ m n}$	$[Pa \ s]$	$19.396\cdot 10^{-6}$ at 60 $^{\circ}\mathrm{C}$	[5] Db 37
N_2				
Molecular weight of O_2	Mo	$[\mathrm{kg} \ \mathrm{mol}^{-1}]$	$2\cdot 16.0\cdot 10^{-3}$	
Molecular weight of	$M_{\rm w}$	$[\mathrm{kg} \ \mathrm{mol}^{-1}]$	$(2 \cdot 1.008 + 16.0) \cdot 10^{-3}$	
H_2O				
Molecular weight of N_2	M_n	$[\mathrm{kg} \ \mathrm{mol}^{-1}]$	$2 \cdot 14.01 \cdot 10^{-3}$	
Knudsen diffusion co-	$\mathrm{DKn}_{\mathrm{j}}$	$[m^2 s^{-1}]$	calculated	Eq. 34
efficients				
slip factor	ω	[—]	$\frac{\pi}{4}$	[4]
Knudsen numbers	$\rm K_j$	[—]	calculated	Eq. 35
Mean free path lengths	$\lambda_{ m j}$	[m]	calculated	Eq. 36
Mean transport pore	$\langle r \rangle$	[m]	$38.5 \cdot 10^{-6}$	measured
radius				
Pore radii distribution	$\langle r^2 \rangle$	$[m^2]$	$1.826 \cdot 10^{-10}$	measured

Tab. 6: Parameters for the calculation equations with the MTPM

Discussion of the results

In the following calculation results of variables within the GDL direct at the reaction layer are compared for Fick's law and the MTPM as transport mechanism. For the results the standard parameters listed above were used (cell voltage 0.6 V) unless otherwise noted. According to Fig. 1 the x discretization starts in the middle of the channel and ends in the middle of the rib. All shown plots were calculated with a grid of 200×201 cells, which was found to result in acceptable calculation errors.

In Fig. 3 the oxygen partial pressure is plotted. As expected the oxygen degrades from the channel to the rib. With the MTPM the oxygen consumption is lower as with Fick's law. The maximum deviation of both models results is approximately 15 %.

In Fig. 4 the water vapour partial pressure is shown. The MTPM leads to lower water vapour partial pressure in the GDL. The maximum deviation according to Fick's law is approximately 15 %. The water vapour saturation pressure for the standard cell temperature of 60 °C is approximately $2 \cdot 10^4$ Pa. Thus as can be seen from Fig. 4 the water vapour partial pressure exceeds the water vapour saturation pressure under the rib, which effect is stronger with Fick's law as transport mechanism. This means, that under the rib water will condense and liquid water could block the transport pores for the gas transport. In the current model condensation and evaporation aren't considered and it is assumed, that all the product water has to be transported through the GDL in the gas phase, although the saturation pressure is exceeded. As the result in Fig. 4 shows in a further model also phase changes should be included.

In Fig. 5 the current density distribution at the reaction layer is plotted. As expected, the current density drops strongly beneath the ribs and there is an inhomogenous current density distribution between the channel and the rib. Within this model just the descent of the oxygen partial pressure causes the drop of the current density in Eq. 8 and two phase effects are neglected, which would enforce the inhomogenity of the current density distribution, as could be seen from Fig. 4. Because of the higher oxygen partial pressure with the MTPM also the current density is higher. The maximal deviation with both models is approximately 10 %.

In fuel cell practice the voltage current density characteristic (U-i-plot) of a fuel cell is often used to evaluate it's behaviour. So some points of an U-i-plot were calculated and shown in Fig. 6.

From Fig. 6 it could be seen, that the deviation between Fick's law and the MTPM as transport mechanism rises with rising current density. Because of convergence problems it wasn't possible to calculate for lower cell voltages, i.e. higher current densities.



Fig. 3: Oxygen partial pressure at the reaction layer for standard conditions



Fig. 4: Water vapour partial pressure at the reaction layer for standard conditions (saturation pressure at 60 $^{\circ}C$ is approximately $2 \cdot 10^4$ Pa)



Fig. 5: Current density at the reaction layer for standard conditions



Fig. 6: U-i characteristic

Conclusion

A two dimensional PEMFC model was examined and the gas transport was modelled with two material transport mechanisms: the simple Fick's diffusion law and the more detailed MTPM.

As one result the maximum deviations of the calculations with both models were found to be in the range of 10 to 15 %. This has to be considered, when using the simple Fick's law instead of the MTPM. Thus for qualitative calculations the simple Fick's law could be sufficient. For more precisely calculations the MTPM has to be used or the Fick's law has to be corrected in an adequate way.

A further result of the calculation within this project is, that at the low operation temperature of 60 °C already at a cell potential of 0.6 V the water vapour saturation pressure could be exceeded beneath the flowfield ribs and thus liquid water could limit the material transport under the ribs and therefore two phase effects should be considered in model refinement.

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Part II

A 2D-Model of a SOFC-Anode operated with methane

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The Solid Oxide Fuel Cell (SOFC)

A major advantage of the solid oxide fuel cell (SOFC) in comparison to other fuel cell types is that it can be operated directly on practical hydrocarbon fuels without the need for a complex and cost intensive external fuel processing unit. Internal reforming allows the direct conversion of hydrocarbon fuel into hydrogen and carbon monoxide at the catalytic active anode. As feed natural gas is preferred because of the high availability and the easy handling of the gaseous components. In order to understand the processes which occur during internal reforming on the anode and to be able to identify processes which limit the conversion of the main component methane, it is necessary to develop multidimensional mathematical models.

The model and the PDE's

In this study a 2D-model is developed considering the processes in the anode and in the anode gas channel of a single cell. Figure 1 shows the calculation region.



Fig. 1. Sketch: Calculation region

The structural and the geometry parameters according to fig.1 are given for the base case in tab.1

II.2

parameter	symbol	unit	value	source
thickness of the	d _A	m	50.10^{-6}	IWE
anode				
height of the	d _K	m	1.10^{-3}	IWE
anode gas channel				
length of the	$l_{\rm K}$	m	35·10 ⁻³	IWE
anode gas channel				

Tab. 1. Structural and geometry parameters (base case)

The model assumptions are as follows:

Steady state and ideal gas behaviour are assumed. The (single) cell is mounted in a furnace. Temperature gradients that might occur by the heat consumption of the reforming reaction are flattened by radiation from the surface of the furnace walls. Therefore the temperature is considered to be uniform in the cell and energy balances are not included in this version of the model. It is assumed that the influence of axial dispersion is low compared to the convective flow in x-direction [1]. For simplification, axial dispersion is therefore not considered in this model. For diffusion, Fick's law is applied. The area, in which the electrochemical reactions occur is restricted to a thin layer at the interface anode-electrolyte [2]. Therefore, these reactions are considered to take place only at the boundary anode-electrolyte.

Below the governing equations and boundary conditions for the anode gas channel are listed

Anode gas channel

• Species balances

$$-\left[\frac{\partial\left(p_{K}\cdot u_{x,K}\cdot Y_{i,K}\right)}{\partial x} + \frac{\partial\left(p_{K}\cdot u_{y,K}\cdot Y_{i,K}\right)}{\partial y}\right] + \frac{\partial\left(D_{i,gas}\frac{\partial\left(p_{K}\cdot Y_{i,K}\right)}{\partial y}\right)}{\partial y} = 0$$
(1)-(4)

where $i = CH_4$, CO, H₂, H₂O

• Equation of continuity

$$\frac{\partial \left(\rho_{K} \cdot u_{x,K}\right)}{\partial x} + \frac{\partial \left(\rho_{K} \cdot u_{y,K}\right)}{\partial y} = 0$$
(5)

• Navier-Stokes equations

$$\rho \cdot \left(u_{x,K} \frac{\partial u_{x,K}}{\partial x} + u_{y,K} \frac{\partial u_{x,K}}{\partial y} \right) = -\frac{\partial p_K}{\partial x} + \frac{\partial}{\partial x} \left(\mu \cdot \left(2 \cdot \frac{\partial u_{x,K}}{\partial x} - \frac{2}{3} \cdot \left(\frac{\partial u_{x,K}}{\partial x} + \frac{\partial u_{y,K}}{\partial y} \right) \right) \right) + \frac{\partial}{\partial y} \left[\mu \cdot \left(\frac{\partial u_{x,K}}{\partial y} + \frac{\partial u_{y,K}}{\partial x} \right) \right]$$
(6)

$$\rho \cdot \left(u_{x,K} \frac{\partial u_{y,K}}{\partial x} + u_{y,K} \frac{\partial u_{y,K}}{\partial y} \right) = -\frac{\partial p_K}{\partial y} + \frac{\partial}{\partial y} \left(\mu \cdot \left(2 \cdot \frac{\partial u_{y,K}}{\partial y} - \frac{2}{3} \cdot \left(\frac{\partial u_{x,K}}{\partial x} + \frac{\partial u_{y,K}}{\partial y} \right) \right) \right) + \frac{\partial}{\partial x} \left[\mu \cdot \left(\frac{\partial u_{x,K}}{\partial y} + \frac{\partial u_{y,K}}{\partial x} \right) \right]$$
(7)

• Dalton's law

$$\sum_{i} Y_{i,K} = 1 \tag{8}$$

One obtains 7 PDEs and one algebraic equation for the 8 dependent variables in the anode gas channel: p_K , $u_{x,K}$, $u_{y,K}$, $Y_{CH_4,K}$, $Y_{CO,K}$, $Y_{H_2,K}$, $Y_{CO_2,K}$ and $Y_{H_2O,K}$. The independent variables are x and y.

The Diffusion coefficient $D_{i,gas}$ of component i in the gas mixture is calculated by the Wilke approach [2]:

$$D_{i,gas} = \frac{1 - Y_i}{\sum_{j \neq i} (Y_j / D_{ij})} \quad i = CH_4, CO, H_2, CO_2, H_2O$$
(9)

The binary diffusion coefficients D_{ij} are obtained by using the theory of Chapman and Enskong (see tab 2).

	CH ₄	СО	H_2	CO_2	H ₂ O
CH ₄	-	2,34e-4	7,46e-4	1,95e-4	2,91e-4
CO	2,34e-4	-	8,05e-2	1,75e-3	2,80e-2
H ₂	7,46e-4	8,05e-4	-	6,91e-3	9,53e-2
CO ₂	1,95e-4	1,75e-4	6,91e-4	-	2,28e-2
H ₂ O	2,91e-4	2,80e-4	9,53e-4	2,28e-4	-

Tab. 2. Binary Diffusion coefficients D_{ij}/ [m²/s], 950 °C [3]

For the calculation of the fluid density the ideal gas law is applied:

$$\rho = \frac{p}{R_{M}T}$$
 in (kg/m³) where $R_{M} = \frac{R}{\sum_{i} Y_{i} \cdot M_{i}}$ and $i = CH_{4}, CO, H_{2}, CO_{2}, H_{2}O$ (10)

The viscosity of the gas mixture is obtained via the equation (see [3])

$$\mu = \sum_{i} \frac{Y_{i} \mu_{i}}{\sum_{j} Y_{j} \Psi_{ij}} \text{ in } 1.10^{-7} \text{ Pa·s } i, j = CH_{4}, CO, H_{2}, CO_{2}, H_{2}O$$
(11)

with
$$\Psi_{ij} = \frac{\left[1 + \left(\frac{\mu_i}{\mu_j}\right)^{0.5} \left(\frac{M_j}{M_i}\right)^{0.25}\right]^2}{\left[8\left(1 + \frac{M_i}{M_j}\right)^{0.5}\right]}$$
 i,j =CH₄, CO, H₂, CO₂, H₂O (12)

The viscosity of the single components is calculated by the expression [3]:

$$\mu_{i} = 844 \frac{\sqrt{M_{i}T}}{\sigma_{i}^{2}\Omega_{v,i}} \qquad \text{in } 1.10^{-7} \text{ Pa·s}$$

$$\tag{13}$$

with
$$\Omega_{v,i} = \frac{1.16145}{\frac{kT}{\epsilon_i}} + \frac{0.52487}{\exp\left(0.773\frac{kT}{\epsilon_i}\right)} + \frac{2.162}{\exp\left(2.438\frac{kT}{\epsilon_i}\right)} i = CH_4, CO, H_2, CO_2, H_2O$$
 (14)

In Tab. 3 the dependent variables of the anode gas channel are listed

Parameter	symbol	units
flow velocity in x-direction	$u_{x,K}$	$\mathrm{m~s}^{-1}$
flow velocity in y-direction	$u_{y,K}$	$\mathrm{m~s}^{-1}$
mole fraction of methane	$Y_{CH_4,K}$	-
mole fraction of carbon monoxide	$Y_{CO,K}$	-
mole fraction of hydrogen	$Y_{H_2,K}$	-
mole fraction of carbon dioxide	$Y_{CO_2,K}$	-
mole fraction of steam	$Y_{H_2O,K}$	-
Pressure	p_K	Ра

Tab.3. Dependent variables (anode gas channel)

Boundary conditions.

• Rib boundary (y=0)

II.4

The rib is assumed to be impermeable for gases

$$u_{y,K} = 0 \tag{15}$$

$$\frac{\partial Y_{i,K}}{\partial y} = 0 \quad i = CH_4, CO, H_2, CO_2, H_2O$$
(16-20)

$$u_{x,K} = 0 \tag{21}$$

• Channel boundary ($y=d_K$)

$$D_{i,gas} \frac{\partial \left(p_K \cdot Y_{i,K} \right)}{R \cdot T \partial y} = D_{i,gas}^{eff} \frac{\partial \left(p_A \cdot Y_{i,A} \right)}{R \cdot T \partial y} \quad i = CH_4, CO, H_2, CO_2, H_2O$$
(22)-(25)

$$u_{y,K} = u_{y,A} \tag{26}$$

$$Y_{i,K} = Y_{i,A}$$
(27)-(32)

$$p_K = p_A \tag{33}$$

• Left boundary (x=0)

A parabolic velocity profile is assumed at the inlet of the anode gas channel

$$Y_{i,K} = Y_i^o$$
 i =CH₄, CO, H₂, CO₂, H₂O (34)-(38)

$$u_{y,K} = 0 \tag{39}$$

$$u_{x,K} = -\frac{4 \cdot u_{x,K,\max}}{d_K^2} y^2 + 4 \frac{u_{x,K,\max}}{d_K} y$$
(40)

This is the parabolic entry profile with $u_{x,K,max}$ in the middle of the channel

• Right boundary $(x=l_K,)$

 $p_K = p_{atm}$

The other variables at the outlet of the anode gas channel are calculated by the governing equations

Tab.4. Parameters for the governing equations and the boundary conditions (anode gas channel)

parameter	symbol	units	value	source
Diffusion coefficient of	Digas	$m^2 s^{-1}$	eg. (9)	[3]
component i in the gas	— 1,ga3	2	- T . (2)	[-]

(41)

mixture				
Binary Diffusion coefficients	D _{ij}	$m^2 s^{-1}$	tab 2	[3]
Molar mass of methane	M _{CH4}	10 ⁻³ kg/mol	16	[3]
Molar mass of carbon monoxide	M _{CO}	10 ⁻³ kg/mol	28	[3]
Molar mass of carbon dioxide	M _{CO2}	10 ⁻³ kg/mol	44	[3]
Molar mass of hydrogen	$M_{\rm H2}$	10 ⁻³ kg/mol	2	[3]
Molar mass of steam	M _{H2O}	10 ⁻³ kg/mol	18	[3]
Maximum flow velocity in x-direction at inlet of gas channel	u ^o _{x,max}	m s ⁻¹	0.5	chosen
Molar fraction of methane at channel inlet	$Y^o_{_{CH_4}}$	-	0.33	chosen
Molar fraction of carbon monoxide at channel inlet	Y^o_{CO}	-	0	chosen
Molar fraction ofhydrogen at channel inlet	$Y^o_{H_2}$	-	0	chosen
Molar fraction of carbon dioxide at channel inlet	$Y^o_{co_2}$	-	0	chosen
Molar fraction of steam at channel inlet	$Y^o_{_{H_2O}}$	-	0.67	chosen
Hard sphere diameter of methane	σ_{CH4}	3.758	Å	[3]
Hard sphere diameter of carbon monoxide	σ_{CO}	3.69	Å	[3]
Hard sphere diameter of carbon dioxide	$\sigma_{\rm CO2}$	3.941	Å	[3]
Hard sphere diameter of hydrogen	$\sigma_{\rm H2}$	2.827	Å	[3]
Hard sphere diameter of	$\sigma_{\rm H2O}$	2.641	Å	[3]

steam				
Lennard-Jones-Parameter of methane	ϵ_{CH4}/k	148.6	К	[3]
Lennard-Jones-Parameter of carbon monoxide	ϵ_{CO}/k	91.7	K	[3]
Lennard-Jones-Parameter of carbon dioxide	$\epsilon_{\rm CO2}/k$	195.2	K	[3]
Lennard-Jones-Parameter of hydrogen	ϵ_{H2}/k	59.7	K	[3]
Lennard-Jones-Parameter of steam	$\epsilon_{\rm H2O}/k$	809.1	K	[3]

Anode

Below the governing equations for the anode are listed.

• Species balances

$$-\left[\frac{\partial\left(p_{A}\cdot u_{x,A}\cdot Y_{CH_{4},A}\right)}{R\cdot T\partial x}\right] - \left[\frac{\partial\left(p_{A}\cdot u_{y,A}\cdot Y_{CH_{4},A}\right)}{R\cdot T\partial y}\right] + \frac{\partial\left(D_{CH_{4},gas}^{eff}\frac{\partial\left(p_{A}\cdot Y_{CH_{4},A}\right)}{R\cdot T\partial y}\right)}{\partial y} + \frac{\partial\left(D_{CH_{4},gas}^{eff}\frac{\partial\left(p_{A}\cdot Y_{CH_{4},A}\right)}{R\cdot T\partial x}\right)}{\partial x} - r_{CH_{4}} = 0$$

$$-\left[\frac{\partial\left(p_{A}\cdot u_{x,A}\cdot Y_{CO,A}\right)}{R\cdot T\partial x}\right] - \left[\frac{\partial\left(p_{A}\cdot u_{y,A}\cdot Y_{CO,A}\right)}{R\cdot T\partial y}\right] + \frac{\partial\left(D_{CO,gas}^{eff}\frac{\partial\left(p_{A}\cdot Y_{CO,A}\right)}{R\cdot T\partial y}\right)}{\partial y} + \frac{\partial\left(D_{CO,gas}^{eff}\frac{\partial\left(p_{A}\cdot Y_{CO,A}\right)}{R\cdot T\partial x}\right)}{\partial x} + r_{CH_{4}} - r_{s} = 0$$
(43)

$$-\left[\frac{\partial\left(p_{A}\cdot u_{x,A}\cdot Y_{H_{2},A}\right)}{R\cdot T\partial x}\right] - \left[\frac{\partial\left(p_{A}\cdot u_{y,A}\cdot Y_{H_{2},A}\right)}{R\cdot T\partial y}\right] + \frac{\partial\left(D_{H_{2},gas}^{eff}\frac{\partial\left(p_{A}\cdot Y_{H_{2},A}\right)}{R\cdot T\partial y}\right)}{\partial y} + \frac{\partial\left(D_{H_{2},gas}^{eff}\frac{\partial\left(p_{A}\cdot Y_{H_{2},A}\right)}{R\cdot T\partial x}\right)}{\partial x} + 3r_{CH_{4}} + r_{s} = 0$$
(44)

$$-\left[\frac{\partial\left(p_{A}\cdot u_{x,A}\cdot Y_{CO_{2},A}\right)}{R\cdot T\partial x}\right] - \left[\frac{\partial\left(p_{A}\cdot u_{y,A}\cdot Y_{CO_{2},A}\right)}{R\cdot T\partial y}\right] + \frac{\partial\left(D_{CO_{2},gas}^{eff}\frac{\partial\left(p_{A}\cdot Y_{CO_{2},A}\right)}{R\cdot T\partial y}\right)}{\partial y} + \frac{\partial\left(D_{CO_{2},gas}^{eff}\frac{\partial\left(p_{A}\cdot Y_{CO_{2},A}\right)}{R\cdot T\partial x}\right)}{\partial x} + r_{s} = 0$$
(45)

 $-r_{s} = 0$

II.8

• Darcy's law

$$\frac{\partial p_A}{\partial x} = -\frac{\mu}{k_p} u_{x,A} \tag{47}$$

$$\frac{\partial p_A}{\partial y} = -\frac{\mu}{k_p} u_{y,A} \tag{48}$$

Dalton's law

$$\sum_{i} Y_{i,A} = 1 \tag{49}$$

One obtains 7 PDEs and one algebraic equation for the 8 dependent variables in the anode: $u_{x,A}$, $u_{y,A}$, p_A , $Y_{CH_4,A}$, $Y_{CO,A}$, $Y_{H_2,A}$, $Y_{CO_2,A}$ und $Y_{H_2O,A}$. The independent variables are x and y. The effective diffusion coefficients $D^{eff}_{i,gas}$ are calculated from the diffusion coefficient $D_{i,gas}$ and from the Knudsen Diffusion coefficient D^{K}_{i} by the equation

$$\frac{1}{D_{i,gas}^{eff}} = \frac{1}{\frac{\varepsilon}{\tau} D_{i,gas}} + \frac{1}{D_i^K}$$
(50)

The porosity ε of the anode is estimated to be 30%. For the tortuosity τ a value of 3 is assumed.

The reactions occurring on the (inner) anode surface are the reforming reaction

$$CH_4 + H_2O \rightarrow CO + 3H_2$$
 (51)

which is accompanied by the shift reaction

$$CO + H_2O \Longrightarrow H_2 + CO_2 \tag{52}$$

For the rate of the reforming reaction on a Ni/YSZ-cermet an expression is employed which was found by [4]:

$$r_{CH_4} = 2.45 \left[\frac{mol}{m^3 s P a^{1.2}} \right] \left(p_A \cdot Y_{CH_4} \right)^{1.2} \exp\left(\frac{-57840 \left[\frac{J}{mol} \right]}{RT} \right)$$
(53)

For the shift reaction, a volumetric expression is used which is calculated from the experimental results presented in [5]:

$$\mathbf{r}_{s} = 0.0437 \left[\frac{\text{mol}}{\text{m}^{3}\text{Pa}^{2}\text{s}}\right] \cdot \exp\left(-\frac{112131 \left[\frac{\text{J}}{\text{mol}}\right]}{\text{R} \cdot \text{T}}\right) p_{\text{A}}^{2} Y_{\text{CO},\text{A}} Y_{\text{H}_{2}\text{O},\text{A}} - 0.425 \left[\frac{\text{mol}}{\text{m}^{3}\text{Pa}^{2}\text{s}}\right] \cdot \exp\left(-\frac{132467 \left[\frac{\text{J}}{\text{mol}}\right]}{\text{R} \cdot \text{T}}\right) p_{\text{A}}^{2} Y_{\text{CO}_{2},\text{A}} Y_{\text{H}_{2},\text{A}} - 0.425 \left[\frac{\text{mol}}{\text{m}^{3}\text{Pa}^{2}\text{s}}\right] \cdot \exp\left(-\frac{132467 \left[\frac{\text{J}}{\text{mol}}\right]}{\text{R} \cdot \text{T}}\right) p_{\text{A}}^{2} Y_{\text{CO}_{2},\text{A}} Y_{\text{H}_{2},\text{A}} - 0.425 \left[\frac{\text{mol}}{\text{m}^{3}\text{Pa}^{2}\text{s}}\right] \cdot \exp\left(-\frac{132467 \left[\frac{\text{J}}{\text{mol}}\right]}{\text{R} \cdot \text{T}}\right) p_{\text{A}}^{2} Y_{\text{CO}_{2},\text{A}} Y_{\text{H}_{2},\text{A}} - 0.425 \left[\frac{\text{mol}}{\text{m}^{3}\text{Pa}^{2}\text{s}}\right] \cdot \exp\left(-\frac{132467 \left[\frac{\text{J}}{\text{mol}}\right]}{\text{R} \cdot \text{T}}\right) p_{\text{A}}^{2} Y_{\text{CO}_{2},\text{A}} Y_{\text{H}_{2},\text{A}} - 0.425 \left[\frac{\text{mol}}{\text{m}^{3}\text{Pa}^{2}\text{s}}\right] \cdot \exp\left(-\frac{132467 \left[\frac{\text{J}}{\text{mol}}\right]}{\text{R} \cdot \text{T}}\right) p_{\text{A}}^{2} Y_{\text{CO}_{2},\text{A}} Y_{\text{H}_{2},\text{A}} - 0.425 \left[\frac{\text{mol}}{\text{m}^{3}\text{Pa}^{2}\text{s}}\right] \cdot \exp\left(-\frac{132467 \left[\frac{\text{J}}{\text{m}^{3}\text{Pa}^{2}\text{s}}\right] + 0.425 \left[\frac{132467 \left[\frac{\text{J}}{\text{m}^{3}\text{Pa}^{2}\text{s}}\right]}{\text{R} \cdot \text{T}}\right] + 0.425 \left[\frac{132467 \left[\frac{\text{J}}{\text{m}^{3}\text{Pa}^{2}\text{s}}\right] + 0.425 \left[\frac{132467 \left[\frac{\text{J}}{\text{m}^{3}\text{Pa}^{2}\text{s}}\right]}{\text{R} \cdot \text{T}}\right] + 0.425 \left[\frac{132467 \left[\frac{132467 \left[\frac{\text{J}}{\text{m}^{3}\text{Pa}^{2}\text{$$

In tab. 5 the dependent variables of the anode are listed

parameter	symbol	units
flow velocity in x-direction	$\mathcal{U}_{x,A}$	$m s^{-1}$
flow velocity in y-direction	$u_{y,A}$	$m s^{-1}$
mole fraction of methane	$Y_{CH_4,A}$	-
mole fraction of carbon monoxide	$Y_{CO,A}$	-
mole fraction of hydrogen	$Y_{H_2,A}$	-
mole fraction of carbon dioxide	$Y_{CO_2,A}$	-
mole fraction of steam	$Y_{H_2O,A}$	_
pressure	p_A	Ра

Tab.5. Dependent variables (anode)

Below the relevant boundary conditions for the anode are listed.

Boundary conditions

• Left boundary (x=0)

The left boundary is assumed to be permeable for the gases.

$$u_{y,A} = 0 \tag{55}$$

$$Y_i = Y_i^0$$
 i = CH₄, CO, H₂, CO₂, H₂O (56)-(60)

• Interface anode-electrolyte ($y = d_A + d_K$)

$$\frac{\partial Y_{CH_4}}{\partial y} = 0 \tag{61}$$

$$-D_{CO,gas}^{eff} \frac{\partial \left(p_A Y_{CO}\right)}{R \cdot T \partial y} = \frac{j_{CO}}{2F}$$
(62)

$$-D_{H_2,gas}^{eff} \frac{\partial \left(p_A Y_{H_2}\right)}{R \cdot T \partial y} = \frac{j_{H_2}}{2F}$$
(63)

$$-D_{H_2O,gas}^{eff} \frac{\partial \left(p_A Y_{H_2O}\right)}{R \cdot T \partial y} = -\frac{j_{H_2}}{2F}$$
(64)

$$-D_{CO_2,gas}^{eff} \frac{\partial \left(p_A Y_{CO_2}\right)}{R \cdot T \partial y} = -\frac{j_{CO}}{2F}$$
(65)

• Right boundary $(x = l_K)$

(66)

The other variables at the outlet of the anode gas channel are calculated by the governing equations

The current densities for H_2 and CO, j_{H2} and j_{CO} , respectively, are calculated from the cell voltage U (eq. (67)-(68)). The equivalent circuit diagram which forms the basis of the model is depicted in figure 2.



Fig. 2. Equivalent circuit diagram for the electrical processes in the SOFC [6]

The SOFC

$$j_{H_{2}} = \frac{\left(U_{Nernst,H_{2}} - U\right)R_{CO} + \left(U_{Nernst,H_{2}} - U_{Nernst,CO}\right)\left(R_{ohm} + R_{K}\right)}{R_{A,H_{2}}\left(R_{ohm} + R_{K}\right) + R_{A,H_{2}}R_{A,CO} + R_{A,CO}\left(R_{ohm} + R_{K}\right)}$$

$$(67)$$

$$j_{CO} = \frac{U_{Nernst,CO} - U_{Nernst,H_2} + J_{H_2} \cdot K_{A,H_2}}{R_{A,CO}}$$
(68)

The expression for the area-specific polarization resistance of H_2 , $R_{A,H2}$, is of the form (see [1])

$$\frac{1}{R_{A,H_2}} = 0.213 \cdot 10^9 \left[A / m^2 \right] \cdot \frac{2F}{RT} \exp\left(-\frac{1.1 \times 10^5 \left[J / mol \right]}{RT} \right) \left(Y_{H_2,A} \right)^{0.25}$$
(69)

For CO, the expression is modified so that $R_{A,CO}/R_{A,H2} = 2.6$ which corresponds to the mean value obtained by Matsuzaki and Yasuda [7]:

$$\frac{1}{R_{A,CO}} = 0.82 \cdot 10^8 \left[A / m^2 \right] \frac{2F}{RT} \exp\left(-\frac{1.1 \times 10^5 \left[J / mol \right]}{RT} \right) \left(Y_{CO,A} \right)^{0.25}$$
(70)

For the cathode, the expression for the area specific polarization resistance is taken from [1]:

$$\frac{1}{R_{K}} = 1.49 \cdot 10^{10} \left[A / m^{2} \right] \frac{4F}{RT} \exp\left(-\frac{1.6 \times 10^{5} \left[J / mol \right]}{RT} \right) (0.21)^{0.25}$$
(71)

The Nernst voltages are calculated according to equations (72) and (73), respectively

$$U_{Nernst,H_2} = U_{Zelle,H_2}^o + \frac{RT}{2F} \ln \frac{Y_{H_2,A} \sqrt{Y_{O_2}}}{Y_{H_2O,A}}$$
(72)

$$U_{Nernst,CO} = U_{Zelle,CO}^{o} + \frac{RT}{2F} \ln \frac{Y_{CO,A} \sqrt{Y_{O_2}}}{Y_{CO_2,A}}$$
(73)

The current density j is calculated by the equation

$$j = j_{CO} + j_{H_2} \tag{74}$$

Tab.4. Parameters for the governing equations and the boundary conditions (anode)

parameter	symbol	units	value	source
Effective Diffusion coefficient of component i in the gas mixture	$D_{i,gas}^{e\!f\!f}$	$m^2 s^{-1}$	Eq. (50)	IWE
Knudsen diffusion coefficient of methane	D ^K _{CH4}	$m^2 s^{-1}$	8.0 10 ⁻⁵	calculated
Knudsen diffusion coefficient of carbon monoxide	D ^K _{CO}	$m^2 s^{-1}$	6.20 10 ⁻⁵	calculated

hydrogen

Knudsen diffusion coefficient of

			11.12
D^{K}_{H2}	$m^2 s^{-1}$	0.0002399	calculated
D ^K _{CO2}	$m^2 s^{-1}$	5.12 10 ⁻⁵	calculated
D ^K _{H2O}	$m^2 s^{-1}$	8.0 10 ⁻⁵	calculated
F	A s mol ⁻¹	96485.4	-

Knudsen diffusion coefficient of carbon dioxide	D ^K _{CO2}	$m^2 s^{-1}$	5.12 10-5	calculated
Knudsen diffusion coefficient of steam	D^{K}_{H2O}	$m^2 s^{-1}$	8.0 10 ⁻⁵	calculated
Faraday constant	F	A s mol ⁻¹	96485.4	-
Current density produced by elecrochem. CO-Oxidation	j_{co}	A m ⁻²	Eq. (67)	-
Current density produced by elecrochem. H ₂ -Oxidation	\dot{J}_{H_2}	A m ⁻²	Eq. (68)	-
Pressure loss coefficient	k _p	m ²	8.5 10 ⁻¹⁴	FZJ
Atmospheric pressure	p _{atm}	Ра	101325	-
Universal gas constant	R	J mol ⁻¹ K ⁻¹	8.3144	-
Area-specific Polarization resistance of el.CO-oxidation	$R_{A,CO}$	Ωm^2	Eq (70)	
Area-specific Polarization resistance of el.H ₂ -oxidation	R_{A,H_2}	Ωm^2	Eq (69)	
Area-specific Polarization resistance of el.O ₂ -reduction	R_{K}	Ωm^2	Eq (71)	
Area-specific Ohm's resistance for 8YSZ	R_{ohm}	Ωm^2	9.78 10 ⁻⁶	IWE
temperature	Т	К	1223	chosen
Cell voltage	U	V	0.7	chosen
Nernst voltage of CO	U _{Nernst,CO}	V	Eq (73)	
Nernst voltage of H ₂	U_{Nernst,H_2}	V	Eq (72)	
Nernst Voltage at standard pressure for CO	$U^{o}_{\it Zelle,CO}$	V	0.9145	calculated
Nernst Voltage at standard pressure for H ₂	$U^o_{\it Zelle,H_2}$	V	0.9342	calculated
Mole fraction of oxygen at cathode	<i>Y</i> ₀₂	-	0.21	chosen
Porosity of the anode	3	-	0.3	chosen
tortuosity of the anode	τ	-	3	chosen

Parameter Variation

For the base case an anode thickness of 50 μ m was assumed. This anode thickness is a realistic value for electrolyte supported cells. In anode supported cells the anode thickness has to be higher. Therefore this value should be varied from 50 μ m to 2mm in order to investigate transport limitations in the porous anode in dependence of the anode thickness. For the anodes with a thickness between 0.5 and 2mm it was assumed that the open porosity is increased. Therefore for the ratio of porosity to tortuosity ϵ/τ a value of 0.21 is supposed [5]. Because of the reduced electrolyte thickness of anode supported cells, the area-specific ohmic resistance R_{ohm} is set to 1.63 10⁻⁶ Ω m² in these cases.

Results and Discussion

In Fig. 3 the results of the molar fractions in the anode gas channel are depicted for the base case (anode thickness of 50 μ m). The strong decrease of the methane and steam fractions in flow direction is due to the reforming reaction taking place in the anode. Accordingly, the fractions of hydrogen and carbon monoxide increase along the anode gas channel. Carbon dioxide is produced by the shift reaction and the electrochemical oxidation of CO. It can be seen that the molar fractions do not vary over the height of the anode gas channel so that diffusion in the channel is fast enough to transport the species to the anode surface or from the anode surface to the channel, respectively.





Fig 3. molar fractions of the components in the anode gas channel (base case)

In figure 4 the molar fractions of the components in the anode are shown for the base case.



Fig 4. molar fractions of the components in the anode (base case)
The gradient of the molar fractions in x-direction is similar to the gradient in the anode gas channel. The low variation of the molar fractions in y-direction indicates that no diffusion limitations occur in the anode with a thickness of 50 μ m.

As a result from the distribution of the species in the anode, the Nernst voltage of H_2 increases along the anode length, whereas the Nernst voltage of CO decreases because the ratio of CO to CO₂ decreases in x-direction (Fig. 5). The distribution of the current densities j_{H2} and j_{CO} is according to the distribution of the Nernst voltages. The mean value of the current density j of 5615 A/m² is high compared to measured values which are around 4000 A/m². This indicates that in further work the electrochemical parameters of the model should be adjusted to results obtained by own experiments





In the remainder the results of the parameter variation are presented. Exemplarily the discussion is confined to cells with an anode thickness of 2mm. Fig. 6 shows the molar fractions of the components in the anode for this case. In evidence the reforming reaction proceeds more quickly in x-direction because of the higher amount of Nickel present in the anode compared to the base case. For every component high gradients occur in y-direction which limit the chemical and electrochemical conversions. The CO_2 content in the upper left corner seems to be too high. Whether this value originates from a numerical error or a bad

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scaled parameter of the electrochemical CO oxidation or of the shift reaction remains to be investigated in further work.



Fig 6. molar fractions of the components in the anode (2mm anode)

Fig. 7 shows the Nernst voltages and current densities of the anode supported cell with 2mm anode. Because of the thinner electrolyte a higher current density can be achieved compared to electrolyte supported cells. The high increase of $U_{\text{Nernst,CO}}$ compared to the base case, can be attributed to the high rate of the reforming reaction which produces CO very fast and therefore leads to an increase in the ratio of $y_{\text{CO}}/y_{\text{CO2}}$ in the first quarter of the cell.



Fig 7. Nernst voltages and current densities j_{H2} , j_{CO} and j (2mm anode)

Conclusions

The internal reforming process of methane on a Ni/YSZ anode was successfully simulated with a 2D model. The impact of the anode thickness was investigated and it could be shown that no diffusion limitations occur in an electrolyte supported cell. In anode supported cells with 2mm anode thickness the reforming reaction proceeds faster than in an electrolyte supported cell but the chemical and electrochemical processes are limited by pore diffusion in the anode. Because of the thinner electrolyte in anode supported cells, the results of the simulation show that a higher current density can be achieved in an anode supported cell, compared to an electrolyte supported cell.

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Part III: The numerical solution with the FDEM

1 The FDEM program package

A detailed report on the FDEM (Finite Difference Element Method) program package is in preparation parallel to this report [1]. There the basic method is described together with three application examples. The third example (Chapter 3.4) is of particular interest with respect to the present report: it is the oxygen diffusion at the cathode side of a PEM fuel cell and has for the first time demonstrated the suitability of FDEM for the numerical simulation of fuel cells.

In the following we give a short outline of FDEM. FDEM [2] is a program package developed at the Computer Center of the University of Karlsruhe that solves by a finite difference method arbitrary nonlinear systems of PDEs (partial differential equations) under arbitrary nonlinear BCs (boundary conditions) on an unstructured FEM grid. The 2-D or 3-D PDEs must be of elliptic type (boundary value problem) or parabolic type (initial-boundary value problem). Here the FEM grid serves only for the structuring of the space, i.e. the determination of the neighbouring nodes. In 2-D we use triangles, in 3-D tetrahedrons. For each node we generate with a sophisticated algorithm by means of neighbouring nodes difference formulas of consistency order q, optionally q = 2 or q = 4 or q = 6. By the use of formulas of consistency order q+2 an estimate of the discretization error is obtained. For parabolic equations we use in time direction (for stability reasons) fully implicit difference formulas of consistency order p < 6, with error estimate by formulas of order p + 1. This means that one gets the exact solution if in the space direction the solution of the PDEs to be solved.

The knowledge of the error permits a selfadaptation of the solution method. In time direction the order p and the time step are always automatically optimized. In space direction the solution can be adapted to a requested accuracy by grid refinement (bisection of triangle or tetrahedron edges). There is also possible an optimization of the consistency order qindividually for each node by the comparison of the discretization errors of the different orders q = 2, 4, 6.

For many technical applications the solution domain is composed from subdomains in which hold different PDEs, e.g. anode material and hydrogen channel in a SOFC. It is not possible to apply difference formulas across the boundaries of the subdomains. Therefore we have introduced in FDEM "dividing lines" (which are in 3-D in effect dividing areas, but we call them nevertheless formally dividing lines). These dividing lines are internal boundaries over which we cannot differentiate. The solutions on both sides of the dividing lines are coupled by coupling conditions (CCs). Thus one gets over the whole domain

(composed of several subdomains) a global solution with global error estimate. The meshes on both sides of a dividing line do not have to coincide, one may have non-matching grids. By interpolation with the consistency order q that holds also for the difference formulas, the order q is maintained also for the CCs and therefore for the whole coupled domain. Because of the possibility of non-matching grid, in the subdomains an independent local grid refinement for the adaptation of the accuracy can be executed. The non-matching grid also allows a relative movement of the subdomains to each other.

Because FDEM must solve arbitrary nonlinear systems of PDEs, the linearization is executed by the Newton-Raphson method. In order to make the method as robust as possible we check after each iteration step if the defect has decreased. If this does not hold we try with a self-adapted relaxation factor to reduce the defect (then there is only linear instead of quadratic convergence). For very good convergence we use (optionally) the simplified Newton method with constant matrix to save computation time. The Newton method is terminated if the Newton defect is smaller than a corresponding discretization error term, that no unnecessary digits are computed.

From the discretization of PDEs result very large and sparse linear systems of equations. These are solved by the LINSOL program package that has also been developed at the Computer Center of the University of Karlsruhe. LINSOL [3] comprises CG (conjugate gradient) methods of quite different types for the iterative solution, between which an automatic optimization in a polyalgorithm can be executed. LINSOL also contains a direct solver with optionally reduced fill-in that can be used as preconditioner for the iterative solvers. The fill-in is reduced by different bandwidth optimizers which leads above all for 3-D problems to a considerable saving of computation time and storage space.

FDEM and LINSOL have been developed from the beginning for efficient data structures on distributed memory parallel computers (in contrast to shared memory computers). Here the distribution of the data to the processors plays the decisive role. We use a 1-D domain decomposition that can be executed automatically and runs over dividing lines. For grid refinement a new distribution of the data is executed after each refinement step. The exchange of the data between the processors takes place by the quasi standard MPI (message passing interface). Thus FDEM is running efficiently on shared and distributed memory computers. FDEM has been tested on many different types of parallel computers all over Germany.

FDEM is a program package for the solution of PDEs that has unique properties. To us no other program package is known that unifies in a single code comparable properties concerning the flexibility of the solution method, of the solution domain, of the error estimate and of the parallelization.

FDEM is a black box solver, i.e. it solves an arbitrary nonlinear system of PDEs and boundary conditions (BCs) on an arbitrary domain. The domain can be composed from subdomains that are separated by dividing lines and whose solutions are coupled by CCs. Which PDEs under which BCs and CCs are to be solved is determined by the entering of the PDEs, BCs and CCs as Fortran code into prescibed program frames. The domain with its boundaries and dividing lines is read from a file as 2-D or 3-D grid according to given rules.

Because we assume nonlinear PDEs and solve them by the Newton-Raphson method,

also the Jacobi matrices for the PDEs, BCs and CCs must be entered as Fortran code into program frames. The Jacobi matrices reflect the dependence of the PDEs, BCs and CCs from their arguments. For strongly nested nonlinear systems of PDEs the formulation and implementation of the Jacobi matrices is the main part of the task.

For the simulation of a fuel cell one will start at first with a simplified 2-D model to get insight in the numerical behaviour of the PDEs. Then the 2-D model is refined as necessary. Here one will at first solve the stationary equations, then eventually the non-stationary ones. With the thus gained experiences one will try to implement a simplified, later a refined 3-D model. The transition from 2-D to 3-D is with respect to computation time and above all to the necessary storage space a very large step. The transition from the stationary to the non-stationary problem results only in a corresponding factor in computation time, 100 time steps need 100 times the computation time of a single stationary step.

The above mentioned procedure would be a research program for several years. Because of the relatively short available time for the project (it was intended as an intermediate financing to gain experience and prepare a larger cooperation project) only stationary 2-D fuel cells were simulated. However, the experiences gained for the formulation of the many parameters in the system of PDEs for the different types of fuel cells are very promissing and prepare the research direction for further more sophiscated models of fuel cells.

2 The numerical solution of the PEMFC PDEs

The model and the PDEs for PEMFCs have been presented in Part I. We refer to equations in Part I, e.g. for equation (1), by I(1), similarly for figures and tables.

Fig. 1 shows the domain of solution. It is a section of the GDL (gas diffusion layer). This is Fig. 11 turned upside down so that we have the x-,y-coordanate system in the usual way. The performance of the PEMFC is determined by activities in the GDL on the cathode side, i.e. on the oxygen side. In the upper part of Fig. 1 we see the domain of solution cut out of the whole GDL so that its left and right boundaries are symmetry lines with vanishing derivatives in x-direction, and its upper boundary is the reaction layer. The left half of the lower boundary is open to the channel with oxygen, the right half is closed by the rib. The oxygen is flowing in z-direction perpendicular to the x-,y-plane. The lower part of Fig. 1 shows the domain of solution with more details and gives the numbering of the different types of boundaries as we use them in the coding.

We got basically two models for the PEMFC from the ZSW, first a simple model which was later, after the investigation of the results, refined to a more complicated model with a more sophisticated condition at the reaction layer (Tafel equation). Here we report only on the latter refined model.

Concerning the diffusion model we got from ZSW the equations with the simple model of Ficks, equations I(1)-I(6) for 6 variables, we call this model ZSW3. Then we got a model with a more sophisticated MTPM (Mean Transport Pore Model) transport mechanism, equations I(18)-I(27) for 10 variables, we call this model ZSW4. This is a much more complicated model concerning the implementation in FDEM. Therefore we discuss in this report only the ZSW4 model.



Figure 1: Upper part: domain of solution in the "environment". Lower part: Details of the domain of solution.

parameter	Symbol		name
	English	German	in code
thickness of GDL	t_{GDL}	d_{GDL}	dGDLc
width of channel	c	k	kc
width of rib	r	s	sc

 Table 1: Structural and geometry parameters.

We got from the ZSW at first a report with the PDEs and BCs in German and for these notations we wrote the code. Later we got the English version. Unfortunately, ZSW has changed the symbols for some parameters so that they fitted to their English names. Therefore we give the symbols for the parameters of the English version, of the German version and additionally the name of the parameter in the Fortran code which usually fits to the German name.

Table 2: Dependent variables for node i, mfd means molar flux density.

no.	parameter	symbol	name in code
1	mfd of oxygen in x-dir.	\dot{n}_o^x	u(i,1)
2	mfd of oxygen in y -dir.	\dot{n}_o^y	u(i,2)
3	mfd of water vapour in x-dir.	\dot{n}_w^x	u(i,3)
4	mfd of water vapour in y-dir.	\dot{n}_w^y	u(i,4)
5	mfd of nitrogen in x-dir.	\dot{n}_n^x	u(i,5)
6	mfd of nitrogen in y-dir.	\dot{n}_n^y	u(i,6)
7	oxygen partial pressure	p_o	u(i,7)
8	water vapour partial pressure	p_w	u(i,8)
9	nitrogen partial pressure	p_n	u(i,9)
10	total pressure	p	u(i,10)
11	current density	i	u(i,11)

Table 1 gives the structural and geometry parameters of Table I1. We do not repeat here the units and values. Table 2 which corresponds to Table I5 gives the dependent variables for ZSW4. In the black-box solver FDEM the variables for node i and solution component j are denoted by u(i,j). In the Fortran code many loops run over the node number i. If the innermost loop runs over the first index of a multidimensional array, in Fortran the elements are accessed contiguously which is the most efficient access. Therefore the node number i is in the first position in u(i,j).

We can see from Table 2 that we have 11 dependent variables. One of them, namely the current density i (do not confuse with node index i), plays a very special role. It occurs only in the boundary condition at the reaction layer. If it appeared explicitly we could express it by the other variables. But it appears in a bad nonlinear way in the Tafel equation I(8). Therefore we proceed as follows: we take the current density i as a variable in the whole

no.	variable	equation		
1	\dot{n}_o^x	I(18) in form (2)		
2	\dot{n}_o^y	I(19) in similar form		
3	\dot{n}_w^x	I(20) in similar form		
4	\dot{n}_w^y	I(21) in similar form		
5	\dot{n}_n^x	I(22) in similar form		
6	\dot{n}_n^y	I(23) in similar form		
7	p_o	I(24)		
8	p_w	I(25)		
9	p_n	I(26)		
10	p	I(27)		
11	i	(1)		

Table 3: Sequence of variables and equations in the interior of the domain.

domain, but it has a physical meaning only at the reaction layer. In the other nodes the current density i plays the role of a dummy variable and there we put

$$i = 0. (1)$$

This is the "PDE" and BC except for the nodes at the reaction layer (boundary ④ in Fig. 1).

As we can see at Table 2 we have 11 variables and therefore we need 11 equations. In Table 3 we show which equation is used in which position in the system of PDEs. As FDEM requests the PDEs in the form $P_i u = 0$ for PDE no. *i*, we take all terms to the l.h.s. of the equations. Therefore I(18) is used in the form

$$\frac{\dot{n}_{o}^{x}}{DKn_{o}} + \frac{p_{w}\dot{n}_{o}^{x} - p_{o}\dot{n}_{w}^{x}}{D_{ow} \cdot p} + \frac{p_{n}\dot{n}_{o}^{x} - p_{o}\dot{n}_{n}^{x}}{D_{on} \cdot p} + \frac{1}{RT}\frac{\partial p_{o}}{\partial x} - \frac{p_{o}}{RTp}\frac{\partial p}{\partial x} + \left[\frac{B_{o}}{DKn_{o}} + \frac{B_{o}p_{w}}{D_{ow} \cdot p}\left(1 - \frac{B_{w}}{B_{o}}\right) + \frac{B_{o}p_{n}}{D_{on} \cdot p}\left(1 - \frac{B_{n}}{B_{o}}\right)\right] \frac{p_{o}}{RTp}\frac{\partial p}{\partial x} = 0.$$
(2)

Similarly we write in equs. I(19)–I(27) all terms to the l.h.s.. Now these equations can be coded in Fortran. Before we can write down code we must give to the coefficients Fortran names. The coefficients that occur in the PDEs are compiled in Tables I3 and I6. There are coefficients that are constants, their names will end by "c" for constant. There are coefficients that depend on the node *i* and there are coefficients that depend on solution component index *j* or *j*, *k*. In Tables I3 and I6 all information about the coefficients is given. Here we give in Table 4 only the Fortran names for the coefficients. In the PDEs appear the following coefficients DKn_j with (*j*) as *o*, *w*, *n*, thus DKno(i), DKnw(i), DKnn(i) for each node *i*, Beff(j) similarly as Beffo(i), Beffw(i), Beffn(i). As the coefficients $D_{j,k}$

	Fortran		Fortran
symbol	name	symbol	name
R	Rc	η	eta
F	Fc	η_o	etaoc
T	Tc	η_w	etawc
ε_o	epsoc	η_n	etanc
$\varepsilon(x)$	epsxc(i)	M_o	Moc
a	aec	M_w	Mwc
kf	kfc	M_n	Mnc
au	tau	DKn_j	Dkn(j)
D_{jk}	D(j,k)	ω	omc
Vd_o	Vdo	K_j	Kn(j)
Vd_w	Vdw	λ_j	lam(j)
Vd_n	Vdn	< r >	rmc
B_j	Beff(j)	$< r^{2} >$	rmqc
$ u_j$	nue(j)	RT	RTc

Table 4: Fortran names for the coefficients that occur for the PDEs.

with j and k as o, w, n appear only in the combination $p \cdot D_{j,k}$ we immediately compute pD_{ow} as pDow(i), pD_{on} as pDon(i) and pD_{wn} as pDwn(i) etc. These coefficients are pre-computed for all nodes i with the equations given in Part I.

Before we present the coding for equ. (2) as an example, we must mention the following items: we have introduced an additional coefficient RT as RTc because R and T always appear in this combination. Derivatives of variables are denoted in the following way: the xand y-derivatives of u(i,1) are denoted and naturally stored as ux(i,1) and uy(i,1). Second derivatives (that do not appear in this section) would be denoted by uxx(i,1), uyy(i,1), uxy(i,1). With these notations and above all with the notations of Table 2 for the variables the coding for equ. (2) looks like this (this is P_1u , the Newton residual of the first PDE in the system) for node i, denoted by p(i,1):

$$\begin{split} p(i,1) &= u(i,1)/Dkno(i) + (u(i,8) * u(i,1) - \\ u(i,7) * u(i,3)/pDow(i) + (u(i,9) * u(i,1) - \\ u(i,7) * u(i,5)/pDon(i) + ux(i,7)/RTc - \\ u(i,7) * ux(i,10)/(RTc * u(i,10)) + \\ Beffo(i) * (1D0/Dkno(i) + u(i,8) * (1D0 - \\ Beffw(i)/Beffo(i)/pDow(i) + u(i,9) * \\ (1D0 - Beffn(i)/Beffo(i))/pDon(i)) * \\ u(i,7) * ux(i,10)/(RTc * u(i,10)) . \end{split}$$

This gives a touch how by mnemonic nomenclature it is rather easy to translate equ. (2)

	Fortran		Fortran
symbol	name	symbol	name
p^{ch}	pKac	γ	gammac
φ	phic	U_0	U0c
$y_{o,a}^{uc}$	yokc	U_z	UZc
i_0	ioc	d_{mem}	dmemc
α	alphac	κ_{mem}	kappac
n	nc	A	Ac
$ ho_o^{ref}$	porefc	В	Bc
f_v	fvc	C	Cc
p_w^S	pwsc		

Table 5: Fortran names for the coefficients that occur for the BCs.

into Fortran code. These p(i, j) for equation j in node i are pre-computed and in a later step entered in a program frame that places them into the right position in the linear system of equations for the computation of the Newton correction. The meaning of p(i, 1) is the Newton residual or Newton defect of the first equation in the block of 11 equations for node i. It is the r.h.s. in the linear system of the computation of the Newton correction.

The next problem we want to discuss are the boundary conditions for the 4 types of boundaries ① to ④ of Fig. 1. At the boundaries for some variables BCs are given. However, we need at each boundary node 11 equations for the 11 variables. So we take the missing equations quite naturally from the set of the interior equations, where no other conditions, e.g. symmetry at boundary ③, are given.

The set of parameters that occur in the BCs is given in Table I4. We give in Table 5 the Fortran names for these parameters.

The BCs for the MTPM transport equations are given in equs. I(37)-I(49). We have to supplement these equations by interior or other PDEs (symmetry) so that we have always 11 equations for the 11 variables. In contrast to Part I we do not use (upper) indices like UC, UR for channel or rib because the index *i* of the node tells where the node is.

BCs at boundary ① (open to channel): Here we need p_w^S with the Fortran name pwsc pre-computed from I(9) which is resolved for p_w^S and gives a constant value. For a node *i* on the boundary ① we have the BCs I(37)–I(40). As we need 11 BCs for the 11 variables, we supplement the conditions by the PDEs I(18)–I(23) and equ. eqrefequ1. In Table 6 we list the variables and the equations at boundary ① that includes the left corner. In order to show how such a BC is translated to Fortran, we show the code for the equation for p_n in Table6 for a node *i* on the boundary ①:

$$p(i,9) = u(i,9) - (pKac - u(i,8)) * (1D0 - yokc)$$
(4)

no.	variable	equation
1	\dot{n}_o^x	I(18) in form (2)
2	\dot{n}_o^y	I(19) in similar form
3	\dot{n}_w^x	I(20) in similar form
4	\dot{n}_w^y	I(21) in similar form
5	\dot{n}_n^x	I(22) in similar form
6	\dot{n}_n^y	I(23) in similar form
7	p_o	$p_{o} - (p^{ch} - p_{w})y_{o,a}^{UC} = 0$
8	p_w	$p_w - \varphi \; p_w^S = 0$
9	p_n	$p_n - (p^{ch} - p_w)(1 - y_{o,a}^{UC}) = 0$
10	p	$p - p^{ch} = 0$
11	i	(1)

Table 6: Variables and equations for the BCs at boundary ①.

The right corner of boundary ① is "avoided" as the separation between boundary ① and ② is put between two nodes. If at the separation of the two boundaries a node would be placed, there would be no unique BC for this node. However, this procedure means that the geometrical location how far the BC ① extends to the right and BC ② to the left changes with the mesh size in the *x*-direction.

BCs at boundary (2) (under rib): Here the impermeability conditions I(41)–I(43) are given. Therefore we need another 8 equations for the 11 variables. In Table7 we list the variables and the equations at boundary (2) that includes the right corner.

BCs at boundary ③ (symmetry lines): Because of the symmetry no x-transport of species takes place, this results in the BCs I(44)–I(46). For the other variables, except current density i for which i = 0 holds also here, we put the x-derivative to zero. Table 8 shows the variables and the equations for boundary ③, excluding the corner nodes.

BCs at boundary 0 (reaction layer): The BCs for boundary 0 are given in I(47)–I(49). However, in these equations appears the current density *i* for which holds the Tafel equation I(8). This extremely nonlinear equation cannot be resolved explicitly for the current density *i*. Therefore we take it in the form

$$i - f_v i_0 \left(\frac{p_o}{p_o^{ref}}\right)^{\gamma} \exp\left[\frac{\alpha n F(U_0 - U_z - \frac{d_{mem}}{\kappa_{mem}}i)}{RT}\right] = 0$$
(5)

and use this as the equation for the current density i. The other two BCs I(47), I(48) are used in the form

$$\dot{n}_{o}^{y} - \frac{1}{4F}i = 0 , \qquad (6)$$

$$\dot{n}_w^y + \frac{1}{2F}i = 0.$$
 (7)

no.	variable	equation
1	\dot{n}_o^x	I(18) in form (2)
2	\dot{n}_o^y	$\dot{n}_o^y = 0$
3	\dot{n}_w^x	I(20) correspond. form
4	\dot{n}_w^y	$\dot{n}_w^y = 0$
5	\dot{n}_n^x	I(22) correspond. form
6	\dot{n}_n^y	$\dot{n}_n^y = 0$
7	p_o	I(24) correspond. form
8	p_w	I(25) correspond. form
9	p_n	I(26) correspond. form
10	p	I(27) correspond. form
11	i	(1)

 Table 7: Variables and equations for the BCs at boundary ②.

 Table 8: Variables and equations for the BCs at boundary ③.

no.	variable	equation
1	\dot{n}_o^x	$\dot{n}_o^x = 0$
2	\dot{n}_o^y	$\partial \dot{n}_o^y / \partial x = 0$
3	\dot{n}_w^x	$\dot{n}_w^x = 0$
4	$\dot{n}_w^{\widetilde{y}}$	$\partial \dot{n}_w^y / \partial x = 0$
5	\dot{n}_n^x	$\dot{n}_n^x = 0$
6	\dot{n}_n^y	$\partial \dot{n}_n^y / \partial x = 0$
7	p_o	$\partial p_o / \partial x = 0$
8	p_w	$\partial p_w / \partial x = 0$
9	p_n	$\partial p_n / \partial x = 0$
10	p	$\partial p/\partial x = 0$
11	i	(1)

no.	variable	equation	
1	\dot{n}_o^x	I(18) in form (2)	
2	\dot{n}_o^y	(6)	
3	\dot{n}_w^x	I(20) correspond. form	
4	\dot{n}_w^y	(7)	
5	\dot{n}_n^x	I(22) correspond. form	
6	\dot{n}_n^y	I(49)	
7	p_o	I(24) correspond. form	
8	p_w	I(25) correspond. form	
9	p_n	I(26) correspond. form	
10	p	I(27) correspond. form	
11	i	(5)	

Table 9: Variables and equations for the BCs at boundary ④.

For the other variables we again take the corresponding equations of Table 3. Table 9 shows the variables and equations at boundary ④.

Again we show how equation (5) is coded in Fortran for a node *i* on the boundary (): at first auxiliary values are computed before the *i*-loop: hU2 = alphac * nc * FchU3 = fvc * iocThen in the *i*-loop for a node *i*, we have

$$p(i,11) = u(i,11) - hU3 * (u(i,7)/porefc) * *$$

$$gammac * exp(hU2 * (U0c - UZc - dmemc * u(i,11)/kappac)/RTc$$
(8)

For FDEM such a nonlinear algebraic equation is included in the black-box scheme and poses no problem.

For the solution of the PDEs by the Newton-Raphson iteration and for the computation of the error estimate the Jacobian matrices, i.e. the dependence of the differential equations from the variables and their derivatives are needed. For a system of m PDEs with m variables we have for the differential operator in 2-D:

$$Pu \equiv P(x, y, u, u_x, u_y, u_{xx}, u_{yy}, u_{xy}) = 0 , \qquad (9)$$

with

$$u = \begin{pmatrix} u_1 \\ u_2 \\ \vdots \\ u_m \end{pmatrix}, \qquad Pu = \begin{pmatrix} P_1 u \\ P_2 u \\ \vdots \\ P_m u \end{pmatrix}.$$
(10)

The Jacobian matrices, see [1, equ. (2.4.6)], are

$$\frac{\partial P}{\partial u} = \begin{pmatrix} \frac{\partial P_1}{\partial u_1} & \cdots & \frac{\partial P_1}{\partial u_m} \\ \vdots & & \vdots \\ \frac{\partial P_m}{\partial u_1} & \cdots & \frac{\partial P_m}{\partial u_m} \end{pmatrix}, \dots, \frac{\partial P}{\partial u_{xy}} = \begin{pmatrix} \frac{\partial P_1}{\partial u_{1,xy}} & \cdots & \frac{\partial P_1}{\partial u_{m,xy}} \\ \vdots & & \vdots \\ \frac{\partial P_m}{\partial u_{1,xy}} & \cdots & \frac{\partial P_m}{\partial u_{m,xy}} \end{pmatrix}.$$
 (11)

We will not give here the formulas for all Jacobians of the system. We rather want to illustrate the procedure by a few examples. The first PDE P_1u in (10) is in our case the first equation in Table 3, i.e. I(18), that we use in the formulation of equ. (2). The first variable in Table 3 is \dot{n}_o^x . Thus in (11) $\frac{\partial P_1}{\partial u_1}$ is the derivative of equ. (2) with respect to \dot{n}_o^x . But before we formulate the derivatives we must check if there are not hidden variables in "coefficients" that appear in the equation. Fortunately, the coefficients do not depend on \dot{n}_o^x , so we get

$$\frac{\partial P_1}{\partial \dot{n}_o^x} = \frac{1}{DKn_o} + \frac{p_w}{D_{ow} \cdot p} + \frac{P_n}{D_{om} \cdot p} \,. \tag{12}$$

However, if we e.g. want to compute $\frac{\partial P_1}{\partial p_o} = \frac{\partial P_1}{\partial u_7}$, i.e. the dependency of the first PDE from the variable p_o , the permeabilities B_o and B_w depend in a complicated way from p_o : In I(31) B_j , j = o, w, n, depends on ν_j , I(32) that depends on p_k , k = o, w, n, and B_j depends also on η , I(33) that depends on p_k , k = o, w, n and finally B_j depends on K_j , I(35) that depends by λ_j on p_j , I(36). Therefore we precompute the $\frac{\partial \nu_i}{\partial p_j}$, i, j = o, w, n and similarly $\frac{\partial(\frac{1}{\eta})}{\partial p_i}$ and $\frac{\partial K_i}{\partial p_j}$. We have I(31)

$$B_o = DKn_o \frac{\omega\nu_o + K_o}{1 + K_o} + \frac{\langle r^2 \rangle \frac{\varepsilon(x)}{\tau}}{8} \cdot p \cdot \frac{1}{\eta}.$$
 (13)

With the pre-computed values we can compute with the chain rule for differentiation e.g.

$$\frac{\partial B_o}{\partial p_o} = DKn_o \frac{(1+K_o)(\omega \frac{\partial \nu_o}{\partial p_o} + \frac{\partial K_o}{\partial p_o}) - (\omega \nu_o + K_o) \frac{\partial K_o}{\partial p_o}}{(1+K_o)^2} + \frac{\langle r^2 \rangle \varepsilon(x)}{8\tau} p \frac{\partial(\frac{1}{\eta})}{\partial p_o}.$$
(14)

In the same way all $\partial B_i/\partial p_j$ and also $\partial B_i/\partial p$ are pre-computed and stored for all nodes *i*. Note that the expressions for $(D_{jk} \cdot p)$ I(30) do not depend on *p*.

Now we can formulate $\partial P_1/\partial u_7$ in the terminology of (11) which is our equ. (2) differentiated to p_o

$$\frac{\partial P_1}{\partial p_o} = -\frac{\dot{n}_w^x}{D_{ow} \cdot p} - \frac{\dot{n}_n^x}{D_{on} \cdot p} - \frac{1}{RTp} \frac{\partial p}{\partial x} + \frac{\partial B_o}{\partial p_o} [*] \frac{p_o}{RTp} + \frac{\partial p}{\partial x} + B_o \left[-\frac{p_w}{D_{ow} \cdot p} \frac{B_o \frac{\partial B_w}{\partial p_o} - B_w \frac{\partial B_o}{\partial p_o}}{B_o^2} - \frac{p_o}{B_o^2} - \frac{B_o \frac{\partial B_n}{\partial p_o} - B_n \frac{\partial B_o}{\partial p_o}}{B_o^2} \right] \frac{p_o}{RTp} \frac{\partial p}{\partial x} + B_o [*] \frac{1}{RTp} \frac{\partial p}{\partial x} .$$
(15)

Here [*] denotes the brackets in (2) which saves writing down twice this large expression. Quite naturally, in the coding one would precompute [*] as an auxiliary variable, so this form is closer to the coding than the written-out form. If you nevertheless imagine written out [*] in (15) you get the impression, in which a complicated way the first PDE of the system depends on the 7th variable. In a similar way the first 6 PDEs depend on the 7th to 10^{th} variable. It would not be possible to handle these Jacobians without a clear scheme for intermediate derivatives as it has been presented above. These expressions then must be translated into Fortran code as it has been shown for equ. (2).

In the same way we must deliver the Jacobians for the BCs. In many cases the interior PDEs are also used for the BCs, so the Jacobians are the same in these cases.

In Table 9 the equations are shown for boundary A, the reaction layer. Here the Tafel equation (5) is the BC for the last variable, the current density *i*. Therefore $\partial P_{11}/\partial u_{11}$ is the derivative of (5) with respect to *i*. That we do not get too complicated expressions and because intermediate results can be used also in other Jacobians, we precompute auxiliary values

$$\begin{split} hu2 &= \alpha nF \quad , \\ hu3 &= \rho_o \; i_0 \quad , \\ hu4 &= \exp[hu2*(U_0-U_z-\frac{d_{mem}}{\kappa_{mem}}i)/(RT)] \quad . \\ \text{With these values we get for the boundary } (12) from equ. (5) \end{split}$$

$$\frac{\partial p_{11}}{\partial i} = 1 + hu3 * \left(\frac{p_o}{p_o^{ref}}\right)^{\gamma} * hu4 * hu2 * \frac{d_{mem}}{\kappa_{mem} RT} .$$
(16)

All these Jacobians are entered in a prescribed program frame of FDEM that then executes with this information the solution process as described in detail in [1]. So by the PDEs and BCs and their Jacobians from the black-box solver a solver for the special problem is created.

Here we present the results that we obtained for the standard data given in Part I for the (more complicated) Mean Transport Pore Model (MTPM) as an example for the information that FDEM delivers as result. We computed on the HP XC6000 parallel supercomputer of the University of Karlsruhe. The processors are Intel Itanium2 processors with 1.5 GHz. We computed with 32 processors in parallel. The grid was 200×201 nodes in *x*-,*y*-direction. We computed with consistency order q = 4. As we have 11 unknowns per node, see Table 2, we have totally 442, 200 unknows. The computation time was 4123sec on the master processor 1.

In Figs. 2–21 the results are plotted as coloured contour plots together with their errors. These plots are black-and-white in the printed version. So it might be recommended to look at the pictures at the computer in the on-line version of the paper.

Fig. 1 shows the domain of solution. At the lower boundary we have in the left half the opening to the oxygen channel and in the right half the domain is closed by the rib. Therefore we have in the middle of the lower boundary an abrupt change in the BCs that causes a singularity in the solution because there is mathematically no smooth transition from the one type of BC to the other type. This singularity is clearly visible in the figures.

For the fuel cell research the behaviour of the partial pressure p_b of oxygen, p_w of water vapour, p_n of nitrogen and the current density *i* at the reaction layer are of greatest interest. Therefore we show in Figs. 22–26 these quantities together with their errors along the reaction layer. We can see that the singularity of the lower boundary has smoothed out at the upper boundary of the solution domain. At the top of Fig. 26 the value i_{nean} is presented which is the mean value of the grid points at the reaction layer and is a measure of the output of the fuel cell. As we have the singularity in the problem, the local error at the singularity will not decrease with finer grid as fast as we expect from the consistency order q = 4.

The discussion of the results from the point of view of the fuel cell researcher is presented in Part I.



Figure 2: Contour plot of molecular flux density of oxygen in x-direction \dot{n}_{o}^{x} .



Figure 3: Contour plot of the global relative error of \dot{n}_{o}^{x} .



Figure 4: Contour plot of molecular flux density of oxygen in y-direction \dot{n}_{o}^{y} .



Figure 5: Contour plot of the global relative error of \dot{n}_{o}^{y} .



Figure 6: Contour plot of molecular flux density of water vapour in x-direction \dot{n}_w^x .



Figure 7: Contour plot of the global relative error of \dot{n}_w^x .



Figure 8: Contour plot of molecular flux density of water vapour in y-direction \dot{n}_w^y .



Figure 9: Contour plot of the global relative error of \dot{n}_w^y .



Figure 10: Contour plot of molecular flux density of nitrogen in x-direction \dot{n}_n^x .



Figure 11: Contour plot of the global relative error of \dot{n}_n^x .



Figure 12: Contour plot of molecular flux density of nitrogen in *y*-direction \dot{n}_n^y .



Figure 13: Contour plot of the global relative error of \dot{n}_n^y .



Figure 14: Contour plot of oxygen partial pressure p_o .



Figure 15: Contour plot of the global relative error of p_o .



Figure 16: Contour plot of water vapour partial pressure p_w .



Figure 17: Contour plot of the global relative error of p_w .



Figure 18: Contour plot of nitrogen partial pressure p_n .



Figure 19: Contour plot of the global relative error of p_n .



Figure 20: Contour plot of total pressure *p*.



Figure 21: Contour plot of the global relative error of *p*.





Figure 22: Oxygen partial pressure p_o along the reaction layer and its global relative error.





Figure 23: Water vapour partial pressure p_w along the reaction layer and its global relative error.





Figure 24: Nitrogen partial pressure p_n along the reaction layer and its global relative error.





Figure 25: Total pressure p along the reaction layer and its global relative error.





Figure 26: Current density i along the reaction layer and its global relative error. On top of the upper frame is the value $i_{mean} = 2981.92$.

3 The numerical solution of the SOFC PDEs

The model and the PDEs for the SOFC have been presented in Part II. We refer to equations in Part II, e.g. for equation (1), by II(1), similarly for figures and tables.

Fig. 27 shows the domain of solution and the numbering of the boundaries. Here we have a coupled domain of anode and gas channel, coupled by the dividing line DL with side 1 und side 2 where we have coupling conditions (CCs).



Figure 27: Domain of solution and numbering of the boundaries.

Table 10 which corresponds to Table II1 gives the names of the geometrical parameters in the Fortran code. The last letter "c" denotes that these values are constants. We do not repeat here the units and values, they are given in Part II. Table 11 shows the 8 dependent variables with their Fortran names. It combines Tables II3 and II5. In Part II the variables have different symbols for gas channel, index K (for Kanal, German word for channel) and index A for anode. However, these are in reality the same variables, only in different domains. That they are computed by different PDEs in the different index K or A is not matter. As the node number i tells where the variable is used, a different index K or A is not necessary. In the black-box solver FDEM the variables for node i and solution component jare denoted by u(i,j). In the Fortran code many loops run over the node number i. If the

parameter	symbol	name in code
thickness of anode	d_A	dac
height of gas channel	d_K	dkc
length of gas channel	l_K	lkc

Table 11: Dependent variables with their Fortran names for node *i*, mf means mole fraction.

no.	variable	symbol	name in code
1	flow velocity in x-direction	u_x	u(i,1)
2	flow velocity in y-direction	u_y	u(i,2)
3	mf of methane	Y_{CH4}	u(i,3)
4	mf of carbon monoxide	Y_{CO}	u(i,4)
5	mf of hydrogen	Y_{H_2}	u(i,5)
6	mf of carbon dioxide	Y_{CO_2}	u(i,6)
7	mf of steam	Y_{H_2O}	u(i,7)
8	pressure	p	u(i,8)

innermost loop runs over the first index of a multidimensional array, in Fortran the elements are accessed contiguously which is the most efficient access. Therefore the node number i is in the first position in u(i,j).

no.	variable	our notation	equation
1	u_x	u_x	II(5) in form (17)
2	u_y	u_y	II(7) in form (18)
3	Y_{CH4}	Y_3	II(1) in form (19)
4	Y_{CO}	Y_4	II(2) in similar form
5	Y_{H_2}	Y_5	II(3) in similar form
6	Y_{CO_2}	Y_6	II(4) in similar form
7	Y_{H_2O}	Y_7	II(8) in form (20)
8	p	p	II(6) in similar form to (18)

Table 12: Sequence of variables and equations in the channel.

Table 12 shows the variables and the equations that we use in the channel. That we do not have to write the chemical indices like CH_4 in Y_{CH_4} we have replaced them by numbers that correspond to the numbering in Table 12, thus instead of Y_{CH_4} we write Y_3 , instead of Y_{CO} we write Y_4 etc. These simplified indices are also used for component indices in the coefficients of the PDEs.

For the numerical solution we must differentiate out the product terms. Therefore the first equation II(5) (continuity equation) in Table 12 becomes

$$\frac{\partial \varrho}{\partial x}u_x + \varrho \frac{\partial u_x}{\partial x} + \frac{\partial \varrho}{\partial y}u_y + \varrho \frac{\partial u_y}{\partial y} = 0.$$
(17)

The second equation in Table 12, the y-momentum equation II(7) becomes, as we must take all terms of the PDEs to the l.h.s.

$$\varrho u_x \frac{\partial u_y}{\partial x} + \varrho u_y \frac{\partial u_y}{\partial y} + \frac{\partial p}{\partial y} - \frac{\partial \mu}{\partial y} \left(\frac{4}{3} \frac{\partial u_y}{\partial y} - \frac{2}{3} \frac{\partial u_x}{\partial x}\right) - \mu \left(\frac{4}{3} \frac{\partial^2 u_y}{\partial y^2} + \frac{1}{3} \frac{\partial^2 u_x}{\partial x \partial y} + \frac{\partial^2 u_y}{\partial x^2}\right) - \frac{\partial \mu}{\partial x} \left(\frac{\partial u_x}{\partial y} + \frac{\partial u_y}{\partial x}\right) = 0.$$
(18)

The third equation in Table 12, the species balance II(1) for CH_4 is with the simplified chemical indices of Table 12

$$-\frac{\partial p}{\partial x}u_{x}Y_{3} - \frac{\partial u_{x}}{\partial x}pY_{3} - \frac{\partial Y_{3}}{\partial x}pu_{x} - \frac{\partial p}{\partial y}u_{y}Y_{3} - \frac{\partial u_{y}}{\partial y}pY_{3} - \frac{\partial Y_{3}}{\partial y}pu_{y} + \frac{\partial D_{3,gas}}{\partial y}\left(\frac{\partial p}{\partial y}Y_{3} + \frac{\partial Y_{3}}{\partial y}p\right) +$$
(19)
$$D_{3,gas}\left(\frac{\partial^{2} p}{\partial y^{2}}Y_{3} + 2\frac{\partial p}{\partial y}\frac{\partial Y_{3}}{\partial y} + \frac{\partial^{2} Y_{3}}{\partial y^{2}}p\right) = 0.$$

The equations no. 4 to 6 in Table 12 are obtained by replacing in Y_3 and $D_{3,gas}$ the index 3 by 4, 5, 6. The 7th equation II(8), Dalton's law, becomes

$$Y_3 + Y_4 + Y_5 + Y_6 + Y_7 - 1 = 0. (20)$$

The 8^{th} equation II(6), the *y*-momentum equation, is written similarly to the *x*-momentum equation (18).

In (19) appears the diffusion coefficient $D_{3,gas}$ which is given in II(9) which is in our notation

$$D_{i,gas} = \frac{1 - Y_i}{\sum_{j \neq i} Y_j / D_{ij}}, \qquad i, j = 3, 4, 5, 6, 7.$$
(21)
However, there appears in (19) also $\partial D_{3,gas}/\partial y$. To get a corresponding expression from (21), we write out the expression for $D_{3,gas}$

$$D_{3,gas} = \frac{1 - Y_3}{\frac{Y_4}{D_{34}} + \frac{Y_5}{D_{35}} + \frac{Y_6}{D_{36}} + \frac{Y_7}{D_{37}}} = \frac{1 - Y_3}{sum'3} , \qquad (22)$$

where we have abbreviated the denominator by sum'i where sum' means that the term Y_j/D_{ij} with j = i, in our case Y_3/D_{33} , does not appear in sum'3. With the quotient rule for differentiation we get from (22)

$$\frac{D_{3,gas}}{\partial y} = -(sum'3)^{-2} \left[sum'3\frac{\partial Y_3}{\partial x} + (1-Y_3) \left(\frac{1}{D_{34}} \frac{\partial Y_4}{\partial y} + \frac{1}{D_{35}} \frac{\partial Y_5}{\partial y} + \frac{1}{D_{36}} \frac{\partial Y_6}{\partial y} + \frac{1}{D_{37}} \frac{\partial Y_7}{\partial y} \right) \right].$$
(23)

The other $\partial D_{i,gas}/\partial y$ are computed similarly. For the anode we will need also $\partial D_{i,gas}/\partial x$ that we get by replacing $\partial/\partial y$ by $\partial/\partial x$.

In (18) appears the "coefficient" μ (viscosity) that is given by II(11)

$$\mu = \sum_{i} \frac{Y_{i}\mu_{i}}{\sum_{j} Y_{j}\psi_{ij}} , \qquad i, j = 3, 4, 5, 6, 7 , \qquad (24)$$

where ψ_{ij} are values that are computed from II(12)–II(14), but do not depend on the variables Y_j . However, there appears also $\partial \mu / \partial x$ and $\partial \mu / \partial y$ in (18). To get these expressions we write out (23):

$$\mu = \frac{Y_{3}\mu_{3}}{\underbrace{Y_{3}\psi_{33} + Y_{4}\psi_{34} + Y_{5}\psi_{35} + Y_{6}\psi_{36} + Y_{7}\psi_{37}}_{sumps3} + \underbrace{Y_{4}\mu_{4}}_{\underbrace{Y_{3}\psi_{43} + Y_{4}\psi_{44} + Y_{5}\psi_{45} + Y_{6}\psi_{46} + Y_{7}\psi_{47}}_{sumps4} + \underbrace{Y_{7}\mu_{7}}_{sumps4} + \underbrace{Y_{7}\mu_{7}}_{\underbrace{Y_{3}\psi_{73} + Y_{4}\psi_{74} + Y_{5}\psi_{75} + Y_{6}\psi_{76} + Y_{7}\psi_{77}}_{sumps7} + \underbrace{Y_{7}\mu_{7}}_{sumps7} +$$

By the quotient rule of differentiation we get

$$\frac{\partial \mu}{\partial x} = (sumps3)^{-2} \left[sumps3\mu_3 \frac{\partial Y_3}{\partial x} - Y_3\mu_3 \underbrace{\left(\psi_{33} \frac{\partial Y_3}{\partial x} + \psi_{34} \frac{\partial Y_4}{\partial x} + \dots + \psi_{37} \frac{\partial Y_7}{\partial x} \right) \right]}_{\frac{\partial sumps3}{\partial x}} + (sumps4)^{-2} \left[sumps4\mu_4 \frac{\partial Y_4}{\partial x} - Y_4\mu_4 \frac{\partial sumps4}{\partial x} \right] + (26)$$

$$\vdots$$

$$(sumps7)^{-2} \left[sumps7\mu_7 \frac{\partial Y_7}{\partial x} - Y_7\mu_7 \frac{\partial sumps7}{\partial x} \right].$$

In the same way we get $\partial \mu / \partial y$ by replacing $\partial / \partial x$ by $\partial / \partial y$.

For equs. (17) and (18) we need the density ρ and for (17) also its derivatives with respect to x and y. From II(10) we have

$$\rho = \frac{p}{R_M T}, \quad with \quad R_M = \frac{R}{\sum_i Y_i M_i}, \quad i = 3, 4, 5, 6, 7$$
(27)

in our notation. If we write out R_M we get

$$R_{M} = \frac{R}{\underbrace{Y_{3}M_{3} + Y_{4}M_{4} + Y_{5}M_{5} + Y_{6}M_{6} + Y_{7}M_{7}}_{sumr}}$$
(28)

and we have

$$\rho = \frac{p \cdot sumr}{RT} , \qquad (29)$$

$$\frac{\partial \rho}{\partial x} = \frac{1}{RT} \left[\frac{\partial p}{\partial x} sumr + p \left(M_3 \frac{\partial Y_3}{\partial x} + M_4 \frac{\partial Y_4}{\partial x} + \dots + M_7 \frac{\partial Y_7}{\partial x} \right) \right] . \tag{30}$$

If we replace $\partial/\partial x$ by $\partial/\partial y$ we get $\partial \rho/\partial y$.

Now we have available all the necessary information for the coding of the PDEs in the channel. But before we can give an example for the coding we must give Fortran names to the parameters in the PDEs, and we want to include here already the parameters for the BCs. For this purpose we repeat only the symbols of Table II4 and give them the corresponding Fortran names in Table 13. Some coefficients, e.g. R, T are given below with the anode data in Table 16.

	Fortran		Fortran		Fortran
symbol	name	symbol	name	symbol	name
$D_{i,gas}$	d <u>i</u> gas	$Y_{CH_4}^0$	y03c	σ_{H_2}	sig6c
D_{ij}	dijc	Y_{CO}^{0}	y04c	σ_{H_2O}	sig7c
M_{CH_4}	m3c	$Y_{H_2}^{0}$	y05c	ε_{CH_4}/k	epk3c
M_{CO}	m4c	$Y_{CO_2}^0$	y06c	ε_{CO}/k	epk4c
M_{CO_2}	m5c	$Y_{H_2O}^{0}$	y07c	ε_{CO_2}/k	epk5c
M_{H_2}	тбс	σ_{CH_4}	sig3c	ε_{H_2}/k	epk6c
M_{H_2O}	m7c	σ_{CO}	sig4c	ε_{H_2O}/k	epk7c
$u_{x,max}^0$	u0xc	$\sigma^0_{CO_2}$	sig5c		

 Table 13: Symbols for the parameters and their Fortran names for the PDEs and BCs of the channel.

Here \underline{i} or \underline{j} must be replaced by i, j=3, 4, 5, 6, 7.

Table 14: Symbols and Fortran names for pre-computed "coefficients".

	Fortran		Fortran		Fortran
symbol	name	symbol	name	symbol	name
ρ	rho	ψ_{ij}	psi <i>ij</i>	$\partial \mu / \partial x$	muex
$\partial ho / \partial x$	rhox	μ_i	mu <u>i</u>	$\partial \mu / \partial y$	muey
$\partial ho / \partial y$	rhoy	$\Omega_{\nu,i}$	omv <u>i</u>	$\partial D_{i,gas}/\partial x$	d <u>i</u> gasx
R_M	rm	μ	mue	$\partial D_{i,gas}/\partial y$	d <u>i</u> gasy

Here \underline{i} or \underline{j} must be replaced by i, $\underline{j}=3, 4, 5, 6, 7$.

But we must give for the coding also names for pre-computed "coefficients" that are given in Table 14. Partly they are mere parameters, partly they contain the variables Y_i . These pre-computed values are stored in corresponding arrays for the nodes *i*.

Now we give the Fortran coding for the first 3 equations in Table 12. These are the Newton residuals P_1u to P_3u in (10). But at first we must say how derivatives of variables are denoted in the code: for node *i* the *x*- and *y*-derivatives of u(i,1), i.e. of the first solution component (here u_x) are denoted and stored as ux(i,1) and uy(i,1), second derivatives are denoted by uxx(i,1), uyy(i,1), uxy(i,1). Similarly the derivatives of other components u(i,j) are denoted by ux(i,j), uy(i,j), uxx(i,j), uyy(i,j).

The Fortran code for P_1u , equation (17), looks like this for node *i*:

$$p(i,1) = rhox(i) * u(i,1) + rho(i) * ux(i,1) + rhoy(i) * u(i,2) + rho(i) * uy(i,2)$$
(31)

The Fortran code for P_2u , equation (18), looks like this for node *i*:

no.	variable	our notation	equation
1	u_x	u_x	II(46) in form (34)
2	u_y	u_y	II(48) in form (35)
3	Y_{CH_4}	Y_3	II(42) in form like (34)
4	Y_{CO}	Y_4	II(43) in form like (34)
5	Y_{H_2}	Y_5	II(44) in form like (34)
6	Y_{CO_2}	Y_6	II(45) in form like (34)
7	Y_{H_2O}	Y_7	II(49) all terms to l.h.s.
8	p	p	II(47) in form like (35)

 Table 15: Sequence of variables and equations in the anode.

$$p(i,2) = rho(i) * u(i,1) * ux(i,2) + rho(i) * u(i,2) * uy(i,2) + ux(i,8) - muey(i) * (4D0 * uy(i,2)/3D0 - (32))$$

$$2D0 * ux(i,1)/3D0 - mue(i) * (4D0 * uyy(i,2)/3D0 + uxy(i,1)/3D0 + uxx(i,2)) - muex(i) * (uy(i,1) + ux(i,2))$$

The Fortran code for the third component of the Newton defect P_3u , equation (19), is

$$p(i,3) = -ux(i,8) * u(i,1) * u(i,3) - ux(i,1) * u(i,3) + ux(i,1) * u(i,8) * u(i,3) - ux(i,3) * u(i,8) * u(i,1) - uy(i,8) * u(i,2) * u(i,8) + u(i,3) - uy(i,3) * u(i,8) * u(i,2) + uy(i,8) * u(i,2) * u(i,3) - uy(i,3) * u(i,3) + uy(i,3) + u(i,3) + uy(i,3) * u(i,8) + u(i,3) + uy(i,3) * u(i,8) + u(i,3) + uy(i,3) * u(i,8) + uy(i,3) * u(i,3) + uy(i,3) * u(i,8)) + uyy(i,3) * u(i,8) + uyy(i,3) * u(i,8))$$

$$(33)$$

So we recognize that by the chosen name conventions and precomputation of the "coeffients", that themselves depend on variables, it is quite easy to translate the equations to Fortran code.

The next problem are the PDEs in the anode (up to now we had discussed the PDEs in the channel). Table 15 shows which equation is used in which position of the r.h.s. (Newton residual) of the linear system for the computation of the Newton correction. It should be recalled that we do not use the indices K and A for variables in the channel and in the anode. For FDEM these are the same variables, only in different domains and the node number i tells where the position is. Here we show the form of the first 2 equations prepared for the coding, the other equations are of the same type or trivial (7^{th} equ.). For the preparation

	Fortran		Fortran		Fortran
symbol	name	symbol	name	symbol	name
$D_{i,gas}^{eff}$	d <u>i</u> gas	kp	kpc	$U_{Nernst,CO}$	uneco
$D_{CH_A}^{K}$	dk3c	p_{atm}	patc	U_{Nernst,H_2}	uneh2
D_{CO}^{K}	dk4c	R	rc	$U^0_{Zelle,CO}$	uzcoc
$D_{H_2}^K$	dk5c	$R_{A,CO}$	raco	U^0_{Zelle,H_2}	uzh2c
$D_{CO_2}^{K^2}$	dk6c	R_{A,H_2}	rah2	Y_{O_2}	yo2c
$D_{H_2O}^{K}$	dk7c	R_K	rk	ε	epsc
\bar{F}	fc	R_{ohm}	rohmc	au	tauc
j_{CO}	jco	T	tc	r_{CH_4}	rch4
j_{H_2}	jh2	U	uc	r_s	rs

 Table 16: Symbols for the parameters and their Fortran names for the PDEs and BCs for the anode.

Here \underline{i} must be replaced by 3, 4, 5, 6, 7.

of equation II(46) which is the first equation in Table 15, we multiply the equation by RT which brings this term as a factor to the last term in II(46). We must differentiate out all terms. In II(46) there are effective diffusion coefficients $D_{\underline{i},gas}^{eff}$ that are computed from II(50). Here, \underline{i} is the component index that takes values 3 to 7 in our notation. In the equations and in the node we drop the upper index "eff" because in the anode domain the $D_{i,gas}$ are computed from II(50) so that we do not need a special identification in the formulas or code. So II(46) becomes

$$-\frac{\partial p}{\partial x}u_{x}Y_{3} - \frac{\partial u_{x}}{\partial x}pY_{3} - \frac{\partial Y_{3}}{\partial x}pu_{x} - \frac{\partial p}{\partial y}u_{y}Y_{3} - \frac{\partial u_{y}}{\partial y}pY_{3} - -\frac{\partial Y_{3}}{\partial y}pu_{y} + D_{3,gas}\left(\frac{\partial^{2}p}{\partial y^{2}}Y_{3} + 2\frac{\partial p}{\partial y}\frac{\partial Y_{3}}{\partial y} + p\frac{\partial^{2}Y_{3}}{\partial y^{2}}\right) + \frac{\partial D_{3,gas}}{\partial y}\left(\frac{\partial p}{\partial y}Y_{3} + \frac{\partial Y_{3}}{\partial y}p\right) + D_{3,gas}\left(\frac{\partial^{2}p}{\partial x^{2}}Y_{3} + 2\frac{\partial p}{\partial x}\frac{\partial Y_{3}}{\partial x} + p\frac{\partial^{2}Y_{3}}{\partial x^{2}}\right) + \frac{\partial D_{3,gas}}{\partial x}\left(\frac{\partial p}{\partial x}Y_{3} + \frac{\partial Y_{3}}{\partial x}p\right) - \frac{RT}{d_{A}}r_{3} = 0.$$
(34)

The equation II(48) which is the equation in the second position in Table 15 becomes

$$\frac{\partial p}{\partial y} + \frac{\mu}{k_p} u_y = 0 . aga{35}$$

Now we have prepared the basic types of the equations for the anode, the other equations have quite similar form, see Table 15. The functions $r_{CH_4} = r_3$ and r_s that appear in the equations II(43)–(46) are computed from II(53), (54).

In Table 16 we have listed the parameters of Table II4 with their Fortran names. As mentioned above, we named the $D_{i,gas}^{eff}$ by $D_{i,gas}$ in the anode domain. However, they are computed there from II(50) in which appear the $D_{i,gas}$ computed from II(9) or from (22) for the example of $D_{3,gas}$. In order to distinguish the two $D_{i,gas}$ we denote the $D_{i,gas}$ from II(9) by $D_{i,gas}^*$ and its derivatives computed like (22) by $\partial D_{i,gas}^*/\partial x$ or $\partial D_{i,gas}^*/\partial y$. Now we need for the equations the derivatives $\partial D_{i,gas}/\partial x$ and $\partial D_{i,gas}/\partial y$ in the anode which are in reality the "eff" values. From II(50) we get in the present notation, resolving for $D_{i,gas}$:

$$D_{i,gas} = \frac{\varepsilon}{\tau} D_i^K \frac{D_{i,gas}^*}{\frac{\varepsilon}{\tau} D_{i,gas}^* + D_i^K}$$
(36)

with i = 3, 4, 5, 6, 7 in our notation. From (36) we get the partial derivative (with intermediate calculation)

$$\frac{\partial D_{i,gas}}{\partial x} = \frac{\varepsilon}{\tau} \frac{D_i^K}{(\frac{\varepsilon}{\tau} D_i^* + D_i^K)^2} \frac{\partial D_i^*}{\partial x} , \qquad (37)$$

with $\frac{\partial D_i^*}{\partial x}$ as shown for $\frac{\partial D_3^*}{\partial y}$ in (22). The formula for $\partial D_{i,gas}/\partial y$ is obtained by replacing $\partial/\partial x$ by $\partial/\partial y$.

The formal translation of these equations is executed as we have shown it above for the translation of (19) to (33) so that there is no new information.

Now we have finished the discussion of the programming of the PDEs in the interior of the domain for the channel, Table 12, and for the anode, Table 15. The next problem is the discussion of the BCs. As we have 8 variables, we need at each boundary a system of 8 equations. Often at a boundary only a few conditions are precribed, e.g. the pressure at the exit of the channel. Then we "fill up" the set of the equations by appropriate equations. The domain with its boundaries is shown in Fig. 27. We discuss the boundaries without their corners and discuss the conditions at the corners later.

We start with the BCs for boundary ①, the left entry of the anode, which is assumed to be permeable. For u_x we take the Darcy law II(47) in the form of the 8^{th} equation of Table 15. The value $u_y = 0$ is prescribed which fulfils with the condition for $p: \partial p/\partial y = 0$ Darcy's law II(48). The condition $\partial p/\partial y = 0$ means constant pressure along ①. We will later take the pressure from the channel at the lower corner of ①. The Y_i are prescribed by their entry values Y_i^0 . In Table 17 the boundary equations for boundary ① are compiled.

For boundary (2), the boundary between anode and electrolyte, the conditions II(61)– (65) are given. For u_x we prescribe Darcy's law like on boundary (1). There is $u_y = 0$ because of closed wall. For p we prescribe Darcy's law II(48), which is no.2 in Table 15. The other conditions are given. For Y_4 we have II(62) which is in our notation and product differentiation

$$-D_4 \frac{1}{RT} \left(Y_4 \frac{\partial p}{\partial y} + p \frac{\partial Y_4}{\partial y} \right) - j_4 \frac{1}{2F} = 0.$$
(38)

The other conditions are in similar form. The equations for boundary 2 are shown in Table 17. For these BCs the values $j_{H_2} = j_5 \text{ II}(67)$ and $j_{CO} = j_4 \text{ II}(68)$ must be precomputed for the nodes of boundary 2, except for the first node (left corner) where for the entry values Y_i a singular value would result. However, for the computation of j_4 and j_5 we need intermediate values R_{A,H_2} , $R_{A,CO}$, R_K , U_{Nernst,H_2} and $U_{Nernst,CO}$ which are given in II(69)–(73). These values are also pre-computed for the nodes of boundary 2. For the given entry value $Y_{CO_2}^o = 0$ we get a singular value for II(73). Therefore we do not compute the j_4, j_5 for the entry values of Y_i .

For boundary ③, exit of anode, which is assumed to be "open", there is prescribed only $p = p_{atm}$. So we use for u_x Darcy's law II(47) (no.8 in Table 15) and for the equations in position 2–7 those of the interior, Table 15. The equations are compiled in Table 17.

Now follow the BCs for the channel. At boundary (4), the right exit of the channel, there only $p = p_{atm}$ is prescribed, II(41). The other equations are like in the interior of the channel, i.e. the same as positions 1–7 in Table 12. The boundary equations for boundary (4) are compiled in Table 18.

The BCs for boundary (5), the rib wall, are given in II(15)–(21), these are the no-slip conditions for the velocity components and zero gradient normal to the wall for the Y_i . For the pressure we take the *x*-momentum equation II(6) like in the interior (no.8 in Table 12). The boundary equations for boundary (5) are compiled in Table 18.

The boundary conditions for boundary (6), the channel entry, are given in II(34)–(41). Here values are prescribed for all variables except the pressure which is computed from the x-momentum equation II(6) (no.8 in Table 12). For u_x a parabolic profile is prescribed with the maximal velocity $u_{x,K,max}$ in the middle of the channel and no-slip condition $u_x = 0$ at the rib wall and at the anode, equ. II(40). However, we must have the same u_x in the channel and in the anode at the interface DL, see Fig. 27. We compute at the anode interface u_x from Darcy's law II(47) and we take this as <u>slip</u> for the channel flow at the anode interface. We call this the "modified parabola II(40)". Else we would have a jump in u_x at the interface. The boundary (6) are compiled in Table 18.

The next problem are the coupling conditions (CCs) at the dividing line DL, see Fig. 27. The DL is geometrically one line, but logically two lines: side 1 belongs to the channel, side 2 to the anode. The CCs are given in II(22)–(33). However, we must clearly distinguish which conditions are applied at side 1 and side 2. The variables are computed at one side and their value is transferred to the other side. In the code the logical nodes on side 1 and 2 have different node numbers i, so the variables can be easily distinguished. In the writing down of the CCs we distinguish the variables and also the variable-dependent coefficients by the index K for channel and A for anode. We have compiled the CCs in Table 19 which we now will discuss.

The value of u_x is computed from Darcy's law in x-direction II(47), the equation is that of position 8 in Table 15, i.e. it is computed with the variables in the anode, index A. So this is the equation for u_x on side 2. This value is taken to the channel, side 1, by the condition $u_{x,K} = u_{x,A}$, this is the slip velocity.

no.	var.	boundary ①	boundary 2	boundary 3
1	u_x	no.8 in Tab. 15	no.8 in Tab. 15	no.8 in Tab. 15
2	u_y	$u_y = 0$	$u_y = 0$	no.2 in Tab. 15
3	Y_3	$Y_3 - Y_3^0 = 0$	$\partial Y_3/\partial y = 0$	no.3 in Tab. 15
4	Y_4	$Y_4 - Y_4^0 = 0$	II(62) in form (38)	no.4 in Tab. 15
5	Y_5	$Y_5 - Y_5^0 = 0$	II(63), similar form	no.5 in Tab. 15
6	Y_6	$Y_6 - Y_6^0 = 0$	II(64), similar form	no.6 in Tab. 15
7	Y_7	$Y_7 - Y_7^0 = 0$	II(65), similar form	no.7 in Tab. 15
8	p	$\partial p/\partial y = 0$	no.2 in Tab. 15	$p - p_{atm} = 0$

 Table 17: Boundary equations for the anode for boundaries ①—③.

no.8, Tab. 15 means the equation in row 8 of Table 15.

Table 18: Boundary equations for the channel for the boundaries (4–6).

no.	var.	boundary ④	boundary 5	boundary 6
1	u_x	like	$u_x = 0$	$u_x = \text{mod.par. II}(40)$
2	u_y	positions	$u_y = 0$	$u_y = 0$
3	Y_3	1–7	$\partial Y_3 / \partial y = 0$	$Y_3 - Y_3^0 = 0$
4	Y_4	in	$\partial Y_4 / \partial y = 0$	$Y_4 - Y_4^0 = 0$
5	Y_5	Table 12	$\partial Y_5 / \partial y = 0$	$Y_5 - Y_5^0 = 0$
6	Y_6		$\partial Y_6 / \partial y = 0$	$Y_6 - Y_6^0 = 0$
7	Y_7		$\partial Y_7 / \partial y = 0$	$Y_7 - Y_7^0 = 0$
8	p	$p - p_{atm} = 0$	no.8 in Tab. 12	no.8 in Tab. 12

mod.par. II(40) means modified parabola II(40), see text.

Similar conditions hold for u_y . The Y_i are computed in the anode from the equality of the diffusion transport for channel and anode, II(22)–(26). From II(22) we get in our notation, differentiating out the products and taking all terms to the l.h.s., the equation for Y_3 :

$$D_{3,gas,A}\left(\frac{\partial p_A}{\partial x}Y_{3,A} + p_A\frac{\partial Y_{3,A}}{\partial x}\right) - D_{3,gas,K}\left(\frac{\partial p_K}{\partial y}Y_{3,K} + p_A\frac{\partial Y_{3,K}}{\partial y}\right) = 0.$$
(39)

Here $D_{3,gas,A}$ is computed from (36) with the $Y_{i,A}$ and $D_{3,gas,K}$ is computed from type (22) with the $Y_{i,K}$. Similar relations hold for the Y_4 to Y_7 . These values are taken by $Y_{i,K} = Y_{i,A}$ to the channel side 1.

The pressure p_k is computed from the x-momentum equation II(6) in the channel which is the equation of position 8 in Table 12. This value is transferred by $p_A = p_K$ to the anode side. This discussion of the CCs at the DL is an illustrative example of the use and of the possibilities of a dividing line. It couples by CCs the two domains channel and anode in

no.	var.	side 1, channel	side 2, anode
1	u_x	$u_{x,K} - u_{x,A} = 0$	no.8 in Tab. 15
2	u_y	$u_{y,K} - u_{y,A} = 0$	no.2 in Tab. 15
3	Y_3	$Y_{3,K} - Y_{3,A} = 0$	II(22) in form (39)
4	Y_4	$Y_{4,K} - Y_{4,A} = 0$	II(23) in similar form
5	Y_5	$Y_{5,K} - Y_{5,A} = 0$	II(24) in similar form
6	Y_6	$Y_{6,K} - Y_{6,A} = 0$	II(25) in similar form
7	Y_7	$Y_{7,K} - Y_{7,A} = 0$	II(26) in similar form
8	p	no.8 in Tab. 12	$P_A - P_K = 0$

 Table 19: Coupling conditions (CCs) at dividing line DL. Index K is variable in channel, index A in anode.

no.8 in Tab. 12 means the equation in position 8 in Table 12.

which hold quite different PDEs. We get a global solution over the two domains with global error estimate.

The next problem are the corners. They belong to two boundaries. At first sight it seems to be of no importance which conditions we take. However, the present problem is very critical and we had experienced that we got large errors and even divergence of the Newton iteration if we did not take the "correct" conditions at the corners. We report here those conditions that we take presently which does yet not mean that these are the optimal conditions. One has to look at Fig. 27 for the corners.

Upper left corner, intersection of boundaries ① and ②: we take the equations of boundary ①, Table 17.

Upper right corner, intersection of boundary 2 and 3: For position 1 to 7 we take the equations of boundary 3, Table 17, for position 8 we take $p-p_{atm} = 0$. At first we had used the conditions of boundary 2 for 1 to 7 and $p - p_{atm} = 0$ for 8. With this choice the errors were 1 to 2 orders of magnitude larger. This shows the extreme sensibility of the problem to such seemingly tiny changes and it shows that the corner nodes play an important role for the solution of the whole problem.

Lower right corner, intersection of boundary (4) and (5): we take the equations of boundary (5), Table 18, for positions 1 to 7 and for position 8 we take $p - p_{atm} = 0$.

Lower left corner, intersection of boundary (5) and (6): we take the equations of boundary (6).

The next problem are the left and right end nodes of the dividing line. Here we have for the one geometrical node again two logical nodes at the end and we have to differ between side 1 (channel) and side 2 (anode). We depict our choice of all CCs in Table 20, it is self-explaining.

Now we have prepared all the information for the coding of the r.h.s. of the linear system for the computation of the Newton correction. You have seen that there was still much to do to formulate clearly the problem. The BCs and CCs have been given "shortly" in Part II, but these are only the *given* conditions that must be "filled up" by other equations to get

		left e	end	right	t end
		side 1	side 2	side 1	side 2
no.	var.	channel	anode	channel	anode
1	u_x	$u_{x,K} - u_{x,A} = 0$			
2	u_y	$u_y = 0$	$u_y = 0$	position	position
3	Y_3	$Y_{3,K} - Y_3^0 = 0$	$Y_{3,K} - Y_3^0 = 0$	1 to 7	1 to 7
4	Y_4	$Y_{4,K} - Y_4^0 = 0$	$Y_{4,K} - Y_4^0 = 0$	like	like
5	Y_5	$Y_{5,K} - Y_5^0 = 0$	$Y_{5,K} - Y_5^0 = 0$	side 1	side 2
6	Y_6	$Y_{6,K} - Y_6^0 = 0$	$Y_{6,K} - Y_6^0 = 0$	Table 19	Table 19
7	Y_7	$Y_{7,K} - Y_7^0 = 0$	$Y_{7,K} - Y_7^0 = 0$		
8	p	no.8, Tab. 12	$P_A - P_K = 0$	$p - p_{atm} = 0$	$p - p_{atm} = 0$

Table 20: CCs at left and right end of DL. Index K is variable in channel, index A in anode.

no.8, Tab. 12 means the equation in position 8 in Table 12.

the necessary 8 equations. And in Part II nothing is said about the corners. So the user of FDEM is forced to formulate exactly all the details of his problem to get the equations that finally are entered in FDEM. The formal translation to Fortran code is easy as has been shown exemplarily in equs. (31)–(33) for the channel flow.

The matrix Q_d of the linear system is composed by FDEM from the difference formulas and the Jacobian matrices, that are also needed for the computation of the error estimate, see the basic paper [2] or the detailed report [1]. The meaning and the form of the Jacobian matrices has been explained above in the equations (9)–(11) and the corresponding context. The system of PDEs for the SOFC is extremely nonlinear, above all by the nonlinear coefficients, e.g. the $D_{i,gas}$ or μ . It will be impossible to give here the formulas for the Jacobian matrices, they would fill many pages with formulas that nobody would read. We rather want to show the procedure how to get the Jacobian matrices in our case.

Let uns consider equ. (17), this is the first equation in Table 12 and therefore P_1u in the notation of (10). for the Jacobians we must look for the dependencies of (17) from the variables. Equ. (17) depends explicitly from $u_x = u_1$, the first variable, from its x-derivative $\partial u_x/\partial x = u_{1,x}$, from $u_y = u_2$, from its y-derivative $\partial u_y/\partial y = u_{2,y}$ in the terminology of (9)–(11). If ρ would be a constant, these would be the (explicit) dependencies of the operator P_1u (17). However, ρ depends by (29) from sumr and sumr depends by (28) from the variables $Y_3 = u_3$ to $Y_7 = u_7$, and ρ depends on $p = u_8$. These are implicit dependencies. So we have purely formal

$$P_{1}u = P_{1}(u_{1}, u_{2}, u_{3}, u_{4}, u_{5}, u_{6}, u_{7}, u_{8}, u_{1,x}, u_{2,y})$$

$$= P_{1}(u_{x}, u_{y}, Y_{3}, Y_{4}, Y_{5}, Y_{6}, Y_{7}, p, \frac{\partial u_{x}}{\partial x}, \frac{\partial u_{y}}{\partial y})$$

$$= P_{1}(u_{x}, u_{y}, \frac{\partial u_{x}}{\partial x}, \frac{\partial u_{y}}{\partial y}, \rho(p, sumr(Y_{3}, \dots, Y_{7})), \qquad (40)$$

$$\frac{\partial \rho}{\partial x}(p, \frac{\partial p}{\partial x}, sumr(Y_{i}), \frac{\partial sumr}{\partial x}(\frac{\partial Y_{i}}{\partial x})),$$

$$\frac{\partial \rho}{\partial y}(p, \frac{\partial p}{\partial y}, sumr(Y_{i}), \frac{\partial sumr}{\partial r}(\frac{\partial Y_{i}}{\partial y})))$$

From (17), (28)–(30) we get

$$\frac{\partial P_1}{\partial u_1} = \frac{\partial P_1}{\partial u_x} = \frac{\partial \rho}{\partial x} \quad \text{(dependence } 1^{st} \text{ PDE from } 1^{st} \text{ variable}), \\
\frac{\partial P_1}{\partial u_2} = \frac{\partial P_1}{\partial u_y} = \frac{\partial \rho}{\partial y} \quad \text{(dependence } 1^{st} \text{ PDE from } 2^{nd} \text{ variable}), \\
\frac{\partial P_1}{\partial u_3} = \frac{\partial P_1}{\partial Y_3} = \left(\frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y}\right) \frac{\partial \rho}{\partial Y_3} + u_x \frac{\partial (\frac{\rho}{\partial x})}{\partial Y_3} + u_y \frac{\partial (\frac{\rho}{\partial y})}{\partial Y_3}, \quad (41) \\
\text{similarly} \quad \frac{\partial P_1}{\partial Y_4} \quad \text{to} \quad \frac{\partial P_1}{\partial Y_7} \\
\frac{\partial P_1}{\partial u_8} = \frac{\partial P_1}{\partial p} = \left(\frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y}\right) \frac{\partial \rho}{\partial p} + u_x \frac{\partial (\frac{\rho}{\partial x})}{\partial p} + u_y \frac{\partial (\frac{\rho}{\partial y})}{\partial p}.$$

This ends the dependencies of P_1 from the variables u_x to p. Now come the dependencies from the x-derivatives of the variables:

$$\frac{\partial P_1}{\frac{\partial u_x}{\partial x}} = \rho \qquad \text{(there is no dep. on } \frac{\partial u_y}{\partial x}\text{)},$$

$$\frac{\partial P_1}{\frac{\partial Y_3}{\partial x}} = u_x \frac{\partial(\frac{\rho}{\partial x})}{\frac{\partial Y_3}{\partial x}}, \qquad \text{similarly for } \frac{\partial Y_4}{\partial x} \quad \text{to } \frac{\partial Y_7}{\partial x} \qquad (42)$$

$$\frac{\partial P_1}{\frac{\partial p}{\partial x}} = u_x \frac{\partial(\frac{\rho}{\partial x})}{\frac{\partial p}{\partial x}},$$

$$\frac{\partial P_1}{\partial u_y} = \rho,$$

$$\frac{\partial P_1}{\partial Y_3} = u_y \frac{\partial(\frac{\rho}{\partial y})}{\partial Y_3}, \quad \text{similarly for } Y_4 \text{ to } Y_7 \quad (43)$$

$$\frac{\partial P_1}{\partial y} = u_y \frac{\partial(\frac{\rho}{\partial y})}{\partial y}.$$

All intermediate quantities are pre-computed and stored, e.g. $sumr, \partial sumr/\partial x, \partial sumr/\partial y$ and their derivatives with respect to the variables. From (28)–(30) we get e.g.

$$\frac{\partial \rho}{\partial Y_3} = \frac{p}{RT} \frac{\partial sumr}{\partial Y_3},$$

$$\frac{\partial sumr}{\partial Y_3} = M_3,$$

$$\frac{\partial \left(\frac{\partial \rho_x}{\partial x}\right)}{\partial Y_3} = \frac{1}{RT} \frac{\partial p}{\partial x} \frac{\partial sumr}{\partial Y_3},$$

$$\frac{\partial \left(\frac{\partial \rho_x}{\partial x}\right)}{\frac{\partial Y_3}{\partial x}} = \frac{1}{RT} p \frac{\partial \left(\frac{\partial sumr}{\partial x}\right)}{\frac{\partial Y_3}{\partial x}},$$

$$\frac{\partial \left(\frac{\partial sumr}{\partial x}\right)}{\frac{\partial Y_3}{\partial x}} = M_3.$$
(44)

This should be sufficient to show you how the Jacobians (11) are computed and why we do not list them all here. We have developed a formalism where we reduce the complicated expression by a chain of intermediate values for which we apply the chain rule of differentiation, so that even the most complex expressions get back to their simple origins. Nevertheless, the formulation of the Jacobians is a hard mental training.

It is now also clear that the Jacobians are the main part of the implementation—and that they are rather error-prone. Therefore we have developed the Jacobi tester, where we check the elements of the Jacobi matrices by difference quotients, see [1]. And indeed, there were a lot of errors found, but finally the Jacobi tester did no longer show errors. Then the numerical solution started.

However, the situation was not quite as simple as it seems to be. For the PEMFC we got rather final models that worked nearly immediately. The situation is much more complicated for the SOFC, especially because of the methane reforming process and by the coupling of the two domains of anode and gas channel. Only by solving the PDEs we could check their validity. At the same time also the used values for the many coefficients that came from different sources were not "safe" values and had to be adapted. So we had to improve the model of the PDEs and the values of the coefficients until we finally came up with the model that has been presented here. Because changing the model means changing the Jacobi matrices this is a hard work.

		channel		anode	
no.	var.	solution	error	solution	error
1	u_x	0.6733E+00	0.36E-02	0.2287E-01	0.76E-01
2	u_y	0.1749E-01	0.39E-01	0.1749E-01	0.91E-02
3	Y_{CH4}	0.3300E+00	0.19E-02	0.3300E+00	0.96E-02
4	Y_{CO}	0.2022E+00	0.15E-01	0.2022E+00	0.42E-01
5	Y_{H_2}	0.5754E+00	0.64E-02	0.5752E+00	0.18E-01
6	Y_{CO_2}	0.8065E-01	0.82E-02	0.1269E+00	0.36E-01
7	Y_{H_2O}	0.6700E+00	0.89E-02	0.6700E+00	0.31E-01
8	p	0.1013E+06	0.11E-05	0.1082E+06	0.16E-02

 Table 21: Maxima of the solution components and of the relative global error estimates for the computation with the 2 mm anode.

The numerical experiments showed that the SOFC PDEs are very critical because of their extreme non-linearity which can be seen by the complicated Jacobian matrices. We computed solutions for 3 different thicknesses d_A of the anode, 0.05, 1 and 2 mm. We could get the solution for 2 mm only by computing the solution for 0.05 mm, using this as starting solution for 1 mm and this solution as starting solution for 2 mm. When we used the entry values of x = 0 for the variables as starting values, the Newton iteration diverged. We used the consistency order q = 4. With the order q = 2 we got errors 10 to 100 times larger. When we used the order q = 6, the Newton iteration diverged, even with the solution of order 4 as initial solution. We used a grid of 80 nodes in the x-direction. When we used for accuracy tests a grid of 160 nodes we could get the solution of order 4. These experiences illustrate how critical the SOFC PDEs are.

The results that we present below were computed on the HP XC6000 parallel supercomputer of the University of Karlsruhe. The processors are Intel Itanium2 processors with 1.5 GHz. We computed with 8 processors in parallel. The grid was 80 nodes in x-direction and 41 nodes in y-direction in the channel and 41 nodes in the anode. We computed with consistency order 4. We will present below the results for the anode with $d_A = 2$ mm, $\varepsilon/\tau = 0.21$, $R_{ohm} = 1.63 \cdot 10^{-6}$, see the section "Parameter Variation" in Part II. We used as starting values the solution for $d_A = 1$ mm and needed 4 Newton iterations. The execution time on the master processor 1 was 510 sec, of which are needed 508 sec by the linear solver LINSOL. As we have 80×82 nodes and 8 unknowns per node, the number of unknows was 52480.

In Table 21 the maxima of the solution components and the maxima of the estimated relative global errors are compiled for channel and anode. Before we will discuss these numbers we look at the result plots in Figs. 28–59. These figures are in grayscale in the printed version of the report, but they are in colour in the on-line version. Therefore you should look at these figures at the computer screen.

We discuss at first the results for the channel, Figs. 28–43. Our discussion is purely

about the numerical behaviour. The physical behaviour is discussed in Part II. The plot for u_x , Fig. 28, shows that in the middle of the channel u_x grows from the entry value of 0.5 m/s to its maximal value 0.67, see Table 21, and then goes down again. The error plot, Fig. 29, shows that the maximal relative error of 0.36E-2 or 0.36% occurs in a small region at the exit. Except this region the error is much smaller. The plot of u_{i} , Fig. 30, shows that the maximal value of 0.017 m/s, Table 21, occurs close to the entry in the upper part which results from the influence of the anode, see Fig. 46. The error plot, Fig. 31, shows a small error below 1%, the max. error of 1.7% of Table 21 is not visible and obviously occurs in a very small region at the exit of the channel. The plots for the chemical components, Figs. 32–41, speak for themselves. It is interesting to see that Y_{CH_4} and Y_{H_2O} drop quite fast from their entry values to lower values by the chemical reactions of the reforming process. The errors of the Y's are quite small, their maximal values occur either in the entry or in the exit region of the channel. The pressure is shown in Fig. 42, you can see in the scale to the right of the plot that the change from entry to exit is only in the 5^{th} digit, this is in the range of the discretization error whose max. value is 0.11E-5 from Table 21. Therefore the error plot, Fig. 43, looks a little weird, but this comes only from the smallness of the error.

Now we want to discuss shortly the results for the anode, Figs. 44–59. The velocity components u_x and u_y are small. The maximal error of u_x of 7.6%, the largest error that occurs in Table 21, is practically not visible in Fig. 45 because it occurs obviously just at the entry. This indicates that there is a singularity or an incompatibility in the BCs at the entry of the anode. The second largest error in Table 21 occurs in the anode for Y_{CO} . Fig. 51 shows that this error occurs in a small region at the exit of the anode, indicating a singularity or incompatibility in the BCs at the entry or exit of the anode. Also for the other Y's the max. errors occur in very small regions at the entry or exit of the anode. The variation of the pressure in the anode, Fig. 58, is much larger than in the channel and is surely caused by the diffusion process of the chemical species.

From the numerical point of view these results are very convincing by the small estimates of the errors. The system of the SOFC PDEs is strongly non-linear and numerically very critical, and it is solved on a coupled domain with different PDEs in channel and anode. How should we trust our solution without the error estimate?



Figure 28: Contour plot of velocity u_x [m/s] in the channel.



Figure 29: Contour plot of the global relative error of u_x in the channel.



Figure 30: Contour plot of velocity u_y [m/s] in the channel.



Figure 31: Contour plot of the global relative error of u_y in the channel.



Figure 32: Contour plot of mole fraction Y_{CH_4} in the channel.



Figure 33: Contour plot of the global relative error of Y_{CH_4} in the channel.



Figure 34: Contour plot of mole fraction Y_{CO} in the channel.



Figure 35: Contour plot of the global relative error of Y_{CO} in the channel.



Figure 36: Contour plot of mole fraction Y_{H_2} in the channel.



Figure 37: Contour plot of the global relative error of Y_{H_2} in the channel.



Figure 38: Contour plot of mole fraction Y_{CO_2} in the channel.



Figure 39: Contour plot of the global relative error of Y_{CO_2} in the channel.



Figure 40: Contour plot of mole fraction Y_{H_2O} in the channel.



Figure 41: Contour plot of the global relative error of Y_{H_2O} in the channel.



Figure 42: Contour plot of pressure p [Pa] in the channel.



Figure 43: Contour plot of the global relative error of p in the channel.



Figure 44: Contour plot of velocity u_x [m/s] in the anode.



Figure 45: Contour plot of the global relative error of u_x in the anode.



Figure 46: Contour plot of velocity u_y [m/s] in the anode.



Figure 47: Contour plot of the global relative error of u_y in the anode.



Figure 48: Contour plot of mole fraction Y_{CH_4} in the anode.



Figure 49: Contour plot of the global relative error of Y_{CH_4} in the anode.



Figure 50: Contour plot of mole fraction Y_{CO} in the anode.



Figure 51: Contour plot of the global relative error of Y_{CO} in the anode.



Figure 52: Contour plot of mole fraction Y_{H_2} in the anode.



Figure 53: Contour plot of the global relative error of Y_{H_2} in the anode.



Figure 54: Contour plot of mole fraction Y_{CO_2} in the anode.



Figure 55: Contour plot of the global relative error of Y_{CO_2} in the anode.



Figure 56: Contour plot of mole fraction Y_{H_2O} in the anode.



Figure 57: Contour plot of the global relative error of Y_{H_2O} in the anode.



Figure 58: Contour plot of pressure p [Pa] in the anode.



Figure 59: Contour plot of the global relative error of p in the anode.



Figure 60: Current densities j, j_{CO} and j_{H_2} [A/m²], $j_{mean} = 6860.67$.

Channel	80:	80x41		x81
	max.	mean	max.	mean
u-x	3,6E-03	9,4E-04	9,1E-02	4,6E-03
u-y	2,6E-01	4,3E-03	1,1E+00	7,1E-03
Y-CH4	8,1E-04	5,0E-04	8,2E-04	4,2E-04
Y-CO	5,1E-03	1,2E-03	3,3E-02	8,5E-03
Y-H2	1,7E-03	6,3E-04	1,3E-02	5,4E-03
Y-CO2	3,8E-03	8,0E-04	2,0E-02	5,8E-03
Y-H2O	2,8E-03	6,6E-04	1,8E-02	6,0E-03
n	1.3E-06	8 0E-07	7 9E-06	5 2E-06

Anode	80x41		160x81	
	max.	mean	max.	mean
u-x	1,9E-01	2,9E-03	1,7E-01	1,4E-03
u-y	2,0E-02	3,3E-03	1,9E-02	3,6E-03
Y-CH4	7,8E-04	4,8E-04	8,2E-04	4,2E-04
Y-CO	6,1E-03	1,2E-03	3,3E-02	8,4E-03
Y-H2	1,7E-03	6,1E-04	1,3E-02	5,3E-03
Y-CO2	7,2E-03	7,7E-04	2,2E-02	5,9E-03
Y-H2O	4,0E-03	6,5E-04	1,8E-02	5,8E-03
р	4,0E-05	1,5E-05	9,6E-05	2,8E-05

Figure 61: Comparison of max. and mean error for grid 80×41 and 160×81 for channel and anode.

For the output of a SOFC the current densities at the interface of the anode to the electrolyte are an essential result. Fig. 60 shows the current densities j [A/m²], equ. II(74), j_{CO} , equ. II(68) and j_{H_2} , equ. II(67). We have also computed the arithmetic mean of j of the node values at boundary 2 which is $j_{mean} = 6860.67 \text{ A/m}^2$. For these quantities we cannot give error estimates as we did it for the PEMFC in Fig. 26, there the current density is named i. For the PEMFC i was a variable that had a meaning only at the reaction layer. If we needed error estimates for j_{CO} and j_{H_2} (j is trivial by equ. II(74)), we had to introduce them as variables that have a physical meaning only at the interface to the electrolyte, just as we did it for i in the PEMFC. However, this would increase the number of variables to 10. But as the entries in the formulas for the j's have errors in the 1% range, we can assume that the j's are accurate also in the 1% range.

As mentioned above the system of SOFC PDEs is numerically very critical and there is the suspicion of a hidden singularity or incompatibility of the BCs. If this would be the case the errors would grow if we use a finer grid because the singularity is better detected, or at least would not go down as expected from the consistency order q = 4. Halving the step size would theoretically reduce the error by a factor $(1/2)^4 = 1/16$ or roughly one order of magnitude. Therefore we computed the solution with a grid of 160×81 for the channel and for the anode and compared the errors to those of 80×41 . As we have seen in the (coloured) figures the error is usually small in the main part of the domain and gets larger values only in very small regions at the entry or exit. Therefore we investigated also the mean error, i.e. the arithmetic mean value of the errors in the domain. The max. and mean errors for grid 80×41 and 160×81 for channel and anode are depicted in Fig. 61. What can we learn from these 64 numbers? Where we have small max. errors, the mean error is not much smaller, so we have a "flat" error distribution. However, where we have large max. errors (compared to their neighbouring values), the mean error is by one to two orders of magnitude smaller, see the following examples in Fig. 61:

anode. $u_{a}: 1.9E-1 \rightarrow 2.9E-3$. $1.7E-1 \rightarrow 1.4E-3$.	channel,	u_y :	$2.6\text{E-1} \rightarrow 4.3\text{E-3},$	$1.1\text{E}0 \rightarrow 7.1\text{E-}3$,
	anode,	u_x :	$1.9\text{E-1} \rightarrow 2.9\text{E-3},$	$1.7\text{E-}1 \rightarrow 1.4\text{E-}3$	

This shows clearly that there are error "peaks" that indicate a singularity or incompatibility, presumably in the BCs. This is what the comparison of max. and mean error tells us.

Now we compare the errors of the two grids. Where we have large errors, e.g. for u_y in the channel, the max. and mean errors for the fine 160-grid are both larger than those of the coarser 80-grid. For u_y we have for max. and mean error:

 $2.6\text{E-1} \rightarrow 1.1\text{E0}, \quad 4.3\text{E-3} \rightarrow 7.1\text{E-3}$.

All max. errors go up from the 80-grid to the 160-grid except u_x , u_y in the anode. Also most of the mean errors go up from the 80-grid to the 160-grid. This shows that there is not the theoretically expected behaviour of an error reduction by a factor of 1/16. This confirms the assumption of a singularity/incompatibility in the system of PDEs and BCs and CCs. This needs further investigation of the problem. However, because the financial means were very short there was not the time to do this. Nevertheless we can trust our results for the 80-grid. This ends the discussion of numerical solution of the SOFC PDEs.

4 Concluding remarks

In chapter 1 we gave a short survey of the FDEM program package and its possibilities. The essential advantage of this exceptional black-box PDE solver is the error estimate. This is a unique feature. To our knowledge nobody else can solve such general nonlinear systems of PDEs with a reliable error estimate. FDEM is an unprecedented generalization of the FDM. As large technical problems make the use of large parallel supercomputers mandatory: Also in this respect the FDEM program package is exemplary because it is efficiently parallelized with MPI for shared and distributed memory parallel computers.

In Chapter 2 we report on a fruitful cooperation with the ZSW Ulm to solve the PDEs of PEMFCs. We solved several models with increasing complexity. Only if one solves the PDEs of a certain model numerically, the properties of the model come to light. Our partner, in this case ZSW, is responsible for the PDEs, we are responsible for the numerical solution. The partner will immediately ask us: How good is the solution, can I trust it? He takes it for granted, that we can solve his PDEs. But he expects also that we can tell him the quality of the solution. As the PEMFCs were rather critical, ZSW asked us for solutions on finer grids until they were satisfied with the errors. In chapter 2 we described how we implemented their most elaborate model in FDEM and we discussed the properties of the PDEs from the point of view of numerics.

In Chapter 3 we report about the numerical solution of the SOFC PDEs that were partly established and improved in a vital cooperation with the IWE of our university. The problem of SOFCs is rather complicated by the methane reforming process and hence there are many parameters in the system that must carefully be adapted to get useful solutions. So much of

the project time was used to tune the model. We report here on the implementation of the final model. Again the knowledge of the error of the numerical solution was an invaluable help that opened the eyes to us and to IWE. As in the PDEs are many "coefficients" that themselves depend in a multistage way on the variables, the generation and implementation of the Jacobian matrices that describe the dependency of the PDEs from the variables was a really hard task. The PDEs of the SOFC are numerically very critical as has been shown in Chapter 3.

For us the cooperation with the ZSW and IWE was extremely useful to demonstrate with practical industry-near problems the usefulness of FDEM and we want to thank the colleagues of these institutes for their engaged cooperation.

As it will be our task to demonstrate the usefulness of FDEM by possibly many examples, we are looking for further cooperation partners to solve in common research projects their problems. The problems may be any type of numerical simulation. If you are interested you may contact us.

References

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http://www.rz.uni-karlsruhe.de/rz/docs/FDEM/Literatur/fdem.pdf

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Remark: The on-line version of this report (with coloured figures) will be available at http://www.rz.uni-karlsruhe.de/rz/docs/FDEM/Literatur/fuelcells.pdf