



Weierstraß-Institut für Angewandte Analysis und Stochastik

New Links between Basic Research and Applied Energy R&D

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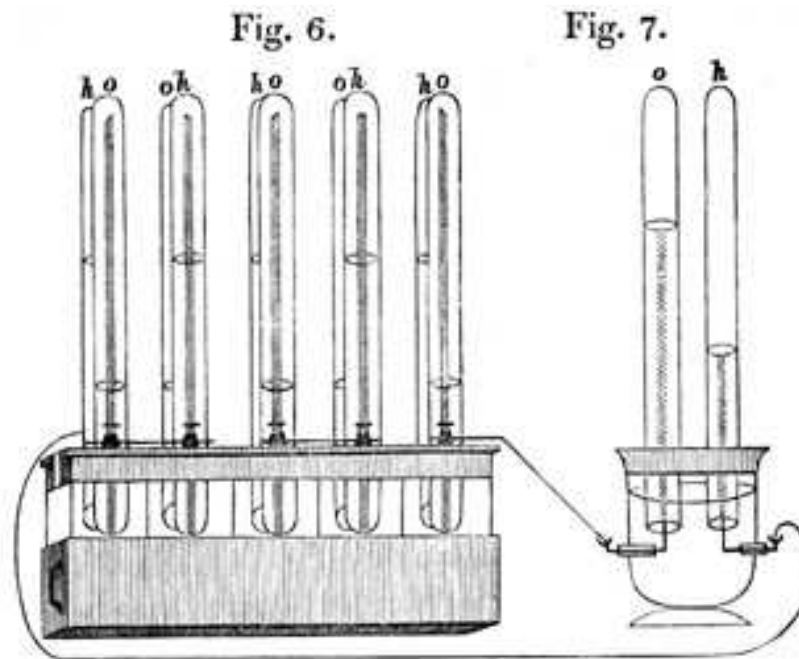
Mathematical Modeling of Direct Methanol Fuel Cells



Leibniz
Gemeinschaft

Fuel Cell Principle

- ▷ Like batteries and rechargeable batteries, **fuel cells** are sources of electrical power based on chemical reactions.
- ▷ Reactions split into two spatially separated steps connected internally by an **electrolyte** and externally by the **electrical circuit**.
- ▷ **Electrons** as intermediate products of these reactions are forced through electrical circuit.



W.R. Groves, 1840

Fuel Cell: Advantages and Classification

- ▷ Continuous mode of operation based on continuous fuel supply.
- ▷ Energy from fuels like hydrogen, natural gas/oil, biogas, **methanol**.
- ▷ Theoretical efficiency is higher than that of thermal engines.

- Main classification by type of electrolyte, e.g.:

- ▷ **PEMFC** (Polymer Electrolyte Membrane Fuel Cell)
Hydrogen (H_2 -PEMFC), Direct Methanol (DMFC) variants.
- ▷ **SOFC** (Solide Oxide Fuel Cell)
- ▷ **MCFC** (Molten Carbonate Fuel Cell)

Some Actual Fuel Cell Modeling Activities in Germany

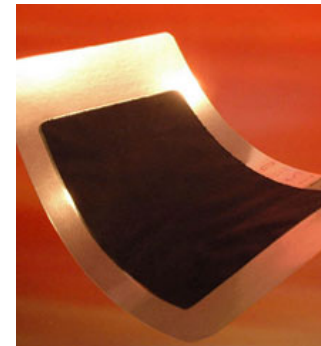
- ▷ **H_2 - PEMFC**: Fraunhofer ISE, Univ. Freiburg (Schumacher, Kröner/Ohlberger)
- ▷ **DMFC**: FZ Jülich, WIAS Berlin (Divisek, Fuhrmann/Gärtner)
- ▷ **SOFC**: FZ Jülich
- ▷ **MCFC**: MPI Magdeburg, Univ. Bayreuth (Heidebrecht/Sundmacher, Pesch)
- ▷ **DMFC/ H_2 -PEMFC Systems**: MPI Magdeburg (Sundmacher)
- ▷ **Membranes**: MPI Stuttgart/MPI Mainz (Kreuer/Meyer)

Direct Methanol Fuel Cells (DMFC)

Advantages

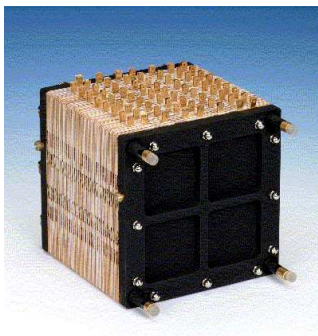
- ▷ Low working temperature – no material problems due to thermal expansion
- ▷ Easy handling of storage and supply of fuel – especially in comparison to H_2
- ▷ Options to create methanol from renewable sources (biogas, syngas from biomass)

- ▷ **Membrane-Electrode Assembly (MEA)**: core unit consisting of PEM, catalyst layers, porous gas diffusion layers (GDL), contact plate.



PEM+GDL

Gore Associates



Stack

FZ Jülich

- ▷ **Fuel Cell Stack**: MEAs connected together.
- ▷ **Fuel Cell System**: Stack combined with tanks, pumps, exhausts and control systems.

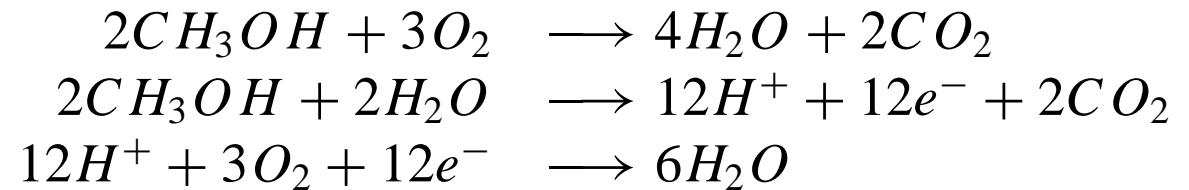
Scales of a Fuel Cell System

- ▷ **Molecular:** Transport mechanisms in membrane, catalytic reactions
- ▷ **Pore space:** simultaneous transport of liquids and gases
- ▷ **MEA:** coupled transport, reaction, conduction processes
- ▷ **Stack:** upscaled MEA processes, heat management
- ▷ **System:** summary models for stack, control facilities

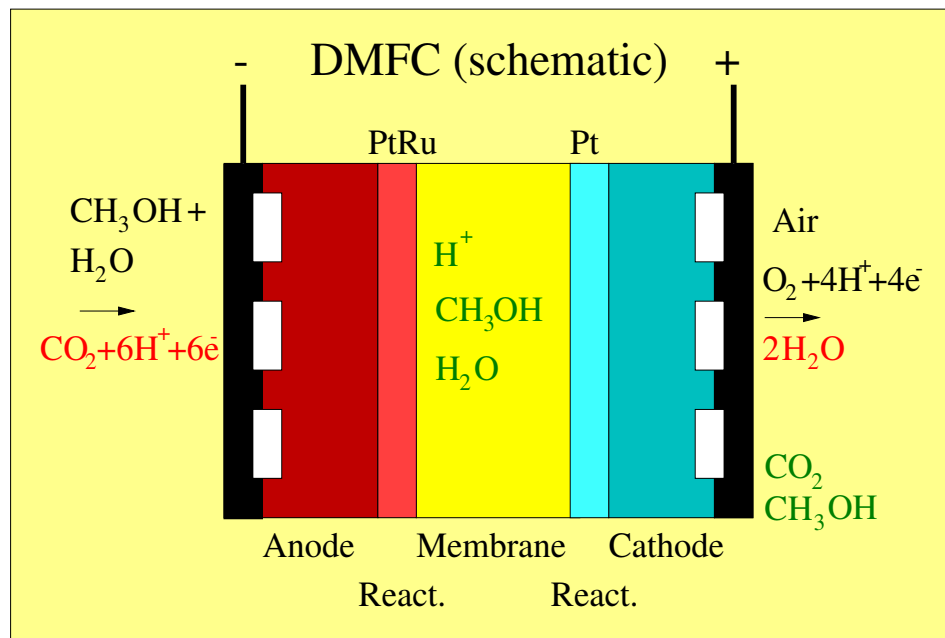
Optimal system \iff optimal materials and design on all scales.

DMFC: Membrane-Electrode Assembly (MEA)

- ▷ In presence of catalyst (Pt, Ru), methanol combustion reaction is split into *anodic part* and *cathodic part*



- ▷ Spatial separation by proton (H^+) conducting polymer membrane



	Anode	Cathode
Supply	methanol, H_2O	O_2 /Air, e^- , H^+
Return	CO_2 , e^- , H^+	H_2O

Physical processes in the DMFC MEA

- ▷ Two-phase flow (Water/Gas).
- ▷ Transport of electrical charge carriers.
- ▷ Catalytic reactions.
- ▷ Flow of a gas mixture (Stefan-Maxwell diffusion).
- ▷ Transport of dissolved species (Methanol, CO_2 in water).
- ▷ Charge and mass transport through PEM.
- ▷ Evaporation, condensation and dissolution reactions.
- ▷ Energy balance.

Mathematical modeling allows to combine all these processes into one model.

Mathematical/Numerical Model of a DMFC MEA

Cooperation WIAS - Forschungszentrum Jülich (J. Divisek, R. Jung).

1D/2D/3D- Numerical model of a DMFC MEA including all the processes described above.

- ▷ MEA processes taken into account in temporal and spatial resolution.
- ▷ 11 coupled nonlinear partial differential equations.
- ▷ 12 nonlinear algebraic equations per discretization node.
- ▷ Resolution of catalytic reaction chains.
- ▷ Two-phase flow model taking into account mixed wettability.
- ▷ Geometrical flexibility due to triangulation-based finite volume discretization.
- ▷ Numerical stability by appropriate upwinding.

J. Divisek, J.Fuhrmann, K. Gärtner and R. Jung: Performance Modeling of a Direct Methanol Fuel Cell, JES 2003

Model Unknowns & Equations

water pressure	p_w ,	temperature T ,
partial gas pressures	$p_1 \dots p_{n_{\text{gas}}}$	($O_2, CO_2, N_2, H_2O, CH_3OH$)
solute concentrations	$C_1 \dots C_{n_{\text{solute}}}$	(CO_2, CH_3OH)
potentials	$\varphi_{e^-}, \varphi_{H^+}$	

$$\partial_t \frac{\rho_w s_w \phi}{M_w} - \nabla \cdot \frac{\rho_w k_f k_{rw}}{M_w \mu_w} (\nabla p_w + n_{\text{drag}} \mathbb{N}_{H^+}) = R_w^{\text{evap}} + R_w^{\text{chem}}$$

$$\partial_t \left(\phi s_g \frac{p_i}{RT} \right) - \nabla \cdot k_{rg} \sum_{j=1}^{n_{\text{gas}}} D_{ij}^{SM} (p_1, \dots, p_{n_{\text{gas}}}) \nabla p_j = R_{\text{gas},i}^{\text{chem}} + R_{\text{gas},i}^{\text{evap}} \quad i = 1, \dots, n_{\text{gas}}$$

$$\partial_t (\phi C_i s_w) - \nabla \cdot \left(D_i^d \phi s_w \nabla C_i + C_i \frac{M_w}{\rho_w} \mathbb{N}_w \right) = R_{\text{solute},i}^{\text{chem}} + R_{\text{solute},i}^{\text{evap}} \quad i = 1, \dots, n_{\text{solute}}$$

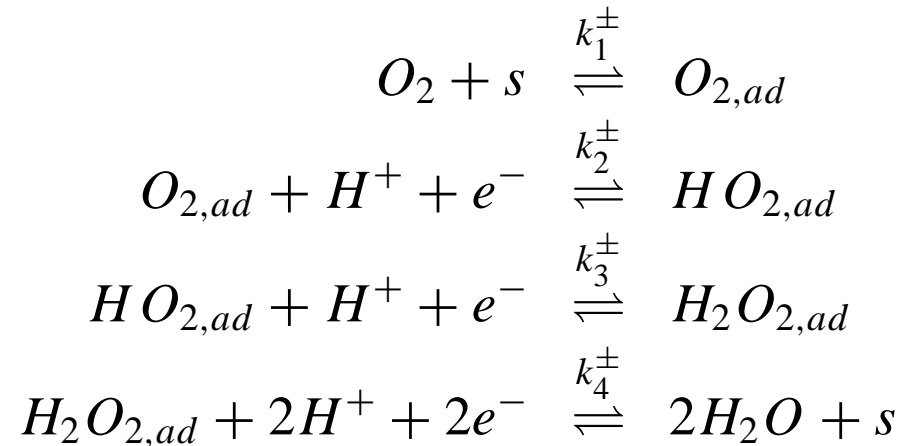
$$-\nabla \cdot \frac{1}{F} \varepsilon_i^2 \sigma_i \nabla \varphi_i = R_{ei}^{\text{chem}} \quad i = e^-, H^+$$

$$\partial_t (\rho_s c_s T) - \nabla \cdot \left(\bar{\lambda}_s(T) \nabla T + T \sum_{i=1}^N c_i M_i \mathbb{N}_i \right) = R_{Temp}$$

\mathbb{N}_i : molar flux of species i ; $s_w = s_w (\sum p_i - p_w)$: water saturation; $s_g = 1 - s_w$

Oxygen Reaction Chain

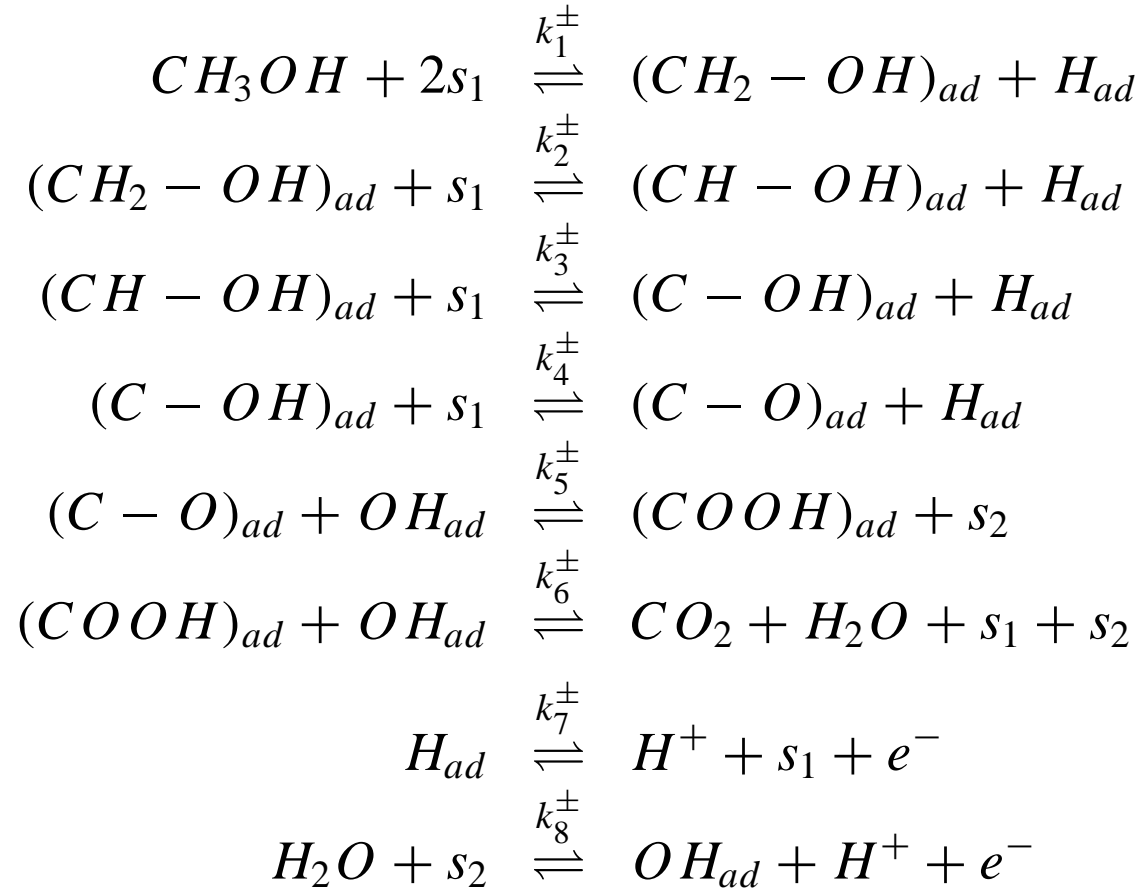
The oxygen reaction at the cathode is split into several steps of a catalytic reaction.
 s – Pt site, \cdot_{ad} – adsorbed species.



Methanol Reaction Chain

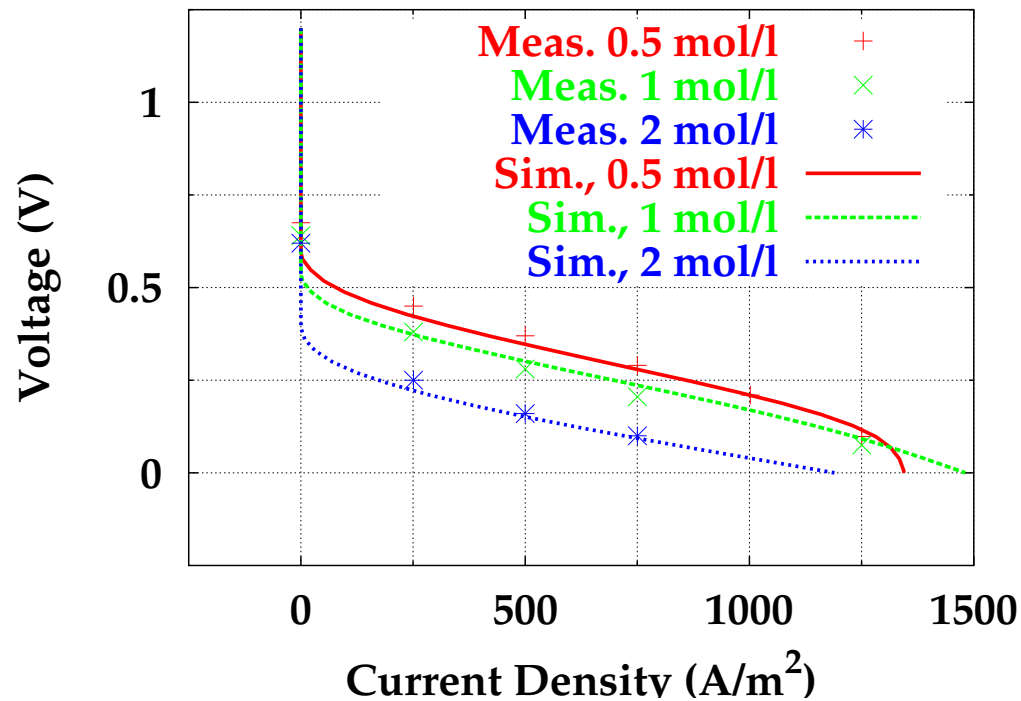
The methanol reactions at anode and cathode are split into several steps.

s_1 : Pt site; s_2 : Ru site; \cdot_{ad} : adsorbed species.



DMFC: Model vs. Experiment

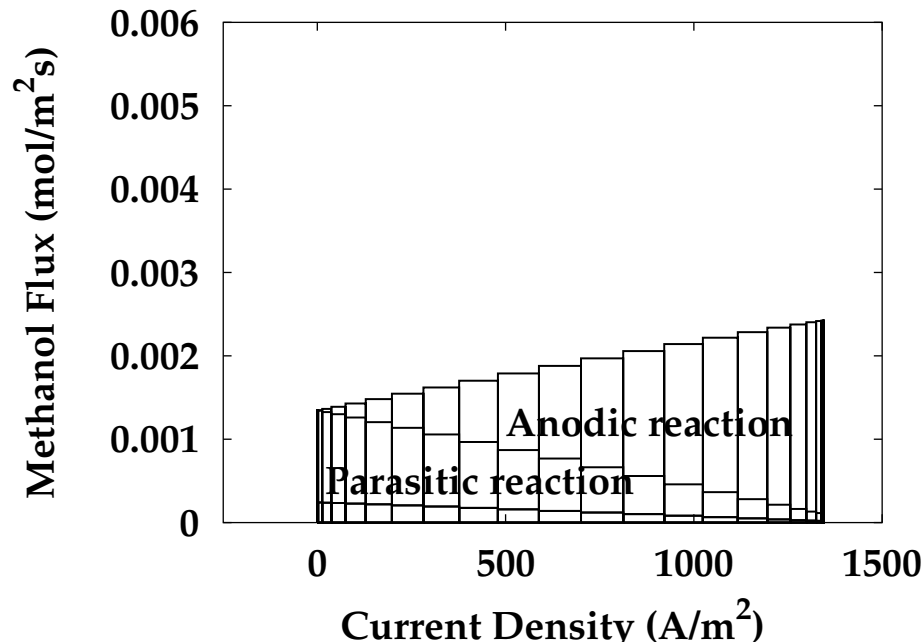
Data taken from experimental setup and literature. 5 of the least reliable parameters fitted.



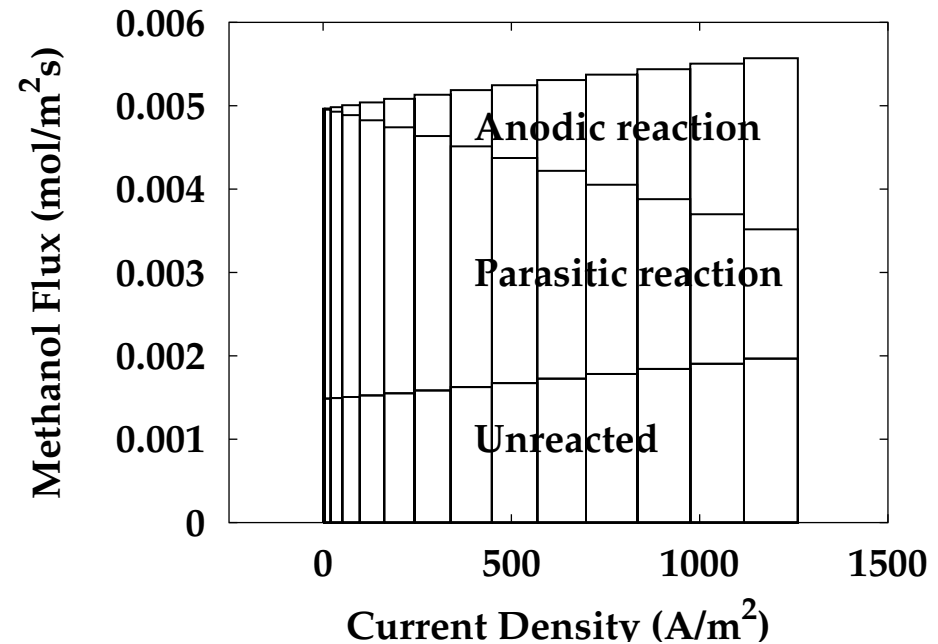
Measured and calculated polarization curves at 60°C. Performance is better for lower methanol concentration ... why ?

Methanol Balance

0.5 mol/l methanol concentration



2 mol/l methanol concentration



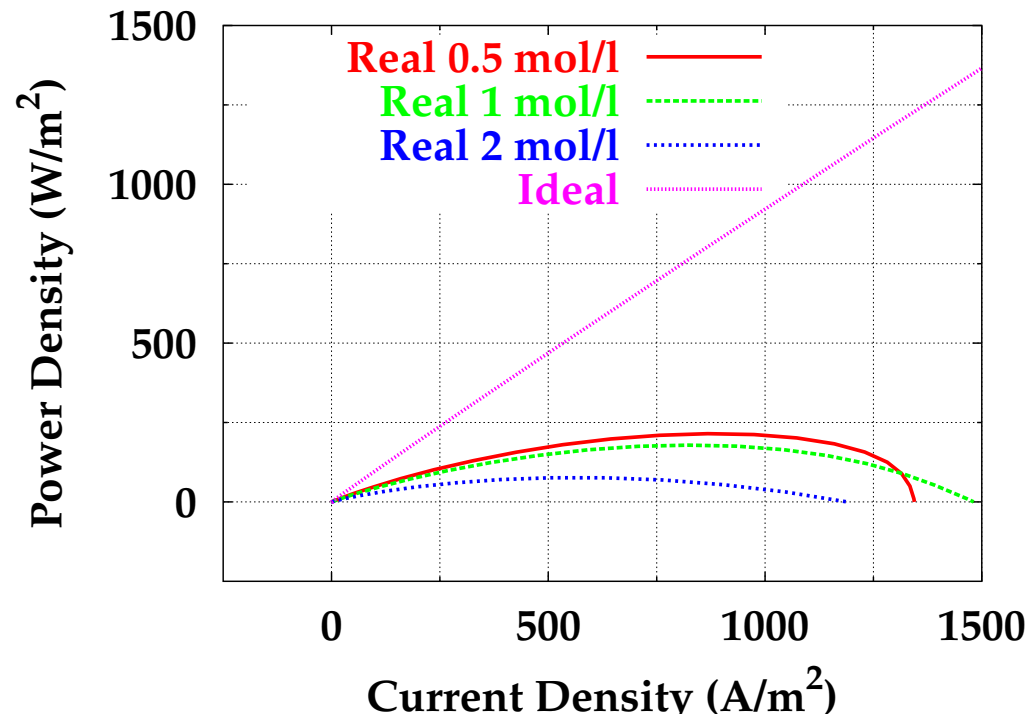
PEM not impermeable for methanol \implies methanol crossover

\implies part of anodic reaction takes place as parasitic reaction at cathode

\implies decrease in performance and efficiency

\implies Need membranes with improved H^+ -ion conductivity/methanol permeability ratio

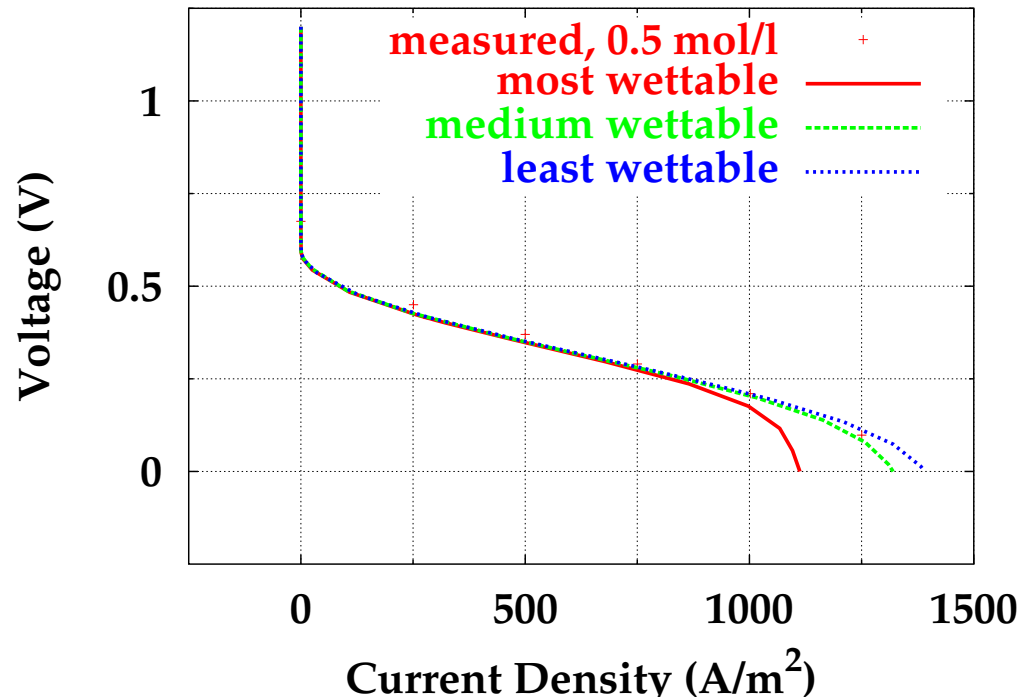
Ideal vs. Real DMFC



- ▷ Hypothetic ideal DMFC would have neither parasitic reactions nor transport inhibitions.
- ▷ Simulation unveils potential of development of better materials and designs.

Mixed Wettability of the Pore Space

Competing transport of gases and water \implies pore space of the GDL is admixed with teflon.



Polarization curves in dependence on wettability (inverse proportional to amount of teflon admixture) of cathode. Decrease of wettability

\implies improved O_2 transport

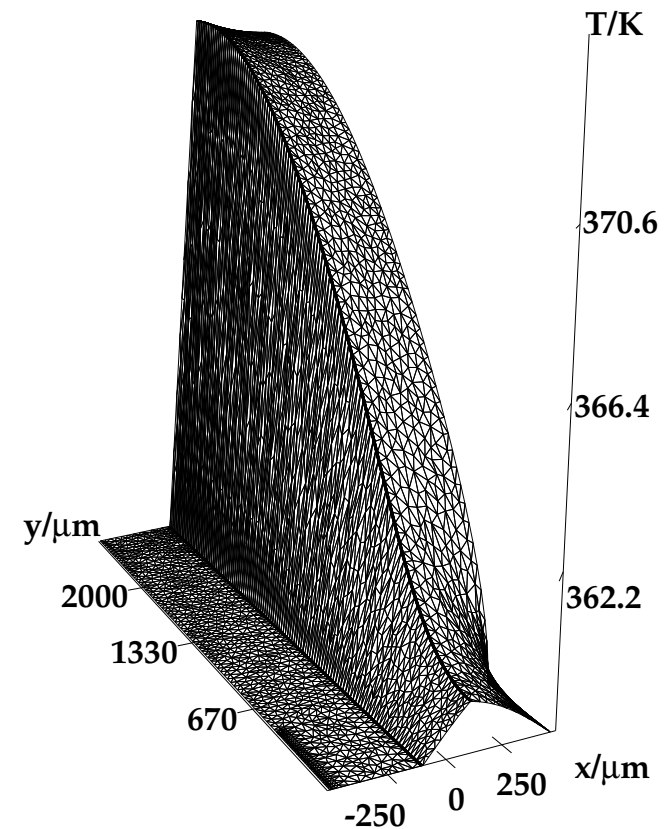
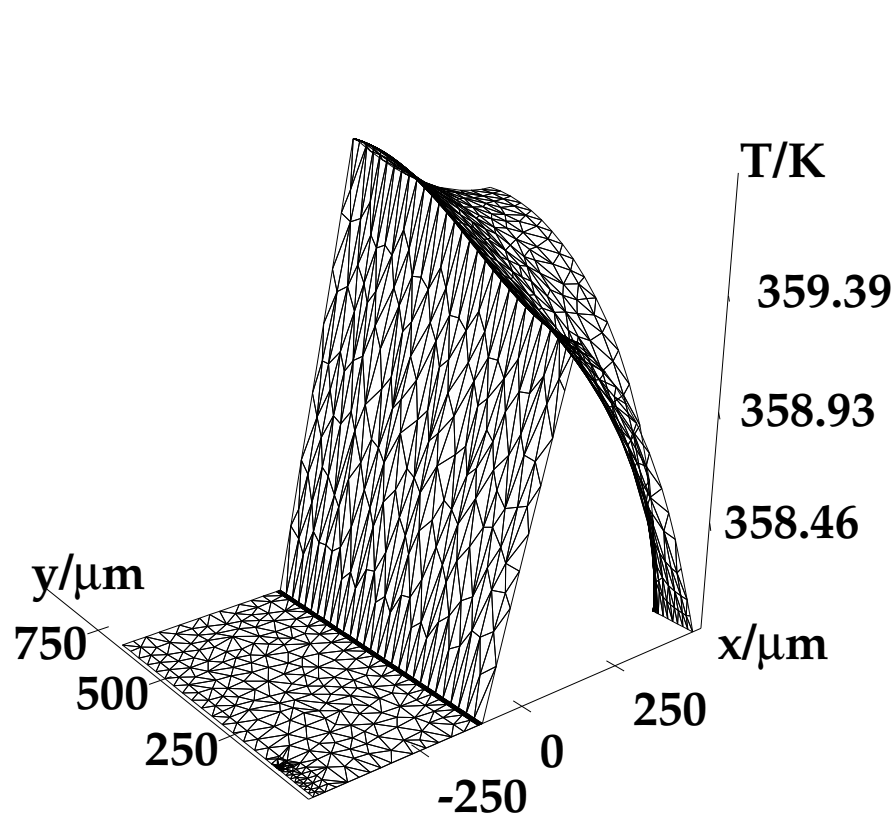
\implies increased power.

Interplay between Heat Management and Geometry

Electrical contacts and gas channels spatially separated

⇒ Ratio contact width/GDL thickness influences max. temperature in reaction zone

⇒ influence on reaction kinetics



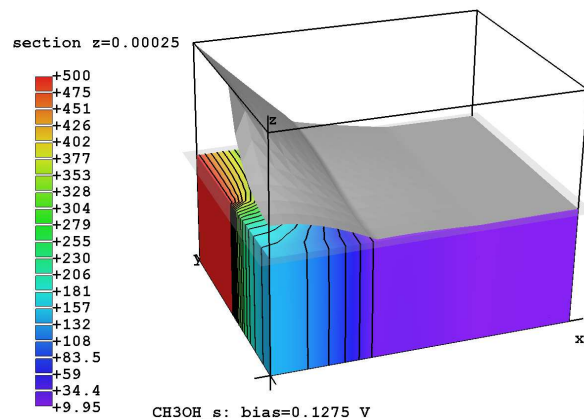
Small contact width / GDL thickness ratio.

4× increased ⇒ higher max. temperature.

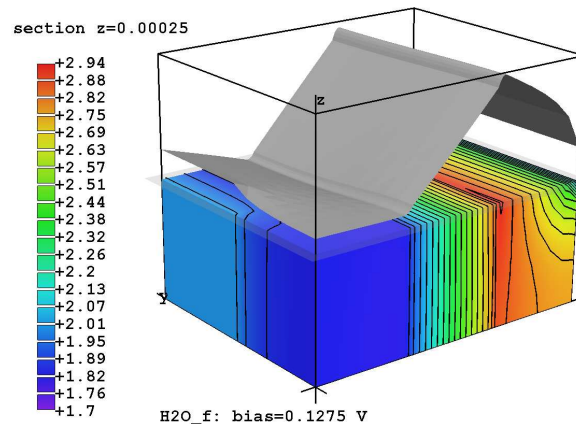
Preliminary 3D Results

Numerical model designed such that, depending on the discretization grid supplied, one-, two- or three-dimensional simulations can be performed.

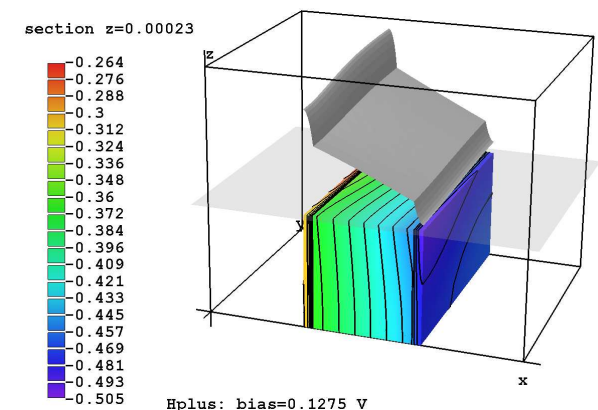
Methanol conc. (mol/m^3)



Water pressure (bar)



Proton potential (V)



Challenges for DMFC Design

Computations show some of the critical points of current DMFC designs.

- ▷ **Catalyst:** DMFC catalyst usage order of magnitude higher than for H_2 -PEMFC
⇒ cheaper and more efficient catalysts are needed.
 - ▷ **Membrane:** model predictions show that proton conductivity/methanol permeation ratio needs to be improved by order of magnitude for decent performance.
 - ▷ **Mass transport:** current designs are diffusion limited, the complete MEA design needs improvement by new techniques and materials.
- ▷ More basic research necessary in membrane science, catalyst chemistry.
- ▷ Mathematical modeling can help to predict implications of particular improvements and to optimize existing designs.

Challenges for Mathematical Modeling

- ▷ improved models (especially for membrane and pore space)
- ▷ bifurcation studies
- ▷ coupling of MEA models to channel transport models
- ▷ modelling of new designs, e.g., MicroDMFC
- ▷ modeling for support of experiments/measurements