European COMSOL Conference, Hannover, Germany 04.-06.11.2008

Modeling Polybenzimidazole/Phosphoric Acid Membrane Behaviour in a HTPEM Fuel Cell

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Outline of this oral presentation

Introduction:

- University of Duisburg-Essen / ZBT-Duisburg GmbH
- High temperature PEM fuel cell (HTPEM)
- Review: 2D HTPEM model (European COMSOL Conference 2007)
- Objectives of this 3D study

Modeling efforts:

- Computational subdomains
- Governing equations
- Boundary conditions

Computational methodology:

- Meshing
- Solver settings and solution procedures

Results:

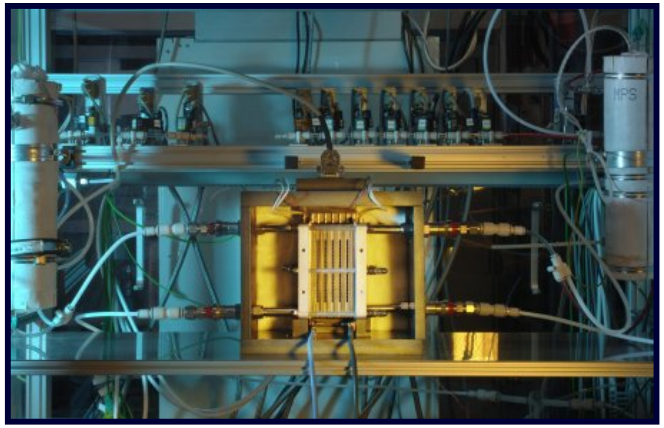
- Modeling base case operating conditions
- Experimental investigations
- Conclusion & outlook

University Duisburg-Essen: Hydrogen and fuel cell R&D since 1996

ZBT-Duisburg GmbH established in 2001

TAZ established in 2008

Hydrogen and fuel cell related activities in 7 divisions



Focusing the HTPEM technology:

- Bipolar-plate development
- Cell and stack design and operation
- System integration
- Theoretical analyses (e.g., modeling and simulation)

High temperature PEM fuel cell (HTPEM)

Fuel Cell - Device which electrochemically converts energy stored in a fuel and oxidant into electricity (e.g. oxygen/hydrogen half - cell reactions)

Some benefits of using higher operating temperatures:

- Reformate gas (higher CO-tolerance)
- No humidification (simplified system design)
- Faster reaction kinetics
- Simplified heat management

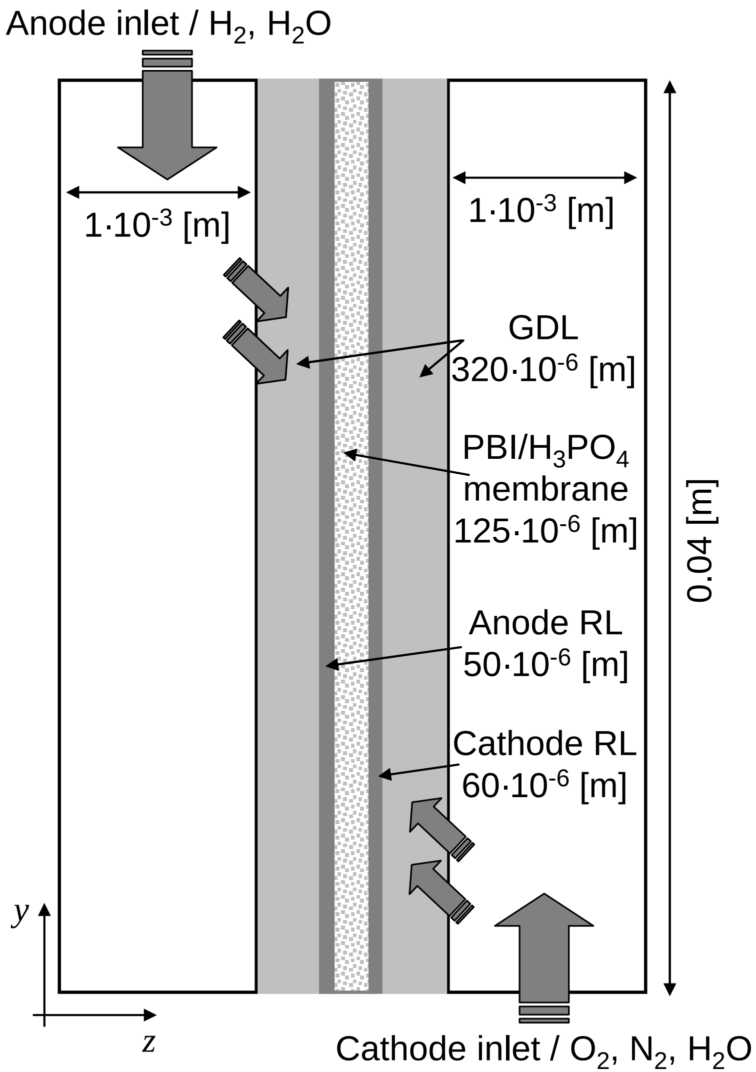
Objectives:

- Development a complete large scale 3D HTPEM model (including structural details)
- Model 'validation' with experimental investigations

Challenges:

- Only few CFD/FEM models available in open literature (*e.g. Cheddie et al., Peng et al., Korsgaard et al.*)
- (Relatively) new technology (some transport processes not fully understood yet)
- Only few material parameters available

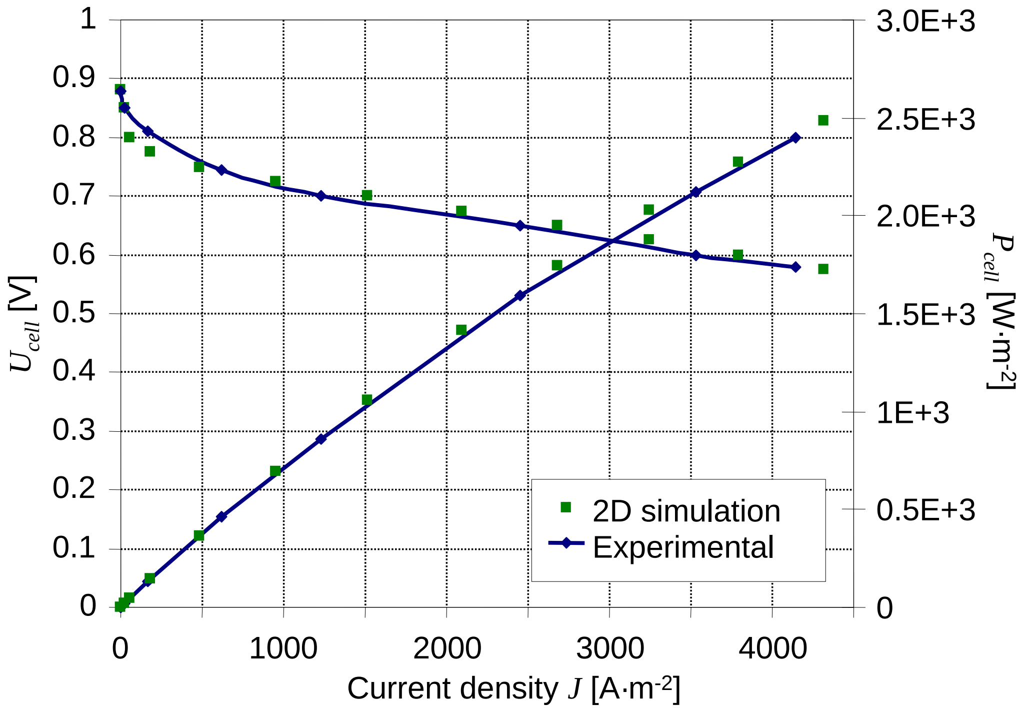
Review: 2D HTPEM (European COMSOL Conference 2007)*



- 2D 'along-the-channel' model
- All conservation laws included
- PBI/H_3PO_4 sol-gel membrane conductivity (empirical equation based on published results)

$$\sigma_m = k_{m,1} - k_{m,2} \cdot T_s^3 + k_{m,3} \cdot T_s^2 - k_{m,4} \cdot T_s$$

- Results



Siegel, C. et al., Proceedings of the European COMSOL Conference – Vol. 1, Numerical simulation of a high-temperature PEM (HTPEM) fuel cell, 428-434, Petit, J.-M., Squalli, O., Grenoble, France (2007)

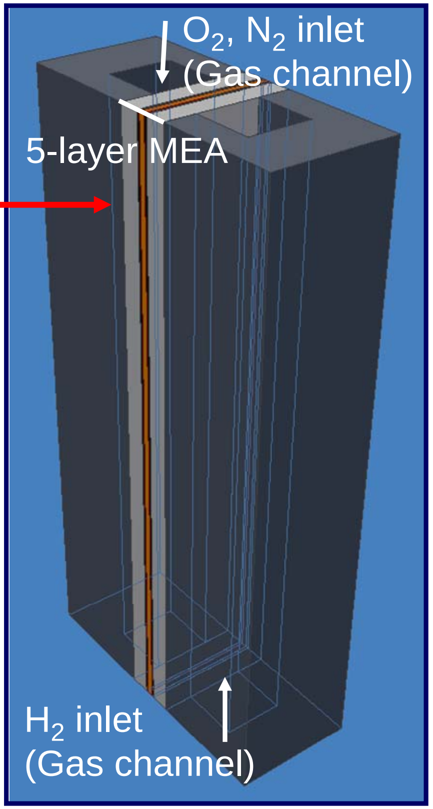
Objectives of this 3D study

- Development of a 3D HTPEM model including gas channels and bipolar-plates
- Enhancement of the already developed and presented 2D study
- All conservation equations (mass, momentum, energy, species, charge) included
- PBI/H_3PO_4 sol-gel membrane conductivity modeled using an Arrhenius equation
- Most physical and material properties updated according the latest publications in the field and personal communications
- More realistic view of HTPEM operation behaviour

Computational subdomains

3D model → extended to the third dimension (here x)

0.005 [m^2] MEA, 6 channel parallel serpentine flow-field (here LTPEM → same for higher temperatures)



Dimensions: 0.002 [m] by 0.003 [m] by 0.01 [m] (x, y, z)

Mass / momentum balance (u,P):

- Gas channel → Navier-Stokes
- Porous media → Brinkmann

Mass / species balance (ω_i):

- Gas channel and porous media → Stefan-Maxwell convection and diffusion

Charge balance (φ_i):

- Bipolar-plate, GDL, RL, PBI/H_3PO_4 sol-gel membrane → Conductive media DC

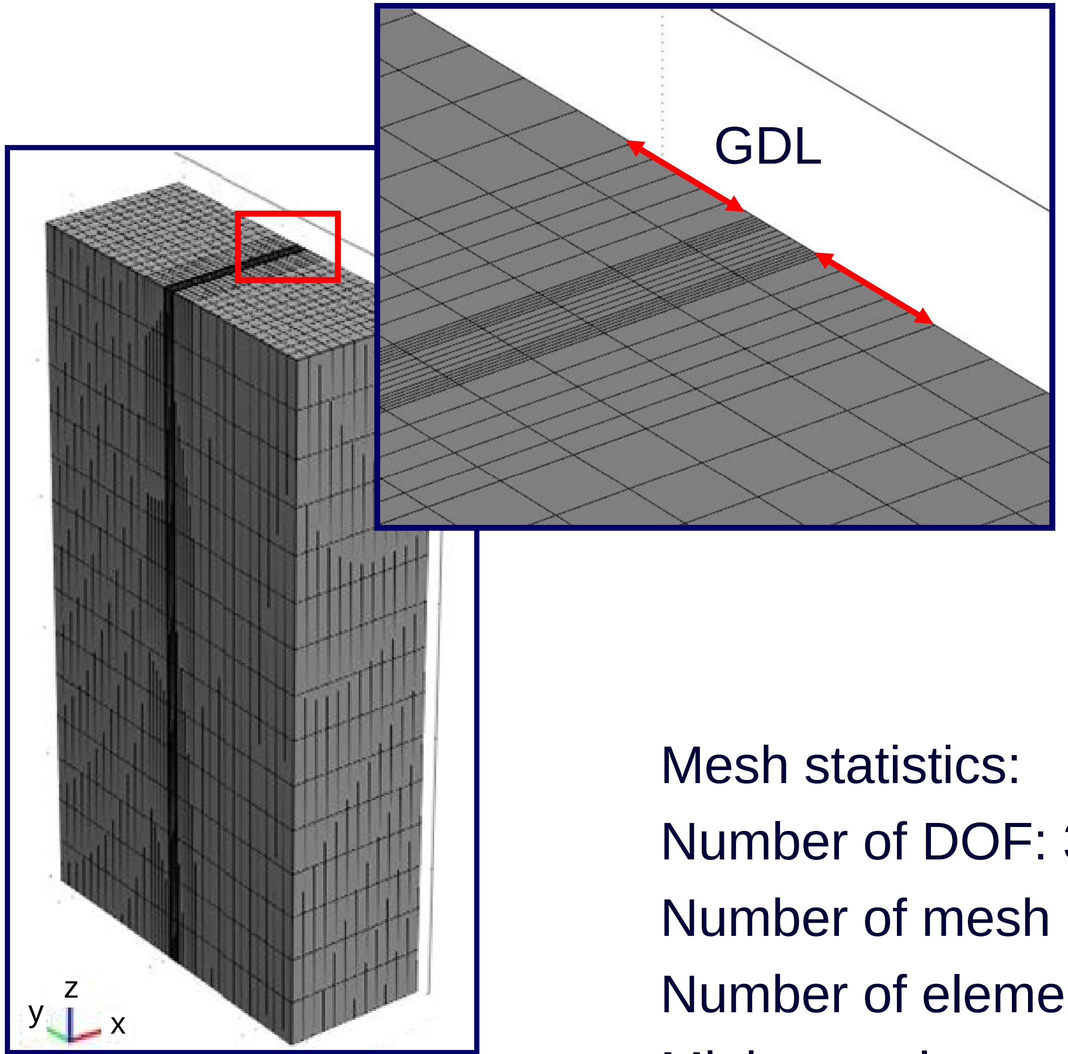
Mass / energy balance (T_i)

- Gas channel, bipolar-plate, GDL, RL, PBI/H_3PO_4 sol-gel membrane → Heat transfer

Boundary conditions

Boundary condition		*Note*	*Experimental data*
Gas flow and pressure	Velocity (inlet) – calculated $u_{i,in} = x_{i,in} \cdot \gamma_i \cdot J \cdot \frac{a_{MEA}}{a_{ch}} \cdot \frac{R \cdot T_f}{n \cdot F} \cdot \frac{1}{P_i}$ $L_e \cdot \nabla_t \cdot \left(P \cdot I - \eta \cdot \left(\nabla_t u + (\nabla_t u)^T\right)\right) = -\vec{n} \cdot P_{0,e}$ $\nabla_t u = 0$ Pressure (outlet) – measured $\eta \cdot \left(\nabla_t u + (\nabla_t u)^T\right) \cdot \vec{n} = 0$ $P = P_{0,out}$	Calculated Measured (ambient pressure)	St. A 1.35 St. C 2.5
Species	Mass fraction (inlet) Convective flux (outlet)	Gas composition Defined	0.25 %RH A 4 %RH C
Charge	Cell voltage (cathode) Reference potential (anode)	Defined	0.95-0.5 [V]
Solid phase temperature	Cell temperature	Defined (controlled)	150-180 [°C]
Fluid phase temperature	Gas temperature (inlet) Convective flux (outlet)	Measured	21 [°C]

Meshing



Structured mesh to reduce the number of degrees of freedom (DOF)

- GDL 5 elements in y
- RL 5 elements in y
- PBI/H_3PO_4 sol-gel membrane 4 elements in y
- Gas channel 6 x 6 x 14 elements in x, y and z

Mesh statistics:

Number of DOF: 378,139

Number of mesh points: 10,400

Number of elements: 8,820

Minimum element quality: 0.0178

Element volume ratio: 0.06

Solver settings and solution procedures

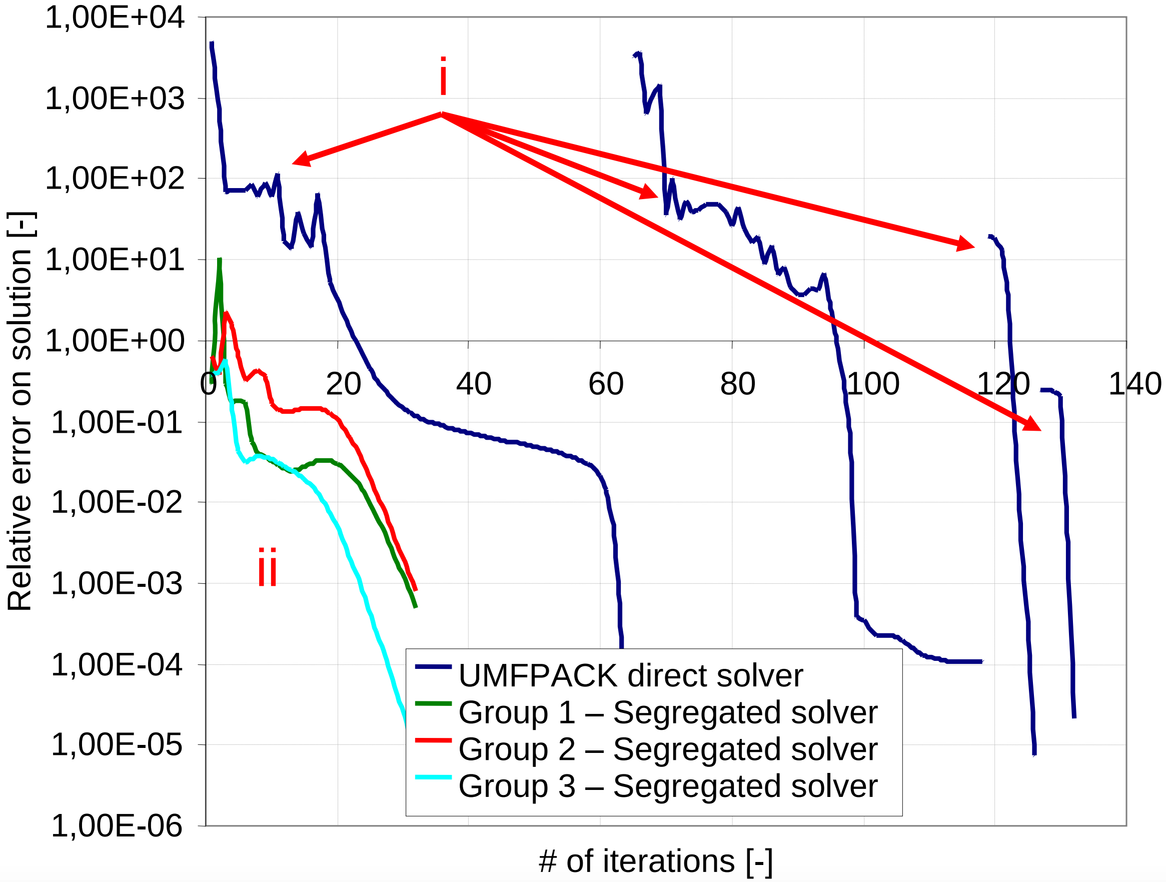
COMSOL MP 3.4 / Quad-core 8GB Ram

i) PARDISO direct solver (±9000 s)

$\varphi_i \rightarrow u, P \rightarrow \omega_i \rightarrow T_i$

ii) Segregated group solver (±4300 s)

$u, P \rightarrow \omega_i \rightarrow T_i, \varphi_i$



Details:

Artificial diffusion (streamline)

Problem solved sequentially using solver scripting

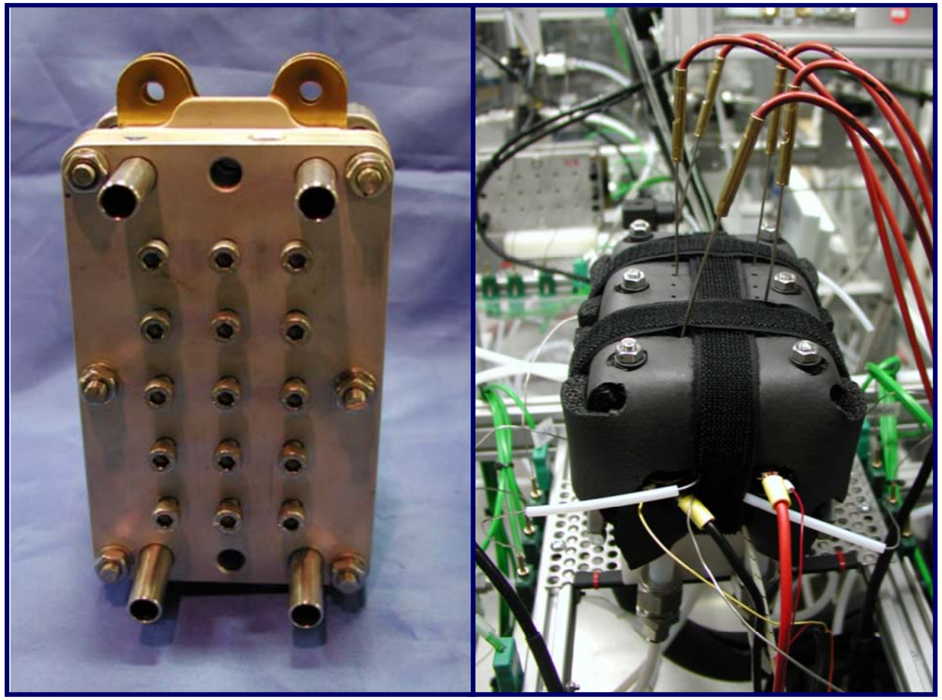
Initial conditions updated

Convergence criteria $1 \cdot 10^{-6}$

Experimental investigations

All tests performed at
the ZBT in Duisburg

Dedicated NI-LabVIEW controlled teststand for model 'validation'



Design:

• HTPEM single cell assembly (temperature controlled – heated aluminum endplate)

Bipolar-plates:

• Highly conductive (electrical and thermal) inhouse bipolar-plates (polyphenylene sulfide (PPS) based)*

• 6 channel parallel serpentine flow field (anode and cathode side)

Membrane electrode assembly:

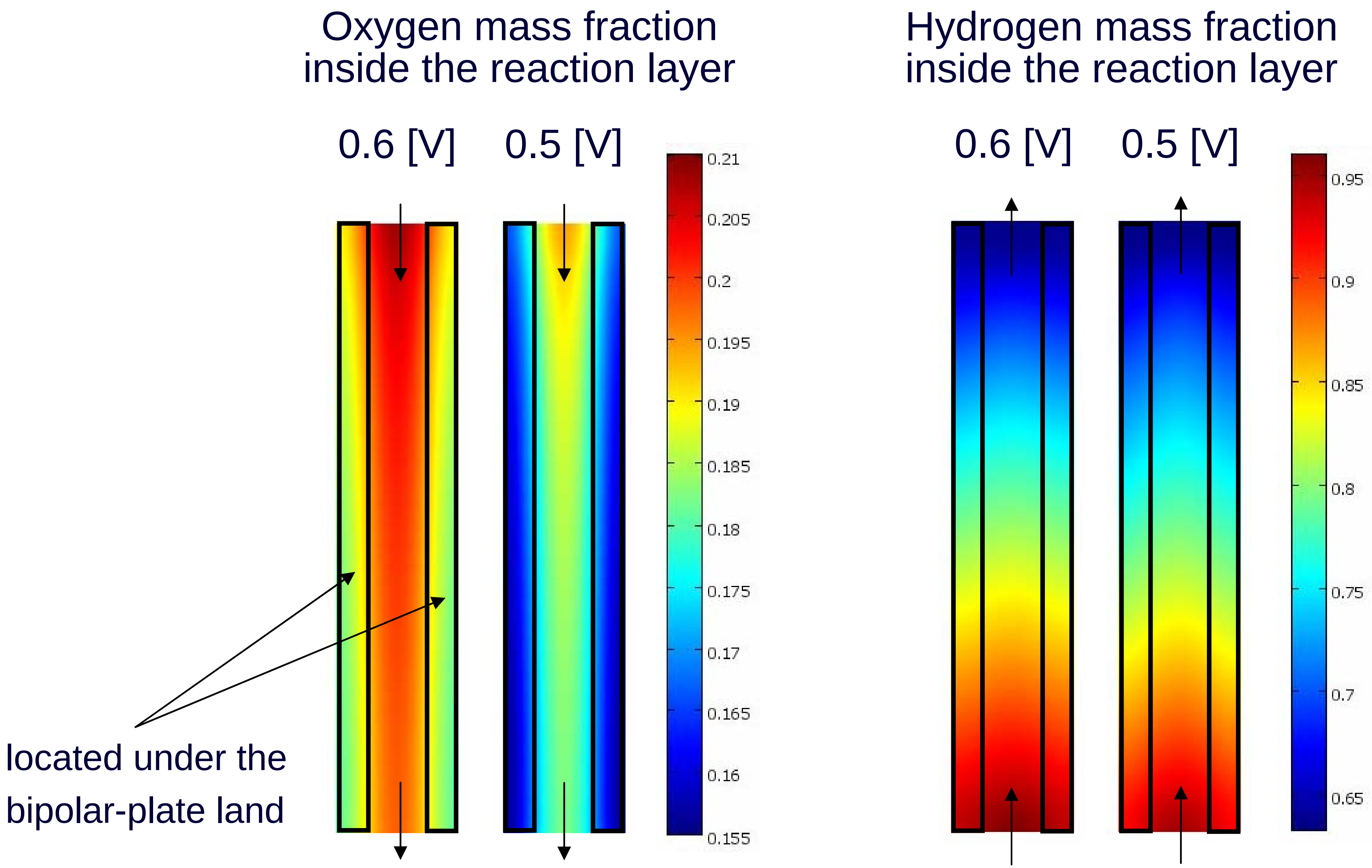
• Highly doped commercially available PBI/H_3PO_4 sol-gel membrane (0.005 [m^2])

• Similar to: GDL → E-tek (ELAT)

• Assumed loading 0.01 [$kg \cdot m^{-2}$] (anode) / 0.0075 [$kg \cdot m^{-2}$] (cathode) with a Pt/C-ratio of 0.3 [-]

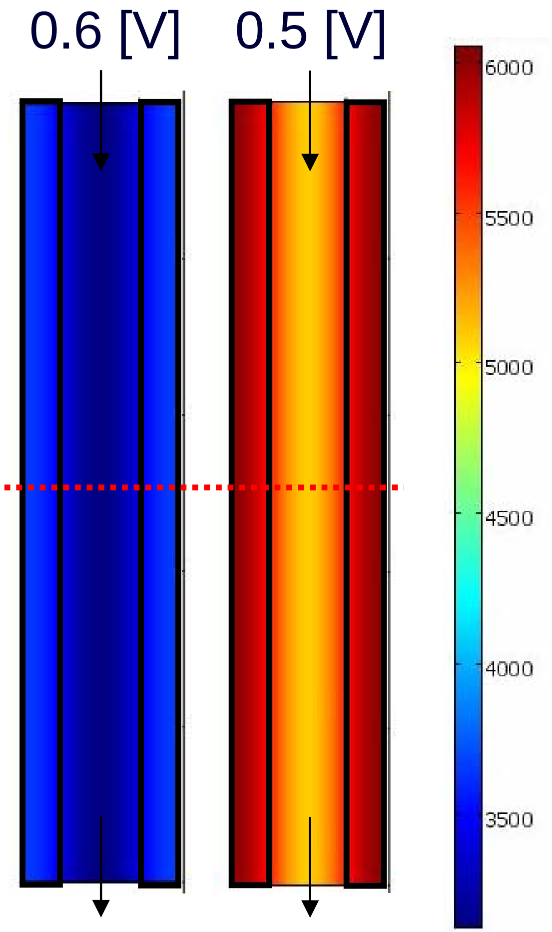
**Derieth, T. et al., Development of highly filled graphite compounds as bipolar plate material for low and high temperature PEM fuel cells, J. New Mat. Electrochem. Systems 11 (2008)*

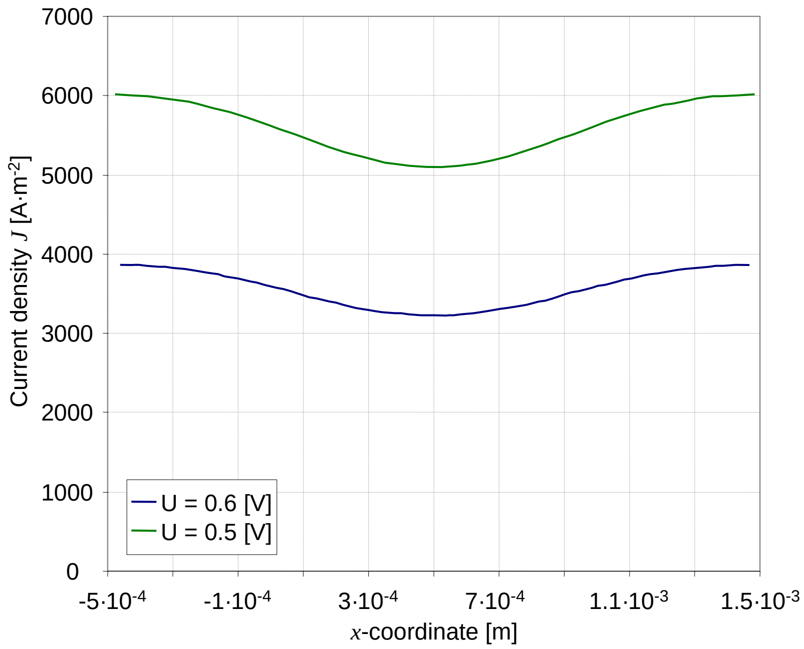
Results (mass/species balance) - Operating conditions 160°C

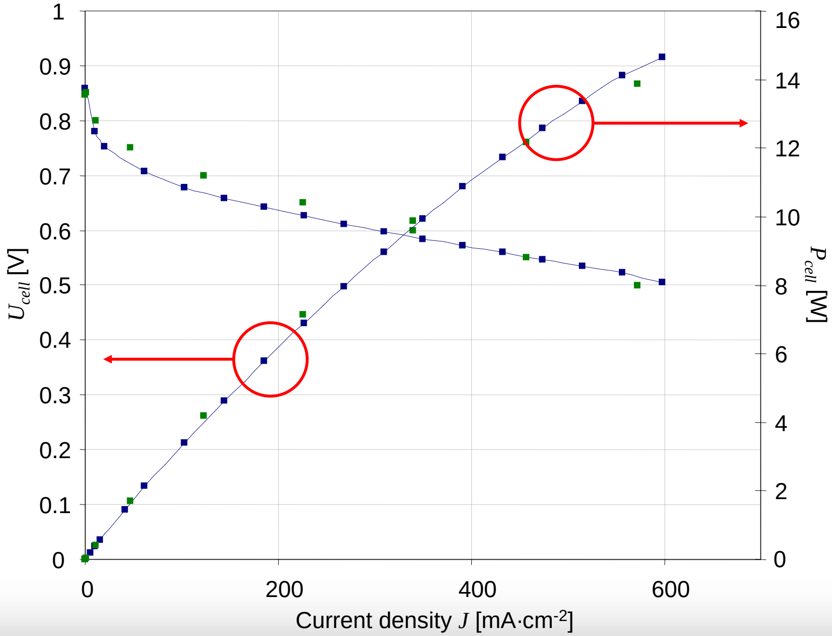


Results (charge balance) - Operating conditions 160°C

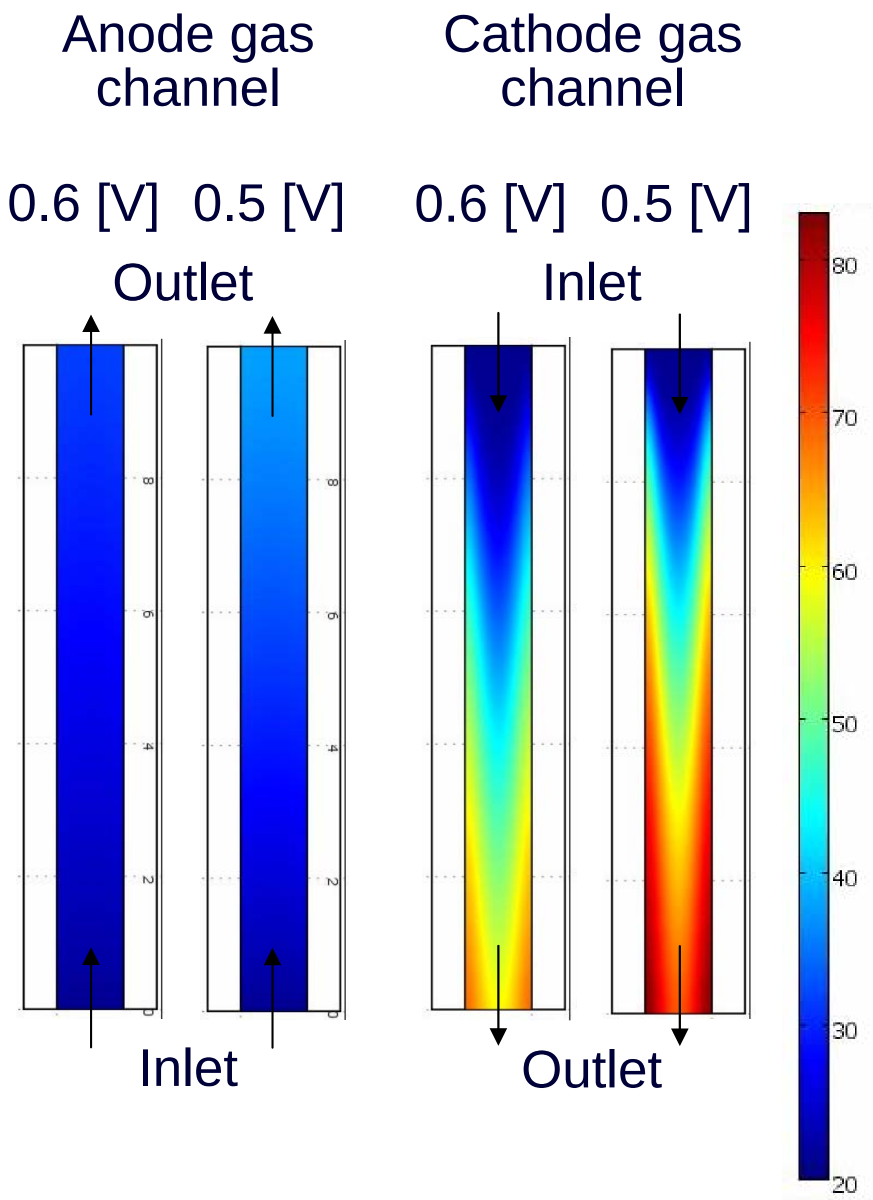
Current density distribution inside the reaction layer (cathode)



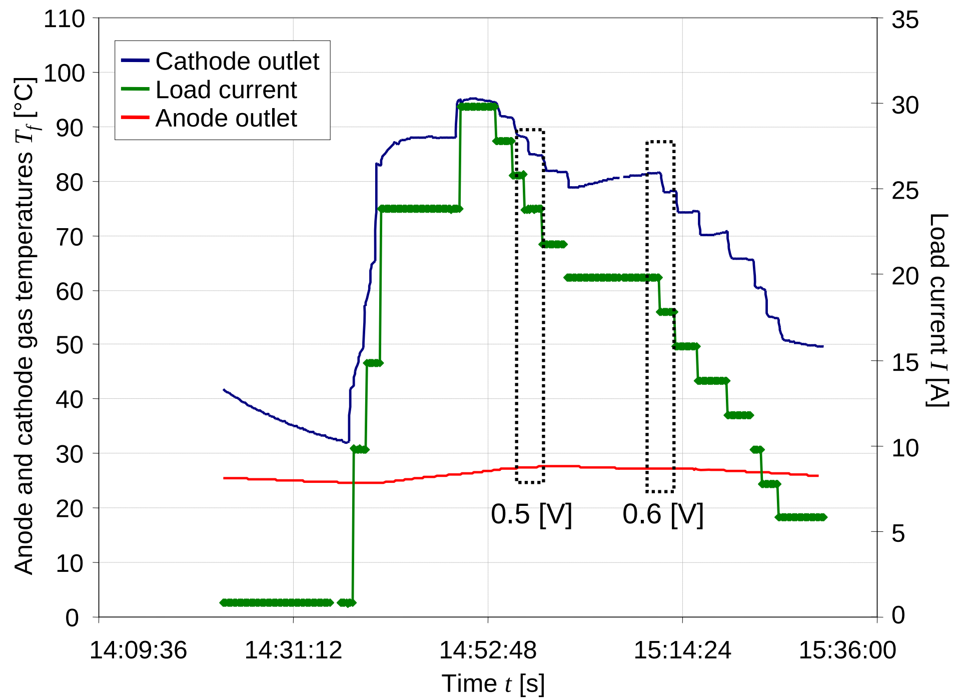




Results (energy balance) - Operating conditions 160°C



Measured gas outlet temperatures over different load currents



PBI/H_3PO_4 sol-gel membrane modeling

Conductivity dependent on H_3PO_4 doping level

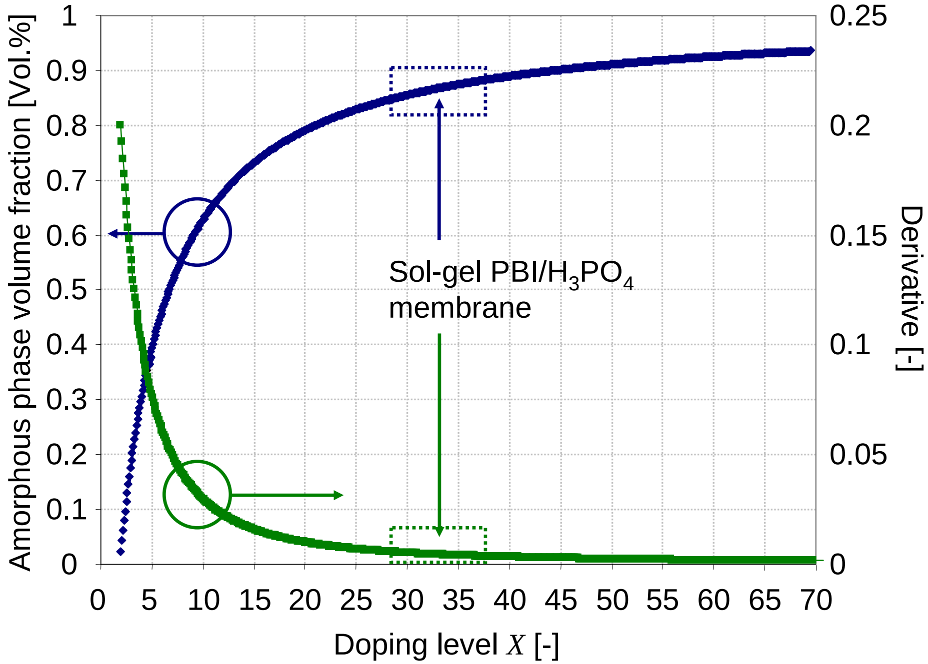
→ Number of H_3PO_4 molecules per PBI repeat unit

→ Here: Doping level X (and X-2) expressed using a density relation (similar to*)

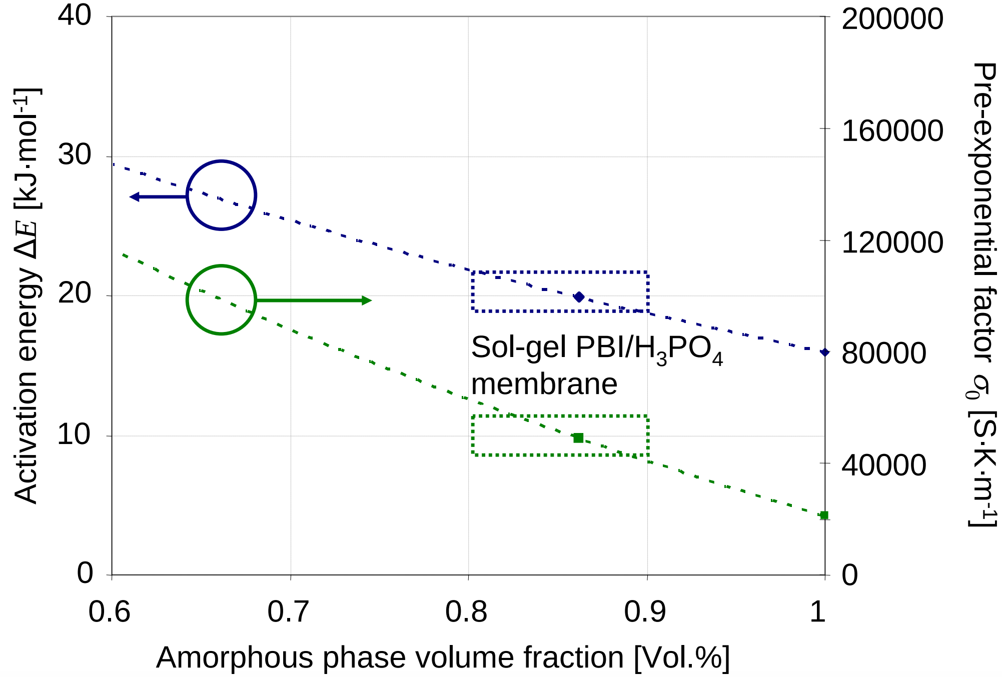
→ Amorphous phase volume fraction used to calculate (empirically) the

- Pre-exponential factor and

- Activation energy



$$\sigma_0, \Delta E = k_1 \cdot \ln(X) + k_2$$

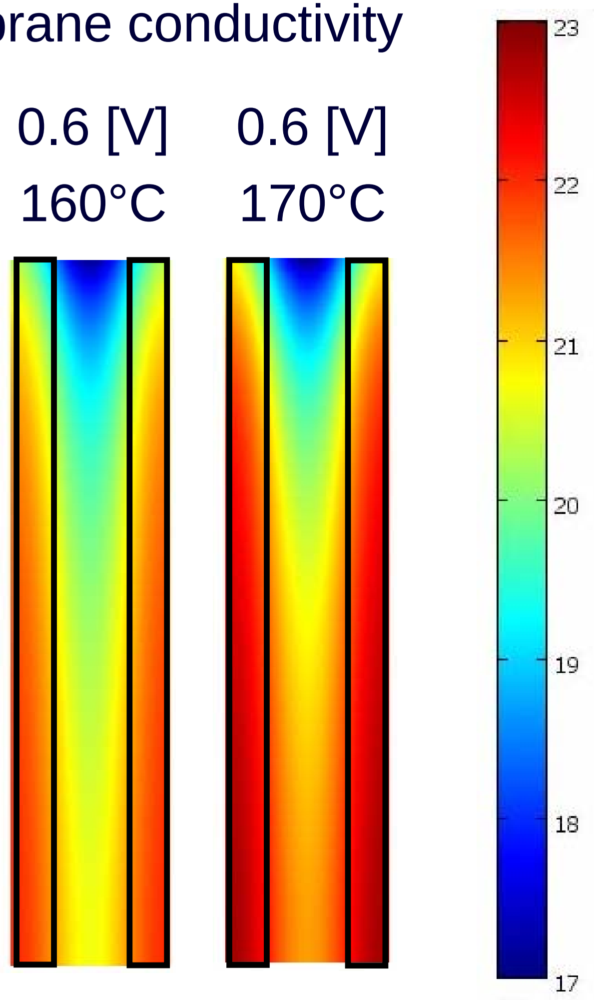


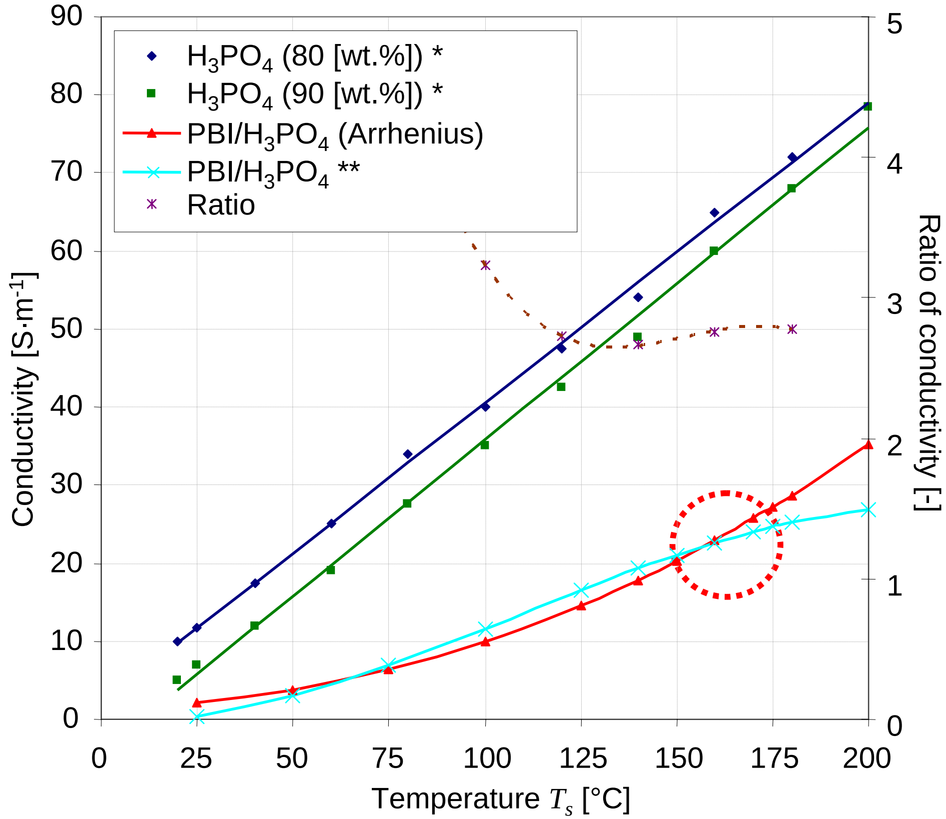
*Cheddie, D. et al., A two-phase model of an intermediate temperature PEM fuel cell, Int. J. of Hydrogen Energy 32 (2007)

Results (charge balance) - Operating conditions 160°C – 170°C

PBI/H_3PO_4 sol-gel membrane conductivity

0.6 [V] 160°C   0.6 [V] 170°C





$$\sigma_0 = \left(\frac{z^2 \cdot F^2}{R}\right) \cdot \alpha \cdot \upsilon_0 \cdot d^2 \cdot C \cdot e^{\frac{\Delta S + \Delta S_f}{R}} \qquad \sigma = \frac{\sigma_0(k_i, X)}{T_s} \cdot e^{\left(-\frac{\Delta E(k_i, X)}{R \cdot T_s}\right)}$$

$$r_{PBI/PA/H_3PO_4} = \frac{\sigma_{H_3PO_4}(85 wt.\%)}{\sigma_{PBI/H_3PO_4}} \approx 2.8 - 3.0$$

Xiao, L. et al., High-temperature polybenzimidazole fuel cell membranes via a sol-gel process, Chem. Mater. 17 (2005)

**Chin, D.T. et al., On the conductivity of phosphoric acid electrolyte, J. Appl. Electrochem., 19 (1989)*

Conclusion & outlook

Development of a 3D HTPEM model

→ Ameliorated PBI/H_3PO_4 sol-gel membrane model development and shortly discussed

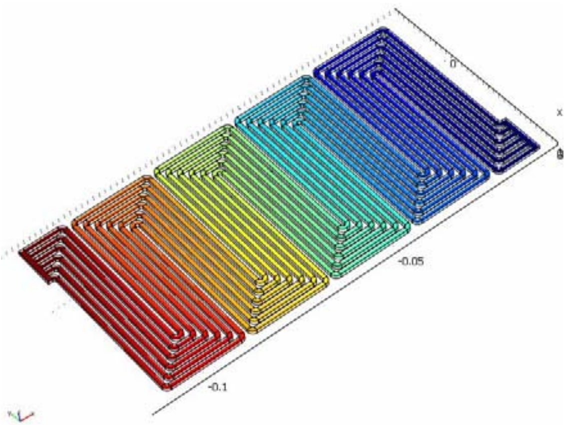
→ Detailed solid- and fluid-phase temperature investigations

→ Model not validated but rather compared with experimental data

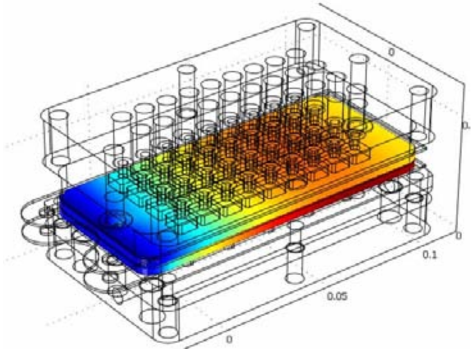
Further development of a complete HTPEM single fuel cell assembly model by our group

• Update material parameters (continuously)

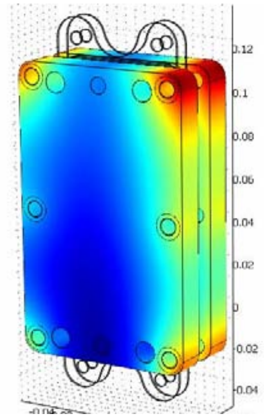
• Enhance electrochemical part of the model (e.g., agglomerate approach, H_3PO_4 distribution modeling?)



Large scale flow-field simulation (e.g., pressure losses)



Tempering concepts (e.g. bipolar-plate temperature distribution)



Structural aspects (e.g., overall displacement)

Thank you very much!

Questions, comments? Discussion!