Computational multiphase modeling of three dimensional transport phenomena in PEFC

Torsten Berning

Department of Energy Technology
Aalborg University
Denmark

Acknowledgements

Dr. Søren Kær
Department of Energy Technology,
Aalborg University

Dr. Chungen Yin
Department of Energy Technology,
Aalborg University

Outline

- Introduction to Computational Fluid Dynamics (CFD)
- Heat and mass transfer processes in Proton Exchange Membrane Fuel Cells (PEMFC)
- Examples for CFD based modeling of PEMFC
  - Commercial codes offered
  - CFD modeling at universities
- Conclusions

INTRODUCTION TO COMPUTATIONAL FLUID DYNAMICS

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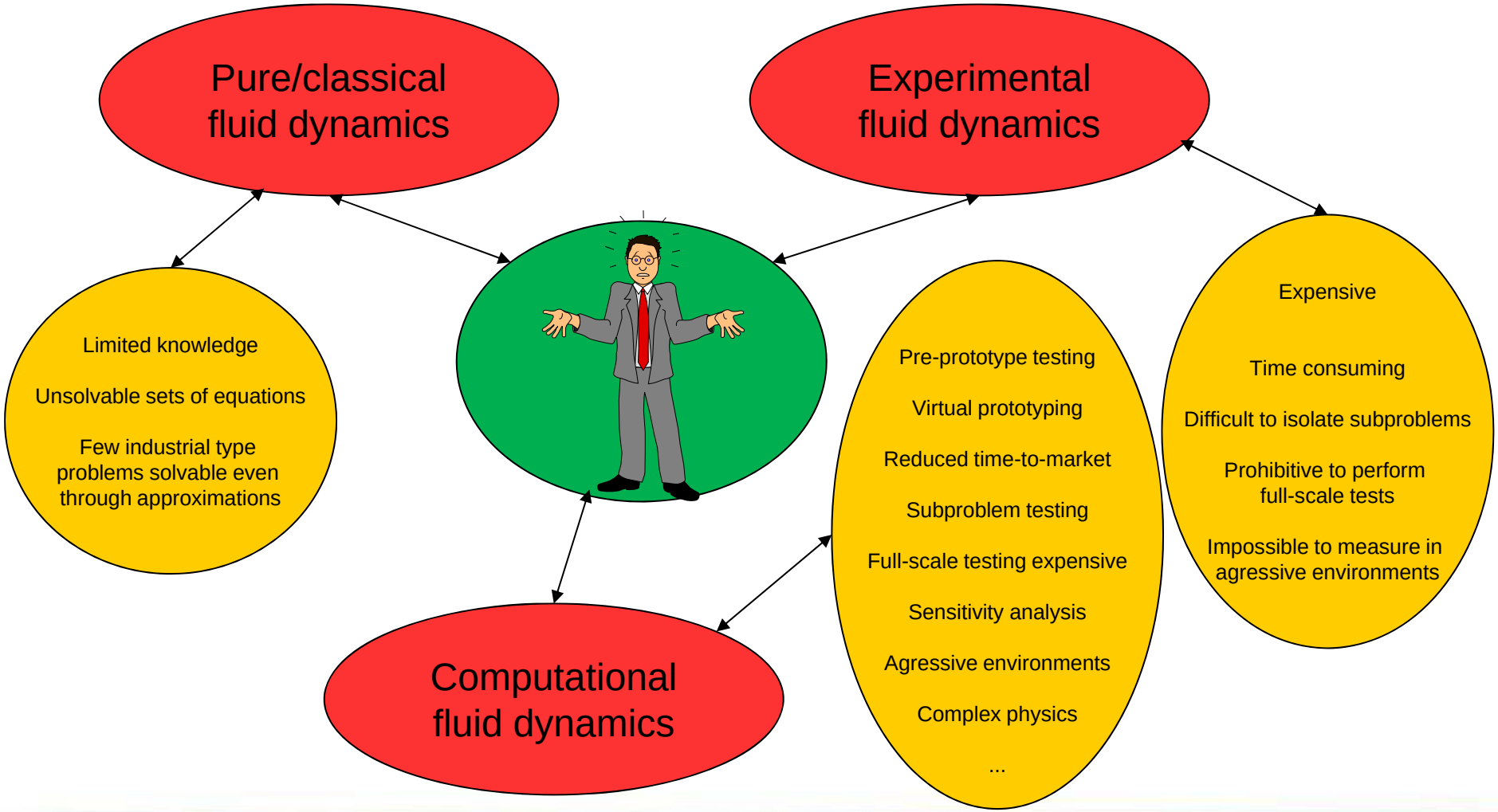
Introduction to CFD

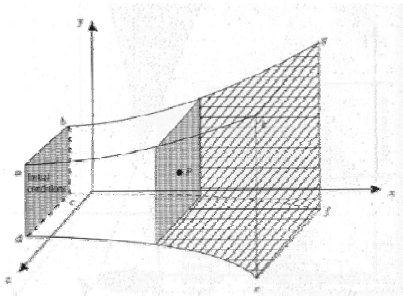
- Fundamental principles of nature include the conservation of mass, momentum, energy, species
- In computational fluid dynamics the partial differential equations (PDEs) are transformed into finite difference equations: $\partial x \rightarrow \Delta x$, $\partial t \rightarrow \Delta t$
- These finite difference equations are solved on a numerical grid for control volumes Δx, Δy, Δz and using a discrete time step Δt <u>in an iterative procedure</u>
- This is done on computers

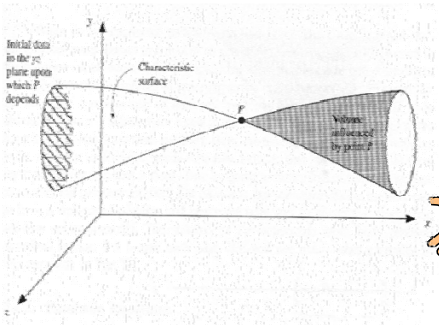
- Various numerical schemes are available for discretizing the equations

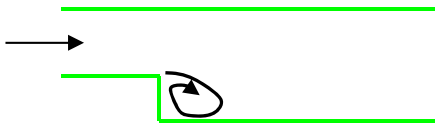
Why use CFD?


Pure/classical fluid dynamics
Experimental fluid dynamics
Limited knowledge
Unsolvable sets of equations
Few industrial type problems solvable even through approximations
Pre-prototype testing
Virtual prototyping
Reduced time-to-market
Subproblem testing
Full-scale testing expensive
Sensitivity analysis
Agressive environments
Complex physics
...
Expensive
Time consuming
Difficult to isolate subproblems
Prohibitive to perform full-scale tests
Impossible to measure in agressive environments
Computational fluid dynamics

A CFD analysis entails







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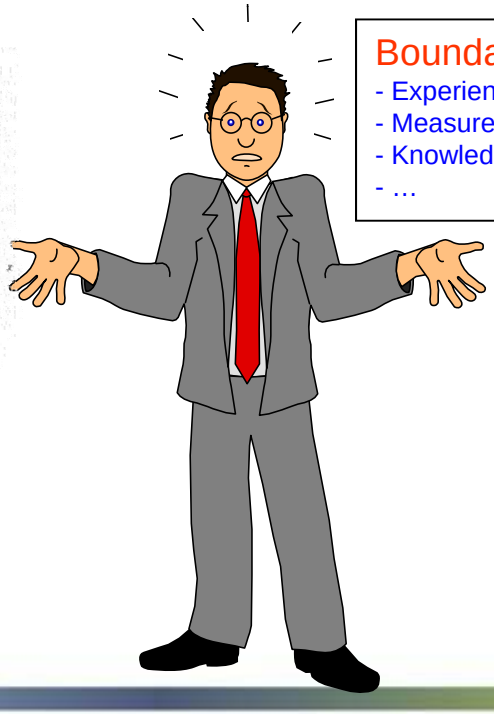

Numerical methods
- Truncation errors
- Stability
- Class of PDE
- …

Physical models
- Turbulence
- Two-phase flow
- Chemistry
- Compressibility
- Heat transfer
- Radiation
- …

Boundary conditions
- Experience from similar problems
- Measurements
- Knowledge from “simple” cases
- …

The Engineer
- Physical insight (choice of models)
- Experience
- Review / evaluation of results
- Choice of approach (exp. or num)
- …

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How CFD works: General conservation equations

Quantity/ property	Equation
Mass	$0 = div(\rho\vec{u}) + \frac{\partial \rho}{\partial t}$
x-momentum	$\rho \frac{Du}{Dt} = -\frac{\partial p}{\partial x} + div(\mu grad\vec{u}) + S_{Mx}$
y-momentum	$\rho \frac{Dv}{Dt} = -\frac{\partial p}{\partial y} + div(\mu grad\vec{u}) + S_{My}$
z-momentum	$\rho \frac{Dw}{Dt} = -\frac{\partial p}{\partial z} + div(\mu grad\vec{u}) + S_{Mz}$
Internal energy	$\rho \frac{Di}{Dt} = -p\, div\,\vec{u} + div(k\, grad\, T) + \Phi + S_i$
Equations of state	$p = p(\rho, T), \quad i = i(\rho, T)$ $p = \rho RT, \quad i = c_v T$
General transport equation	$\frac{\partial(\rho\phi)}{\partial t} + div(\rho\phi\vec{u}) = div(\Gamma\, grad\, \phi) + S_\phi$

Diffusion coefficient

Governing equations

The general transport equation is:

$$\frac{\partial(\rho\phi)}{\partial t} + div(\rho\vec{u}\phi) = div(\Gamma\, grad\,\phi) + S$$

rate of change with time — convection — diffusion — source term

Examples:

Continuity:	$\phi = 1$ $\Gamma = 0$ $S = 0$
U-momentum:	$\phi = u$ $\Gamma = \mu$ $S = -dp/dx$

Discretization of Partial Differential Equations (PDEs)

We are beginning with the diffusion term (not only due to a concentration gradient but in general):

$$\frac{\partial(\rho\phi)}{\partial t} + div(\rho\,\bar{u}\,\phi) = div(\Gamma\, grad\,\phi) + S$$

As an example, consider 1-dimensional conduction of heat:

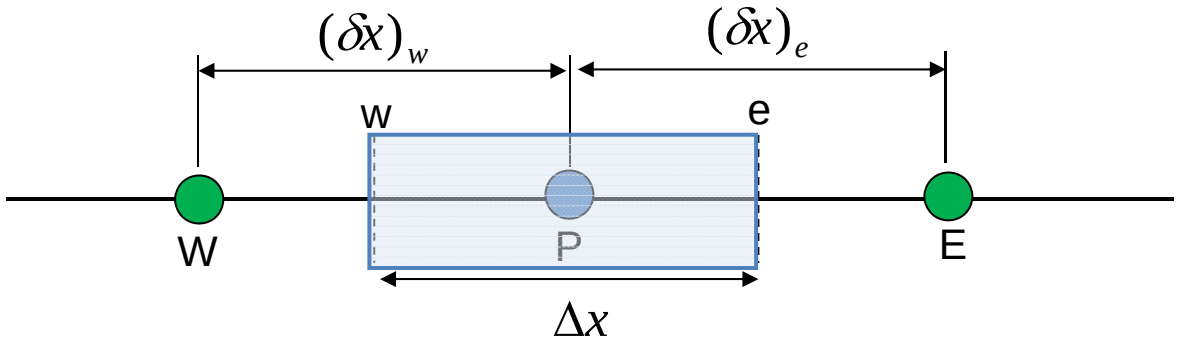
$$\frac{d}{dx}\left(k\frac{dT}{dx}\right) + S = 0$$

where:

k = thermal conductivity
T = temperature
S = rate of heat generation per unit volume

Discretization of Partial Differential Equations (PDEs)

Consider the 1-dimensional grid system (Δy and Δz = 1):



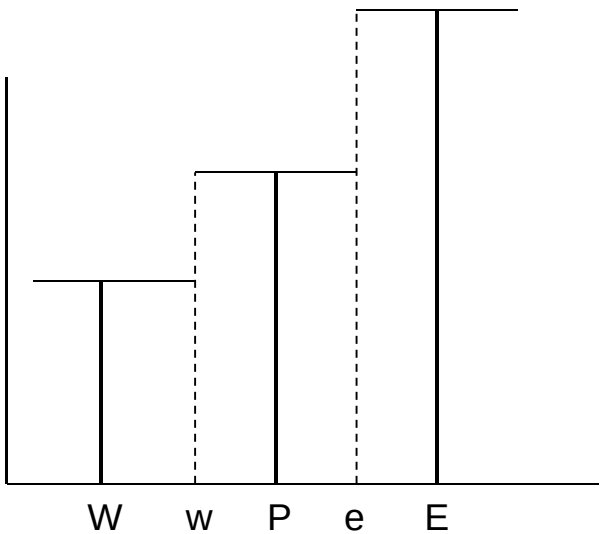
We integrate the heat equation over this volume:

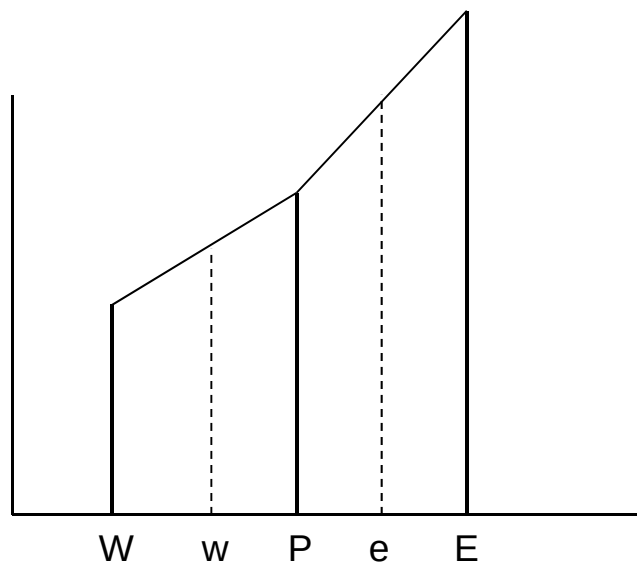
$$\left(k\frac{dT}{dx}\right)_e - \left(k\frac{dT}{dx}\right)_w + \int_w^e S\,dx = 0$$

Discretization of Partial Differential Equations (PDEs)

$$\left(k\frac{dT}{dx}\right)_e - \left(k\frac{dT}{dx}\right)_w + \int_w^e S\,dx = 0$$

We need to assume a profile to evaluate the gradient terms:



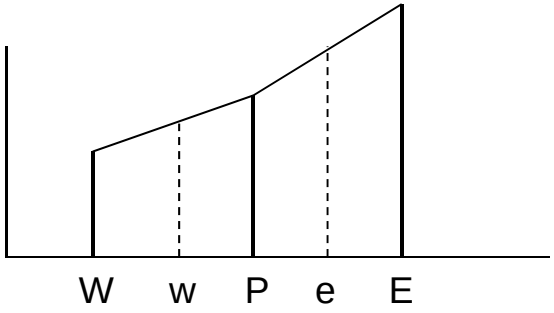


dT/dx NOT defined for this profile!

Discretization of Partial Differential Equations (PDEs)

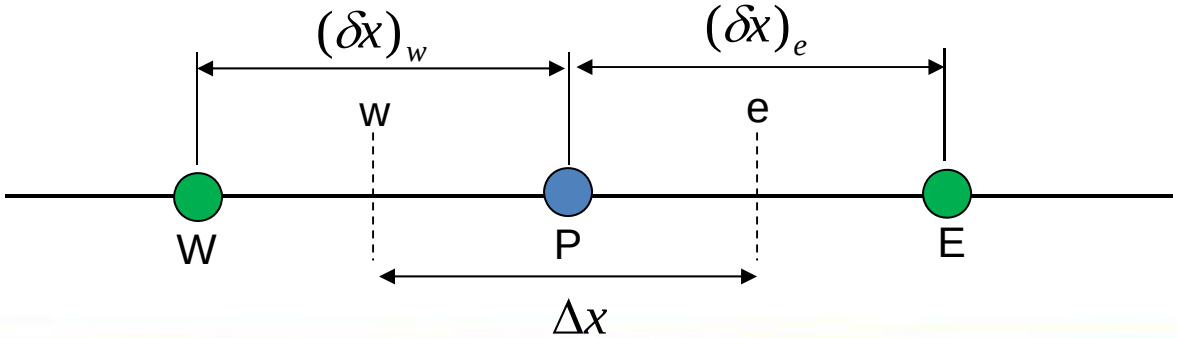
If we use the linear profile assumption:

$$\left(k\frac{dT}{dx}\right)_e - \left(k\frac{dT}{dx}\right)_w + \int_w^e S\,dx = 0$$



We arrive at the following discretized equation (with uniform cells):

$$\frac{k_e(T_E - T_P)}{(\delta x)_e} - \frac{k_w(T_P - T_W)}{(\delta x)_w} + \bar{S}\,\Delta V = 0$$



Discretization of Partial Differential Equations (PDEs)

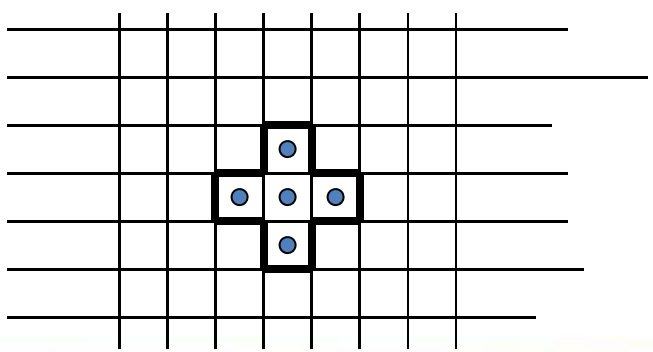
The discretized equation is written as:

$$a_P T_P = a_E T_E + a_W T_W + b = \sum a_{nb} T_{nb} + b$$

where:

$$a_E = \frac{k_e}{(dx)_e} \qquad a_W = \frac{k_w}{(dx)_w} \qquad a_P = a_E + a_W \qquad b = \bar{S}\,\mathrm{D}x$$

In 2 dimensions, this is often illustrated as an amoeba:



From the Fluent manual

1.4.1 Planning Your CFD Analysis

When you are planning to solve a problem using FLUENT, you should first give consideration to the following issues:

- **Definition of the Modeling Goals:** What specific results are required from the CFD model and how will they be used? What degree of accuracy is required from the model?
- **Choice of the Computational Model:** How will you isolate a piece of the complete physical system to be modeled? Where will the computational domain begin and end? What boundary conditions will be used at the boundaries of the model? Can the problem be modeled in two dimensions or is a three-dimensional model required? What type of grid topology is best suited for this problem?
- **Choice of Physical Models:** Is the flow inviscid, laminar, or turbulent? Is the flow unsteady or steady? Is heat transfer important? Will you treat the fluid as incompressible or compressible? Are there other physical models that should be applied?
- **Determination of the Solution Procedure:** Can the problem be solved simply, using the default solver formulation and solution parameters? Can convergence be accelerated with a more judicious solution procedure? Will the problem fit within the memory constraints of your computer, including the use of multigrid? How long will the problem take to converge on your computer?

Careful consideration of these issues before beginning your CFD analysis will contribute significantly to the success of your modeling effort. When you are planning a CFD project, take advantage of the customer support provided to all FLUENT users.

Fuel cell modeling versus experiments I

Modeling

+ cheap, once a realistic model has been developed

+ easy to conduct ”what if” scenarios, parametric studies, possible to isolate the effect of a single parameter

- Danger of over-interpreting results, ”Colourful Fluid Dynamics”, easy to obtain results, but are they meaningful?

- Models tend to idealize, compromise between large computational domain and physical accuracy

- ”Overselling” of commercial models

- Commercial software licenses are expensive

Experiments

+ obtain ”real life” data

+ amazing techniques have been developed (NMR, NR, Neutron scattering, …) yielding very high resolution (2-3 μm)

- ”Frano’s law”: One can not change only one parameter in a fuel cell – change of one parameter causes a change in at least two parameters, and at least one of them has an opposite effect of the one expected to be seen

- Often intrusive

- Tedious and time consuming

- Fuel cell test stations are expensive

Fuel cell modeling versus experiments II

- At the current stage, neither experiments nor a computational model can stand alone!
- An important strength of a model is the ”design of experiments”: Identify the effect of a critical parameter and have it counter-checked by experiments.
- In case of doubt, experiments will always be given priority!

As a general rule:

- when someone at a conference presents modeling work NOBODY believes the results – except the person who did the modeling work;

- however, when someone presents experimental work EVERYBODY believes the results – except the person who did the experiments.

HEAT AND MASS TRANSFER IN PROTON EXCHANGE MEMBRANE FUEL CELLS (PEMFC)

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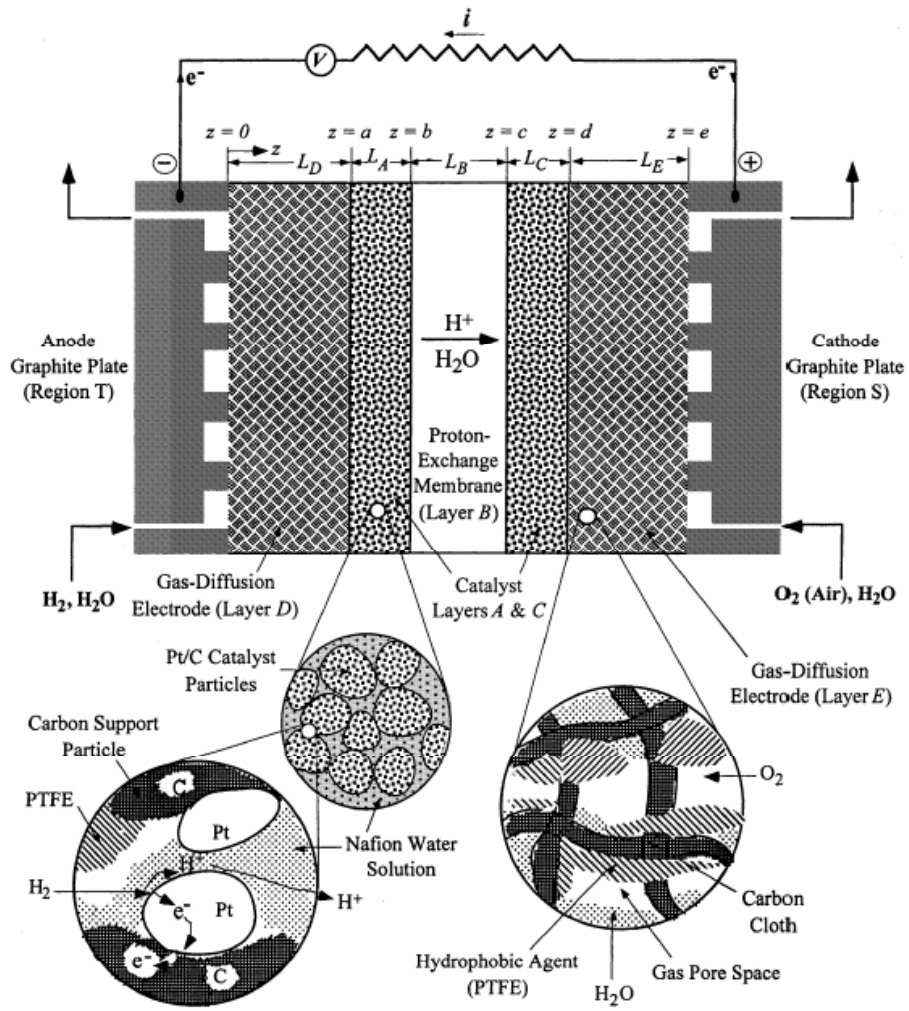
Fuel Cell Schematic



Source: Thampan, PEM Fuel Cell as a Membrane Reactor

Transport phenomena in PEMFC

- Convection in the gas flow channels
- Convection and diffusion of reactants in flow channels and porous media
- Electro-chemical reactions
- Electron and proton transport
- Heat transfer
- Water transport via diffusion (gas phase) and capillary action (liquid phase)
- Phase-change of water
- Water transport through the polymer electrolyte membrane (”electro-osmotic drag”, diffusion, absorption/desorption)
- …

CFD modeling of PEMFC

- Due to the plethora of transport phenomena, CFD is a very good approach to try and cover all (or most) of these physics.
- Commercial CFD codes (e.g. Fluent, Star-CD, CFX 13, CFD ACE) offer tools to solve time dependent transport equations for mass, momentum, species, and energy, and can be modified in order to model heat and mass transfer in fuel cells.
- For complex geometries, one or two-dimensional models are not sufficient to investigate all these phenomena (but are suitable to pick a few aspects and study those in greater detail using analytical modeling)…

Examples of fuel cell modeling using CFD

- Commercial tools available:
  - Star CD (CD Adapco)
  - ANSYS Fluent
  - COMSOL (multiphysics modeling, but not truly CFD)

- University research groups (examples):
  - Pennsylvania State University (PSU)
  - University of Victoria (UVic)
  - Aalborg University (AAU)

COMMERCIAL FUEL CELL MODELS EMPLOYING CFD

Star CD (CD Adapco) fuel cell module

- Originally developed by Dutta et al. (U. South Carolina)
- Implemented into commercial CFD package Star CD (CD Adapco), first published in 2000-2001
- Modeling features:
  - + Three dimensional, large computational domain (full flow field plate)
  - + Complex geometries (serpentine flow fields)
  - + Electrochemical model (catalyst layers, but thickness neglected)
  - + Capable of calculating polarization curve

  - – Greatly simplified multi-phase model
  - – Ultrathin, two-dimensional CLs
  - – Physically incorrect membrane model (membrane water content not calculated, water balance most likely incorrect)

Star CD (CD Adapco) fuel cell module

Approach:

- Use the CFD solver as a vehicle to solve the time-dependent three-dimensional conservation equations of mass, momentum, species and energy.
- Apply sink and source terms in order to account for porous resistances, electrochemical reactions, heat generation, …
  - E.g. inside the porous media there is a momentum sink to account for the additional resistance (increased pressure drop)
  - Inside the CLs there are sink and source terms for the species equations due to the electrochemical reactions.
- Local current density has to be calculated out of combination of field and species equations.
- Also: Apply specific boundaryu conditions for fuel cells (inlet velocities, species concentrations, electrical field values, …)

Source: Dutta et al., J. Applied Electrochem. 30, 2000

Table 1. Governing equations and source terms

Source: Dutta et al., J. Applied Electrochem. 30, 2000

Governing equations	Mathematical expressions	
Conservation of mass	$\frac{\partial(\rho u)}{\partial x}+\frac{\partial(\rho v)}{\partial y}+\frac{\partial(\rho w)}{\partial z}=S_{\mathrm{m}}$	(1)
Momentum transport	$u\frac{\partial(\rho u)}{\partial x}+v\frac{\partial(\rho u)}{\partial y}+w\frac{\partial(\rho u)}{\partial z}=-\frac{\partial P}{\partial x}+\frac{\partial}{\partial x}\left(\mu\frac{\partial u}{\partial x}\right)+\frac{\partial}{\partial y}\left(\mu\frac{\partial u}{\partial y}\right)+\frac{\partial}{\partial z}\left(\mu\frac{\partial u}{\partial z}\right)+S_{\mathrm{p}x}$	(2)
	$u\frac{\partial(\rho v)}{\partial x}+v\frac{\partial(\rho v)}{\partial y}+w\frac{\partial(\rho v)}{\partial z}=-\frac{\partial P}{\partial y}+\frac{\partial}{\partial x}\left(\mu\frac{\partial v}{\partial x}\right)+\frac{\partial}{\partial y}\left(\mu\frac{\partial v}{\partial y}\right)+\frac{\partial}{\partial z}\left(\mu\frac{\partial v}{\partial z}\right)+S_{\mathrm{p}y}$	
	$u\frac{\partial(\rho w)}{\partial x}+v\frac{\partial(\rho w)}{\partial y}+w\frac{\partial(\rho w)}{\partial z}=-\frac{\partial P}{\partial z}+\frac{\partial}{\partial x}\left(\mu\frac{\partial w}{\partial x}\right)+\frac{\partial}{\partial y}\left(\mu\frac{\partial w}{\partial y}\right)+\frac{\partial}{\partial z}\left(\mu\frac{\partial w}{\partial z}\right)+S_{\mathrm{p}z}$	
Hydrogen transport (anode side)	$u\frac{\partial(\rho m_{\mathrm{H_2}})}{\partial x}+v\frac{\partial(\rho m_{\mathrm{H_2}})}{\partial y}+w\frac{\partial(\rho m_{\mathrm{H_2}})}{\partial z}=\frac{\partial(J_{x,\mathrm{H_2}})}{\partial x}+\frac{\partial(J_{y,\mathrm{H_2}})}{\partial y}+\frac{\partial(J_{z,\mathrm{H_2}})}{\partial z}+S_{\mathrm{H_2}}$	(3)
Water transport (anode side)	$u\frac{\partial(\rho m_{\mathrm{aw}})}{\partial x}+v\frac{\partial(\rho m_{\mathrm{aw}})}{\partial y}+w\frac{\partial(\rho m_{\mathrm{aw}})}{\partial z}=\frac{\partial(J_{x,\mathrm{aw}})}{\partial x}+\frac{\partial(J_{y,\mathrm{aw}})}{\partial y}+\frac{\partial(J_{z,\mathrm{aw}})}{\partial z}+S_{\mathrm{aw}}$	(4)
Oxygen transport (cathode side)	$u\frac{\partial(\rho m_{\mathrm{O_2}})}{\partial x}+v\frac{\partial(\rho m_{\mathrm{O_2}})}{\partial y}+w\frac{\partial(\rho m_{\mathrm{O_2}})}{\partial z}=\frac{\partial(J_{x,\mathrm{O_2}})}{\partial x}+\frac{\partial(J_{y,\mathrm{O_2}})}{\partial y}+\frac{\partial(J_{z,\mathrm{O_2}})}{\partial z}+S_{\mathrm{O_2}}$	(5)
Water transport (cathode side)	$u\frac{\partial(\rho m_{\mathrm{cw}})}{\partial x}+v\frac{\partial(\rho m_{\mathrm{cw}})}{\partial y}+w\frac{\partial(\rho m_{\mathrm{cw}})}{\partial z}=\frac{\partial(J_{x,\mathrm{cw}})}{\partial x}+\frac{\partial(J_{y,\mathrm{cw}})}{\partial y}+\frac{\partial(J_{z,\mathrm{cw}})}{\partial z}+S_{\mathrm{cw}}$	(6)

Nonzero volumetric source terms and location of application (Fig. 2)

$$S_m = S_{H_2} + S_{aw} \text{ at } z = z_3$$
$$S_m = S_{O_2} + S_{cw} \text{ at } z = z_2 \quad (7)$$

$$\left.\begin{aligned} S_{px} &= -\frac{\mu u}{\beta_x}; \\ S_{py} &= -\frac{\mu v}{\beta_y}; \\ S_{pz} &= -\frac{\mu w}{\beta_z} \quad \text{at } z_1 \le z \le z_4 \end{aligned}\right\} \quad (8)$$

$$S_{H_2} = -\frac{I(x,y)}{2F} M_{H_2} A_{cv} \text{ at } z = z_3 \quad (9)$$

$$S_{aw} = -\frac{\alpha(x,y)}{F} I(x,y) M_{H_2O} A_{cv} \text{ at } z = z_3 \quad (10)$$

$$S_{O_2} = -\frac{I(x,y)}{4F} M_{O_2} A_{cv} \text{ at } z = z_2 \quad (11)$$

$$S_{cw} = \frac{1 + 2\alpha(x,y)}{2F} I(x,y) M_{H_2O} A_{cv} \text{ at } z = z_2 \quad (12)$$

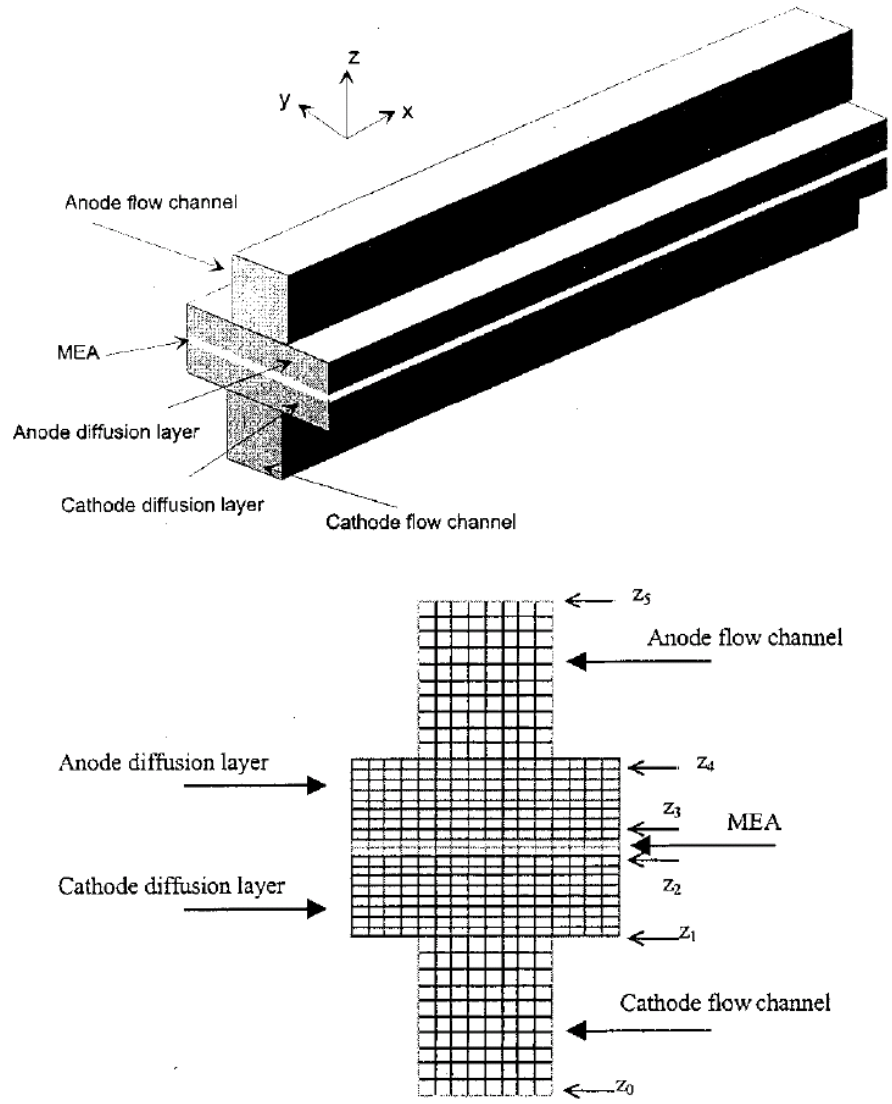


Fig. 2. Schematic of the computation domain for a straight channel fuel cell with diffusion layers in the anode and cathode sides of the membrane electrode assembly (MEA). A typical cross section of the domain and the location of diffusion layers are also shown.

Source: Dutta et al., J. Applied Electrochem. 30, 2000

Table 2. Equations for modelling electrochemical effects

Source: Dutta et al., J. Applied Electrochem. 30, 2000

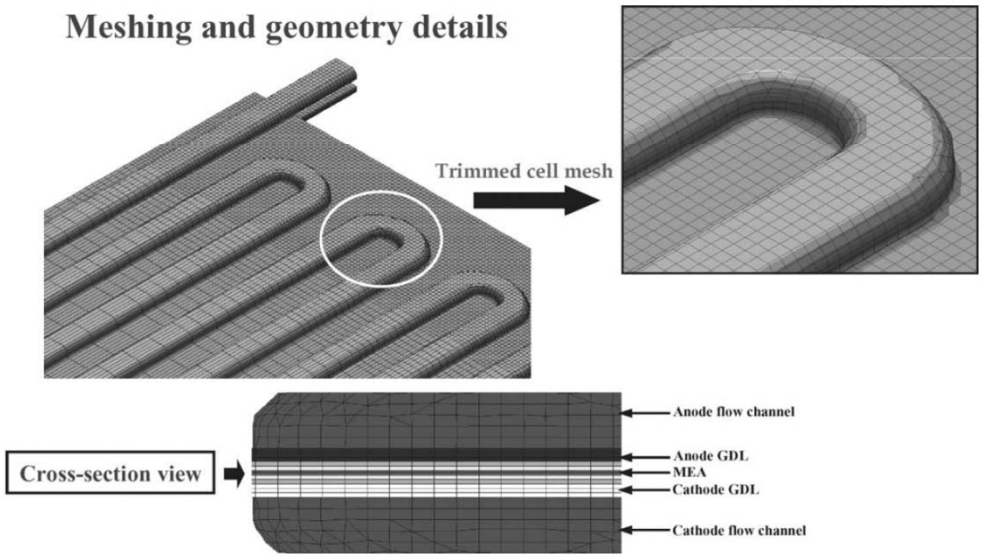
Diffusion mass flux of species l in ξ direction	$J_{i,l} = -\rho D_{i,l} \dfrac{\partial m_{K,l}}{\partial \xi}$	(13)
Binary diffusion coefficient [10]	$\dfrac{PD_{i,j}(x,y)}{(P_{c-i} \times P_{c-j})^{1/3} \times (T_{c-i}T_{c-j})^{5/12} \times \left(\frac{1}{M_i} + \frac{1}{M_j}\right)^{1/2}} = 3.64 \times 10^{-8} \left(\dfrac{T_{\text{cell}}}{\sqrt{T_{c-i}T_{c-j}}}\right)^{2.334}$	(14)
Net water transfer coefficient per proton	$\alpha(x,y) = n_{\text{d}}(x,y) - \dfrac{F}{I(x,y)} D_{\text{W}}(x,y) \left(\dfrac{C_{\text{wc}}(x,y) - C_{\text{wa}}(x,y)}{t_{\text{m}}}\right)$	(15)
Electroosmotic drag coefficient	$n_{\text{d}}(x,y) = 0.0049 + 2.02a_{\text{a}} - 4.53a_{\text{a}}^2 + 4.09a_{\text{a}}^3;\ a_{\text{a}} \le 1$ $= 1.59 + 0.159(a_{\text{a}} - 1);\ a_{\text{a}} > 1$	(16)
Water diffusion coefficient for cases similar to Yi and Nguyen [6]	$D_{\text{W}} = n_{\text{d}} 5.5 \times 10^{-11} \exp\left[2416\left(\dfrac{1}{303} - \dfrac{1}{T_{\text{s}}}\right)\right]$	(17)
Water diffusion coefficient for cases similar to Fuller and Newman [4]	$D_{\text{W}} = 3.5 \times 10^{-6} \lambda \exp\left(-\dfrac{2436}{T_{\text{s}}}\right)$	(18)
Water concentration for anode and cathode surfaces of the MEA	$C_{\text{w}K}(x,y) = \dfrac{\rho_{\text{m,dry}}}{M_{\text{m,dry}}}(0.043 + 17.8a_K - 39.8a_K^2 + 36.0a_K^3);\ a_K \le 1$ $= \dfrac{\rho_{\text{m,dry}}}{M_{\text{m,dry}}}(14 + 1.4(a_K - 1));$ for $a_K > 1$, where $K = a$ or c	(19)
Water activity	$a_K = \dfrac{X_{\text{w},K} P(x,y)}{P_{\text{w},K}^{\text{sat}}}$	(20)
Local current density	$I(x,y) = \dfrac{\sigma_{\text{m}}(x,y)}{t_{\text{m}}} \{V_{\text{oc}} - V_{\text{cell}} - \eta(x,y)\}$	(21)
Local membrane conductivity	$\sigma_{\text{m}}(x,y) = \left(0.005\,14 \dfrac{M_{\text{m,dry}}}{\rho_{\text{m,dry}}} C_{\text{wa}}(x,y) - 0.003\,26\right) \exp\left(1268\left(\dfrac{1}{303} - \dfrac{1}{T_{\text{s}}}\right)\right) \times 10^2$	(22)
Local overpotential	$\eta(x,y) = \dfrac{RT_{\text{s}}}{0.5F} \ln\left(\dfrac{I(x,y)}{I_0 P_{\text{O}_2}(x,y)}\right)$	(23)

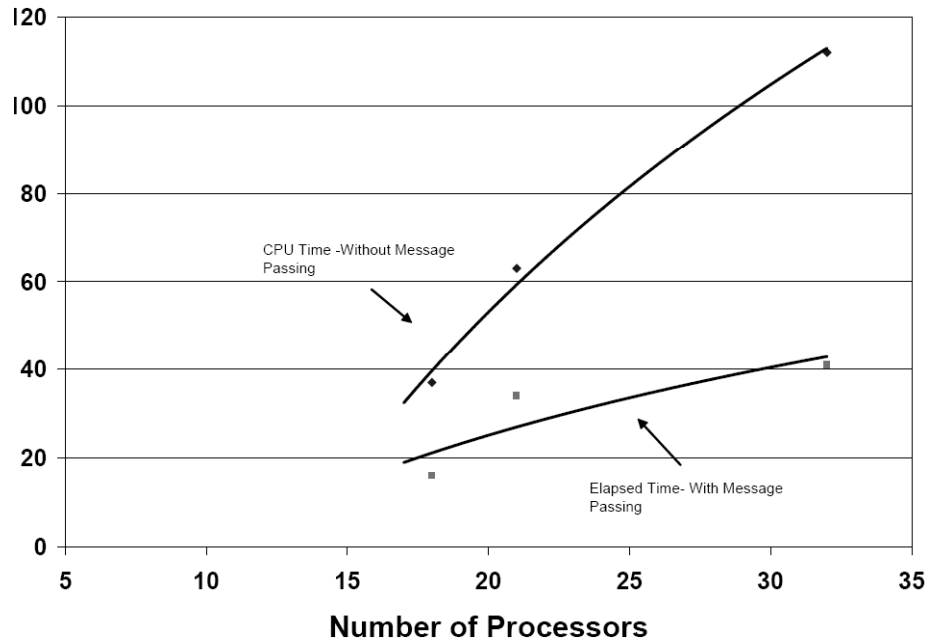
A critical note on commercial CFD modules

- It can be seen from the previous equations that altogether there are as many unknowns as there are equations:
  - Continuity equations and the coupling with three momentum equations yield p, u, v, w.
  - Energy equation: T.
  - Electrical field equation: ϕ.
  - Butler-Volmer equation, Nernst Planck equation: electrical overpotential η, local current density i.
- Hence it is ensured that there is a solvable system of equations

- The need for user convenience ensures that the user will get a solution to this system of equations, but it must be asked, whether all the physical equations and the model is correct!

CD Adapco commercial tool (”ES PEMFC”)





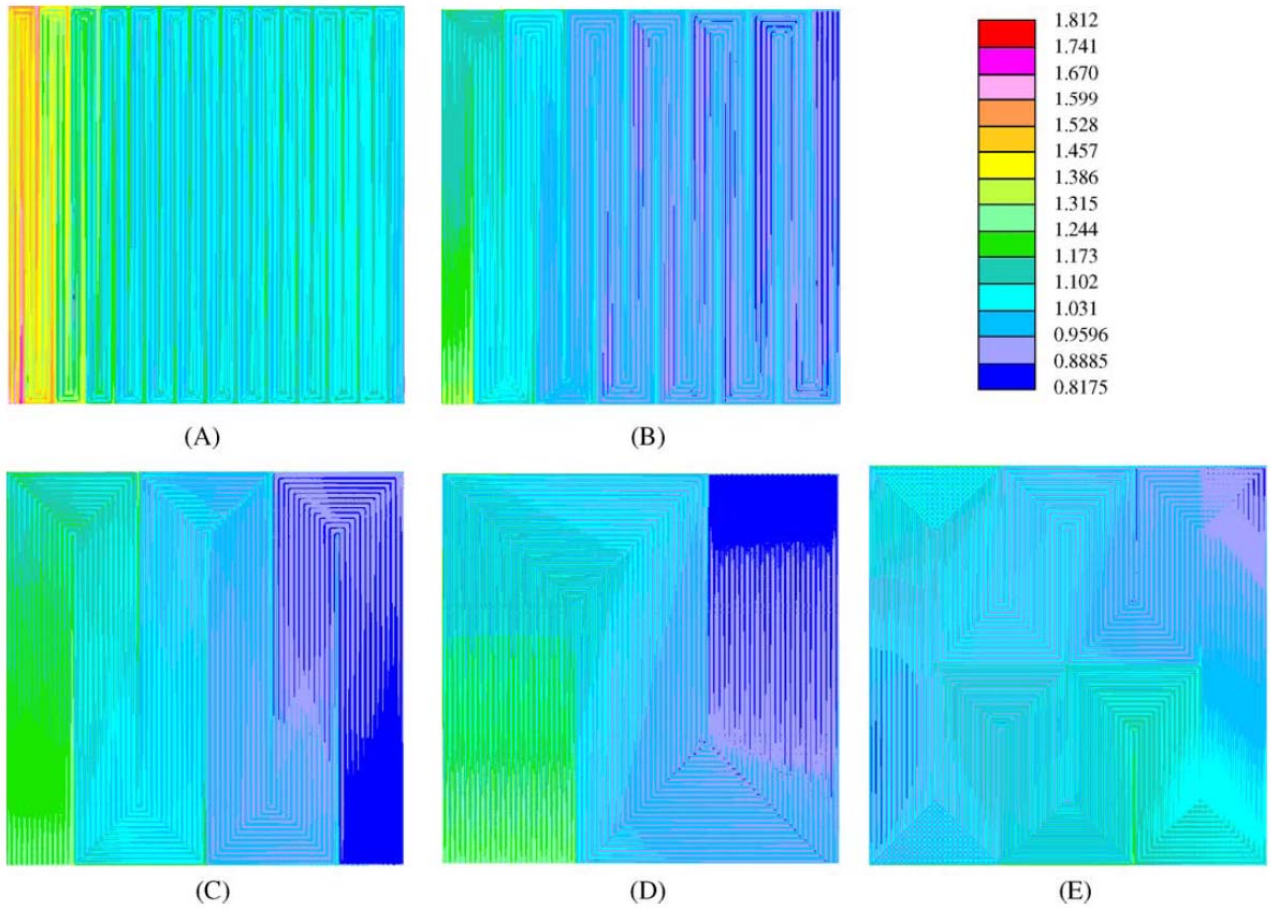
- Complex, realistic commercial-size geometries, nearly 5 million grid cells
- Only affordable with parallel computing
- Note: Generally 1000 - 2000 iterations are required

Source: Shimpalee et al., JPS 135, 2004

Study of the impact of channel length, 2006

- Authors investigated the impact of the channel length, number of serpentines on the predicted cell performance
- One set of operating conditions investigated
- Reactants entered cell at 100 % RH, but model is essentially single-phase

➢Nice pictures, but very probably completely unrealistic!

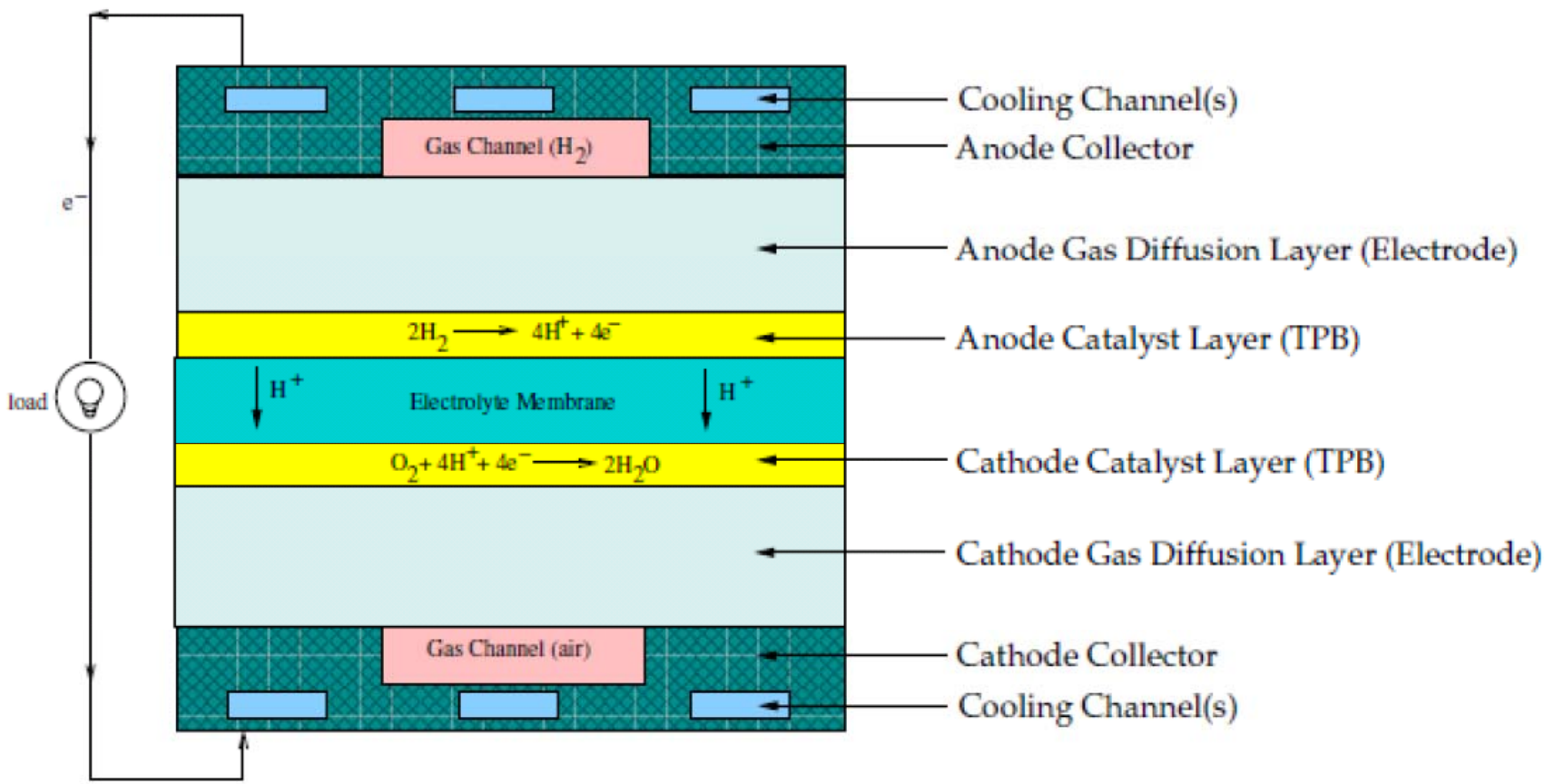


Source: Shimpalee et al., JPS 160, 2006

Summary: Commercial module *es-pemfc* (CD Adapco)

- First commercial tool, state-of-the-art in 2000.
- In general, many of the physics are encountered and highly complex, commercial size geometries can be calculated (on parallel computers one case can take up to 50h).
- Trade-off between physical accuracy (membrane model, multi-phase flow) versus the need of obtaining a result.
- Since development of that model, advances have been made in the understanding of multi-phase flow issues in porous media and channels, not yet accounted for in this model.
- On balance, this model was the first commercial tool and state-of-the-art in 2000, but it has not been further developed to a sufficient degree.
- Results are questionable, but polarization curves can be easily measured (validation possible).
- It is not recommended to use this model for PhD research!

Fluent fuel cell module (ANSYS Inc.)



Physics implemented in Fluent CFD Module

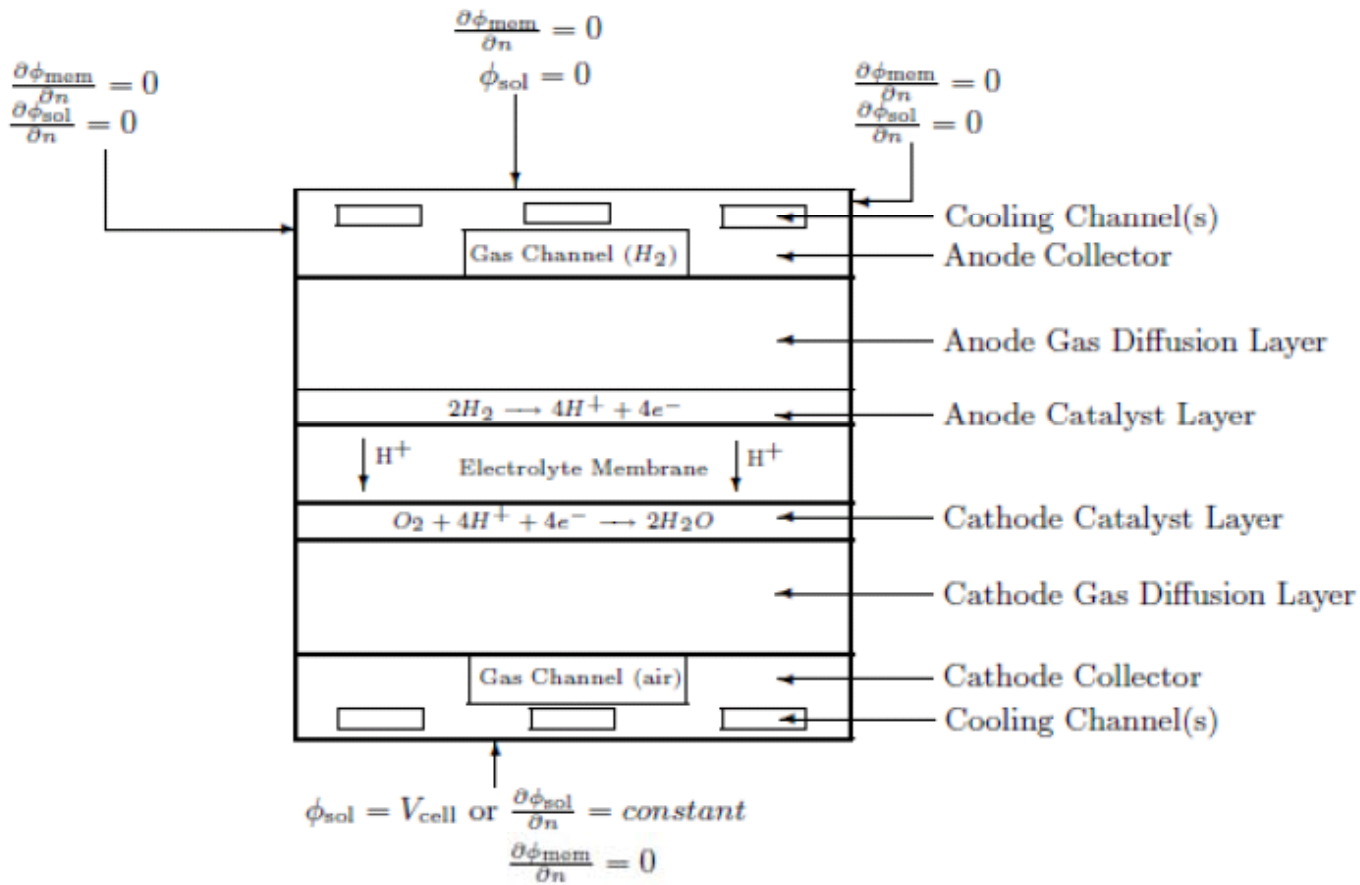
+ Three-dimensional convection and diffusion of multiple species inside the flow channels and porous media
+ Heat transfer and electrical field equations are solved
+ Bipolar plates are included
+ Electrochemical reactions according to Butler-Volmer equations in three-dimensional catalyst layers

– ”Conservation equation” for liquid water, diffusion only
– Water transport through the membrane according to Springer et al.

o Numerical behaviour unknown, so far most publications include a single channel section only (which, however, is sufficient to understand the basic physics)

Boundary conditions

Figure 1.2 Boundary Conditions for the Electric Potential (Solid and Membrane) and — PEMFC Used as an Example



Fluent commercial PEMFC module –membrane model

2.1.3 Membrane water transport

$$J_w^{osm} = \frac{n_d M_{h2o}}{F} i \qquad (18)$$

where n_d is the drag coefficient. Measurements by Springer *et al* [17] suggested the following for Nafion membrane,

$$n_d = \frac{2.5\lambda}{22} \qquad (19)$$

where λ is the water content, number of water molecules per solfonic acid. It is noted that Zawodzinski *et al* [19] reported a unity drag coefficient for Nafion membrane that is equilibrated with water vapor.

The back diffusion flux is computed as,

$$J_w^{diff} = -\frac{\rho_m}{M_m} M_{h2o} D_w \nabla\lambda \qquad (20)$$

where ρ_m and M_m are the dry membrane density and equivalent weight, respectively. The water diffusivity is a function of both water content and temperature, according to [7].

$$D_w = D_\lambda \exp\{2416(\frac{1}{303} - \frac{1}{T})\} \qquad (21)$$

where D_λ is a function of λ [7].

The net water flux is thus,

$$J_w = J_w^{osm} + J_w^{diff} \qquad (22)$$

- Model for membrane water transport is based on earlier work by Springer et al., but has become questionable (n_d specification)
- Slight lack of clarity

Source: Li and Becker, Proc. FuelCell 2004 ASME

Fluent commercial PEMFC module – water transport

2.1.4 Liquid water formation and transport

In the present study, a transport equation of liquid water saturation, s, that is based upon the work of Nguyen and his co-workers [16-17],

$$\frac{\partial}{\partial t}(\rho_l s) + \nabla \cdot (\rho_l \vec{V}_l s) = \nabla \cdot [\frac{\rho_l K s^3}{\mu_l} \frac{dp_c}{ds} \nabla s] + r_w$$

(23)

where ρ_l is the liquid water density, $\vec{V}_l$ is the liquid velocity vector, K is the absolute water permeability. The capillary pressure and the condensation rate are computed by Eq. (24) and Eq. (25), respectively,

$$p_c = \frac{\sigma \cos\theta_c}{(K/\varepsilon)^{0.5}} (1.417 s' - 2.12 s'^2 + 1.263 s'^3) \quad (24)$$

$$r_w = c_r \max[(1-s)\frac{P_{wv} - P_{sat}}{RT} M_{h2o}, -s\rho_l] \quad (25)$$

where $s' = (1-s)$, c_r is the condensation rate constant, σ is the surface tension and θ_c is the contact angle.

In the present study, it is assumed that inside the porous GDL capillary diffusion dominates and therefore the convective term in Eq. (23) becomes negligibly small; also it is assumed that in the gas channel, the liquid water is treated as fine mist that shares the same velocity with the gas mixture.

- Liquid water transport not rigorous, but yields results.
- No irreducible saturation (hydrophilic pores) accounted for.
- Convergence behavor unknown, Fluent almost discourages from switching on multi-phase simulations.

Source: Li and Becker, Proc. FuelCell 2004 ASME

Sample results: Fluent PEMFC model

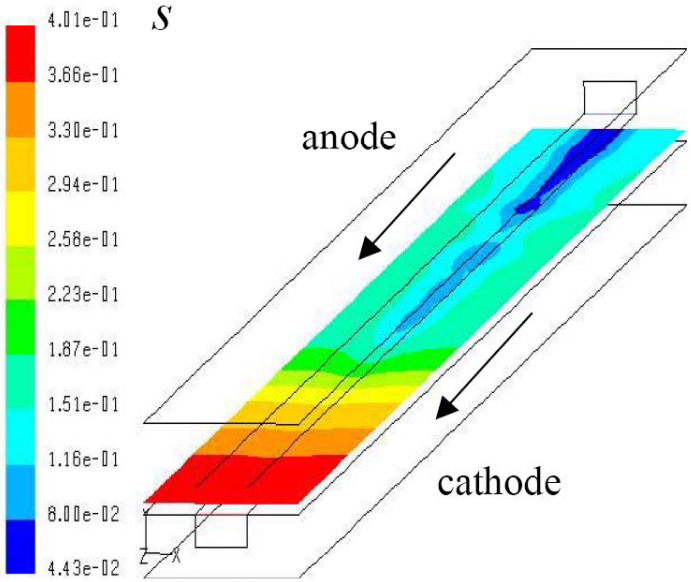


Fig. 4 Contours of liquid water saturation inside the cathode catalyst layer (**baseline case**)

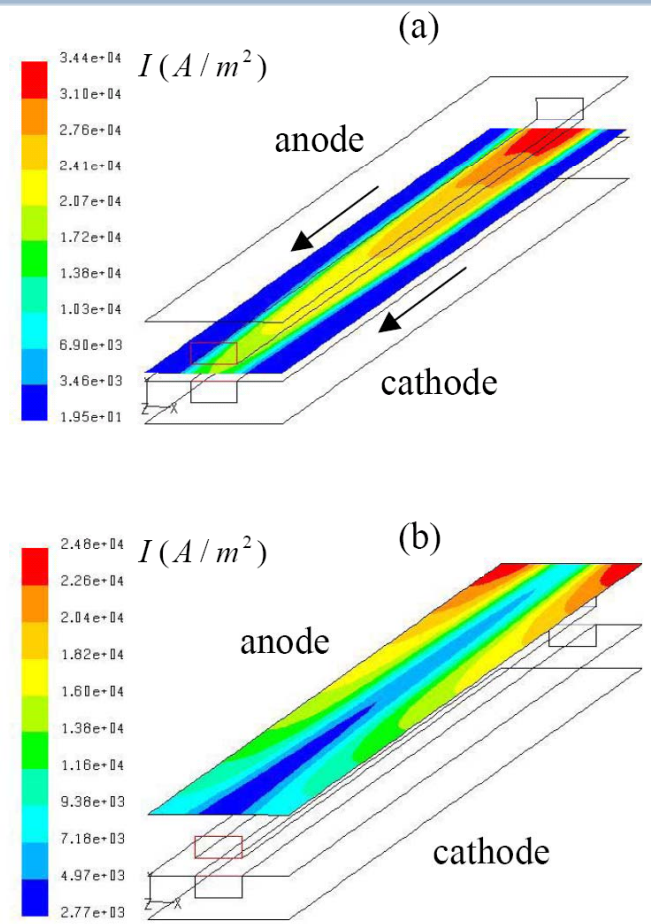


Fig. 6 Contours of local current density (**baseline case**): (a). Membrane (b) Anode collector plate

- Predicted liquid water distribution and current density.
- Calculation of membrane current density unclear.
- Convergence behaviour not mentioned.

Source: Li and Becker, Proc. FuelCell 2004 ASME

Summary of commercial fuel cell modules (Star CD & Fluent)

- Neither *ES PEMFC* by CD Adapco nor the Fluent Fuel Cell Module (ANSYS Inc.) have generally predictive capabilities in terms of multi-phase flow in porous media and correct water transport through the membrane
- Specification of electro-osmotic drag coefficient is by now known to be incorrect
- Validation was done by fitting to polarization curves for chosen operating conditions – predictive capabilities of the models are uncertain!

- Commercial tools need to find compromise between physical modeling of highly complex phenomena and the customer demand to *obtain a numerical solution* and *user friendliness*
- For fundamentally oriented university research neither of the commercial modules can be recommended: Try to build your own model! ☺

UNIVERSITY FUEL CELL MODELS EMPLOYING CFD

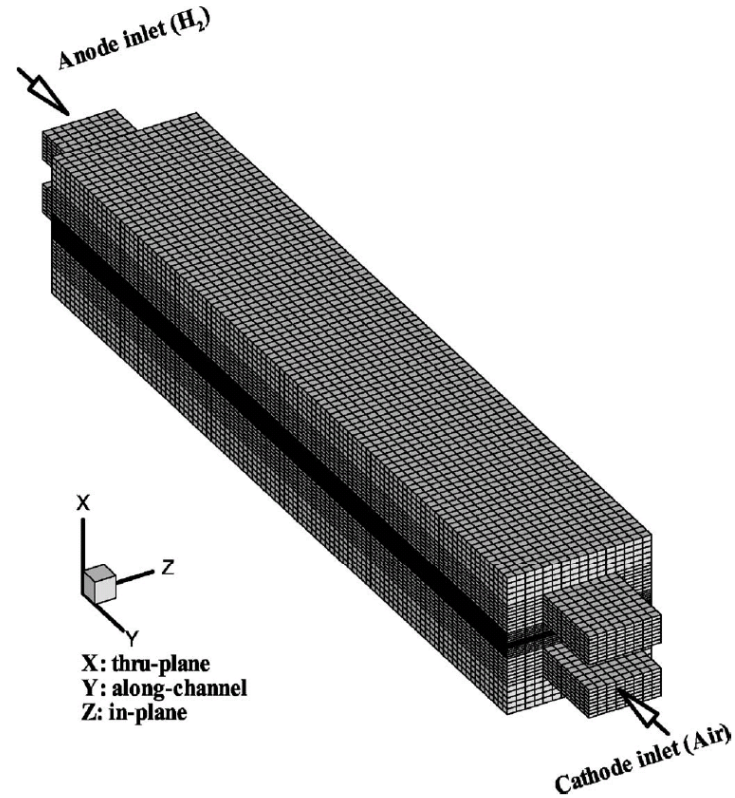
University modeling efforts: PSU (I)

- PSU has strong tradition in electrochemical and multi-phase flow modeling (pioneering work by Prof. CY Wang)
- Typically employs the so-called ”multi-phase mixture model” (M^2 model) to simulate two-phase transport
- Typically implement M^2 model into commercial single-phase solvers such as *Fluent* or *Star CD*
- Very strong, complete three-dimensional model includes all computational domains, even micro-porous layer (MPL).
- Transient results published, full fuel cell plates possible
- Potential weaknesses:
  - Water transport model through the membrane slightly simplified
  - Some approximations included in the M^2 model
- But: M^2 model is substantially better than water transport models in commercial fuel cell modules

University modeling efforts: PSU (II)

Table I. Geometrical and operating parameters.

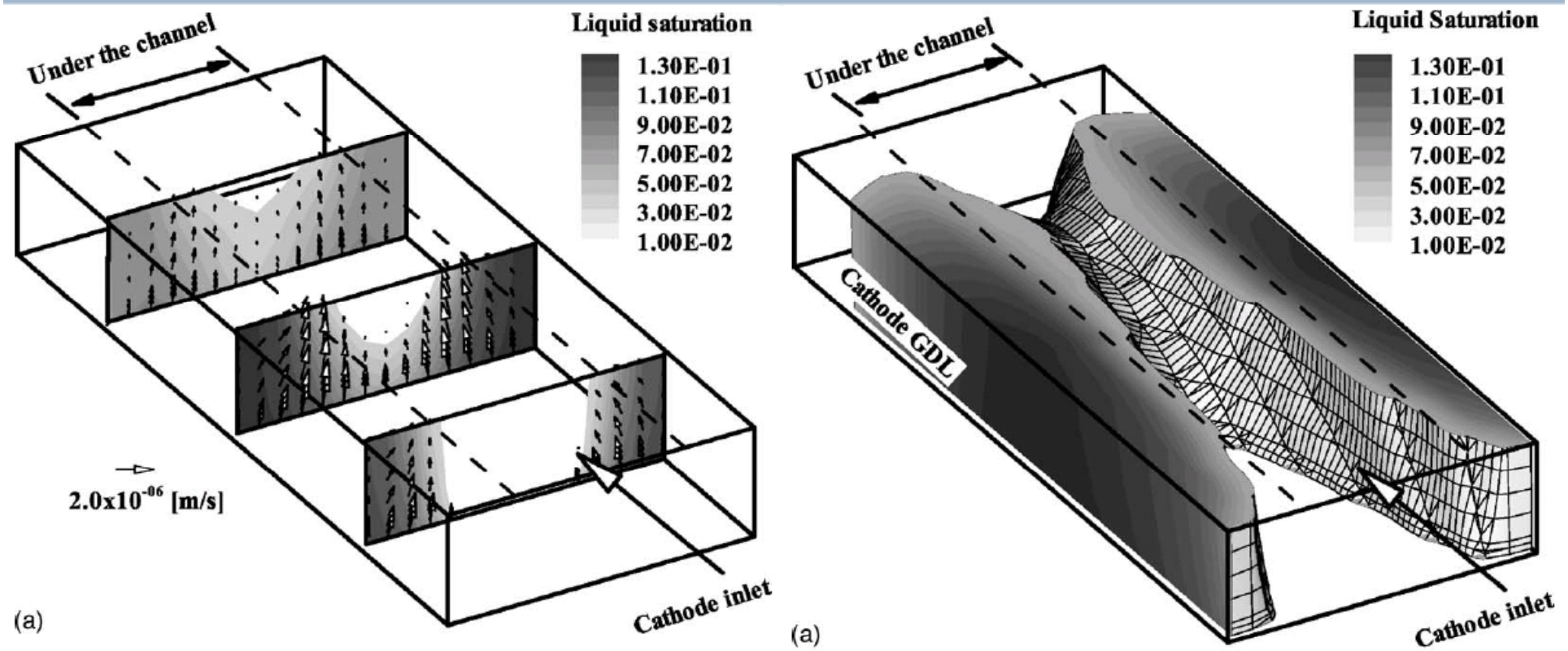
Description	Value
Cell length	70.0 mm
Gas channel depth	0.5 mm
Gas channel width	1.0 mm
Land width	1.0 mm
Anode/cathode DM thickness	0.210 mm
Anode/cathode catalyst layers thickness	0.010 mm
Membrane thickness	0.018 mm
Porosity of anode/cathode DM, ε_{DM}	0.6
Porosity of anode/cathode catalyst layers, ε_{CL}	0.6
Volume fraction of ionomer in anode/cathode catalyst layers, ε_e	0.18
Hydraulic permeability of anode/cathode DM, K_{DM}	3.0×10^{-12} m^2
Hydraulic permeability of membrane, K_{mem}	5.0×10^{-20} m^2
Contact resistance between catalyst layer and DM, R_{CDM}	$1.0 \times 10^{-6}\ \Omega \cdot$ m^2
Anode/cathode inlet pressure, P_{in}	1.5 atm
Cell temperature, T_{cell}	80°C
Anode/cathode stoichiometry, ξ_a/ξ_c	2/2



- Typical domain includes three dimensional CL, MPL, GDL and bipolar plates
- Large number of physical effects and material properties accounted for (e.g. contact resistances which significantly contribute to polarization curve)

Source: Luo, Ju, Wang, J. Electrochem. Soc. 154, 2007

University modeling efforts: PSU (III)



- Cathode and anode inlet 50 % RH at a stoich of 2, P_{cell} = 1.5 atm
- Note: It is numerically very challenging to correctly capture the dry-to-wet interface using the M^2 model (here captured very nicely!)

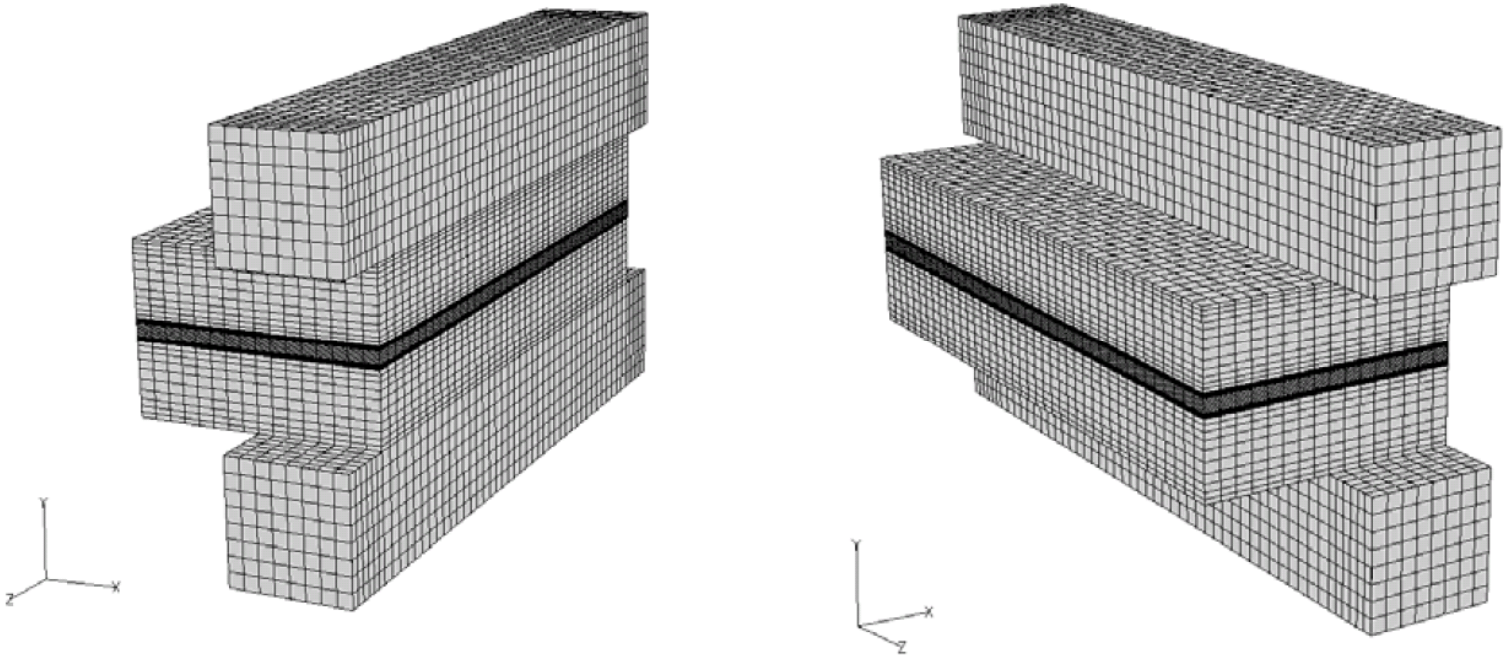
Source: Luo, Ju, Wang, J. Electrochem. Soc. 154, 2007

University modeling efforts: AAU

- Among the few groups that employ the multi-fluid approach to simulate multi-phase flow (other groups: Gurau et al.)
- Use formerly commercial software CFX-4 (AEA Technology, later ANSYS Inc.)
  - Initial work by M. Bang at AAU
  - Later on combination with Berning and Djilali (UVic), also utilizing publication by Gurau et al.

- Salient features of CFX-4
  - Currently appears to be the only model that utilizes multi-fluid approach to simulate two-phase flow (stand alone feature)
  - No parallel code, only small computational domains possible (one ”repeat unit”)
  - Structured grid: only simple geometries are possible (but this is no disadvantage for PEFC)

Sample results, Bang (AAU Dissertation), 2001



- Computational grid: typically a few thousand cells for each channel segment.
- Computational domain includes channels, gas diffusion layer, catalyst layers and membrane.
- Often only half of a channel (or one ”repeat unit”) is modeled because of symmetry.

Sample results, Bang (AAU Dissertation), 2001

- Three different load cases:
  - 0.02 A/cm^2, 0.80 V,
  - 0.52 A/cm^2, 0.49 V,
  - 0.98 A/cm^2, 0.03 V.

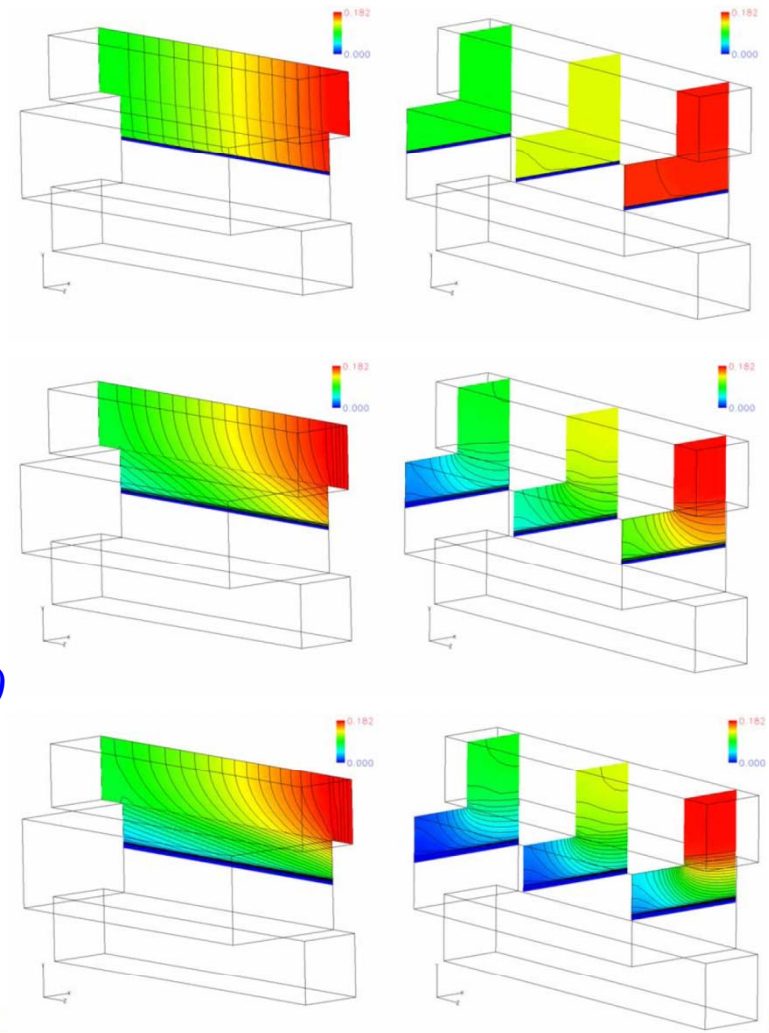
- O_2 distribution reveals effect of mass transport limitations due to porous medium:

Dry porosity (70 – 80 %)

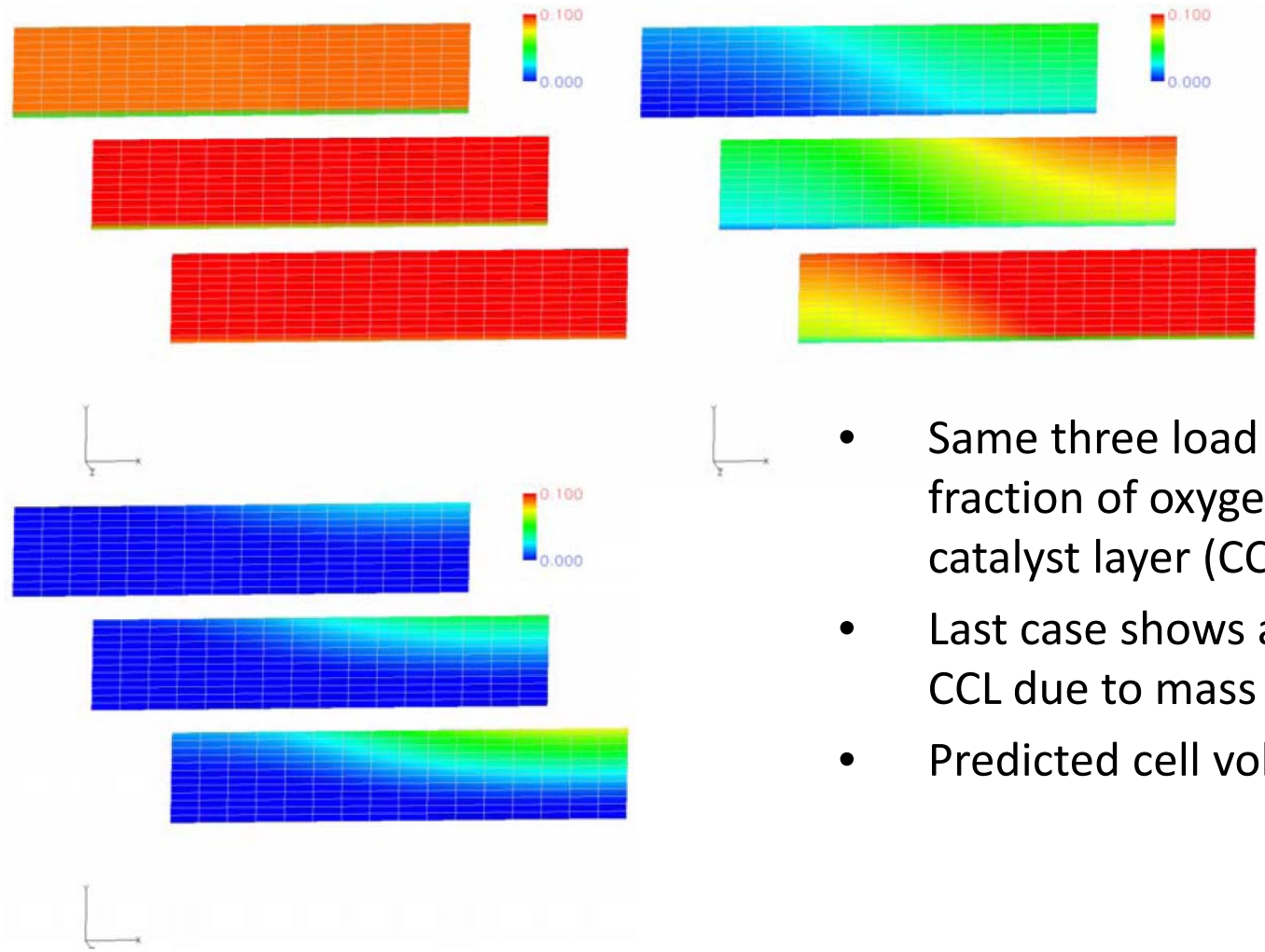
$$D_{O_2-m}^{eff} = D_{O_2-m} \frac{\varepsilon}{\tau} g(s)$$

Function of liquid saturation

Tortuosity (2-4)

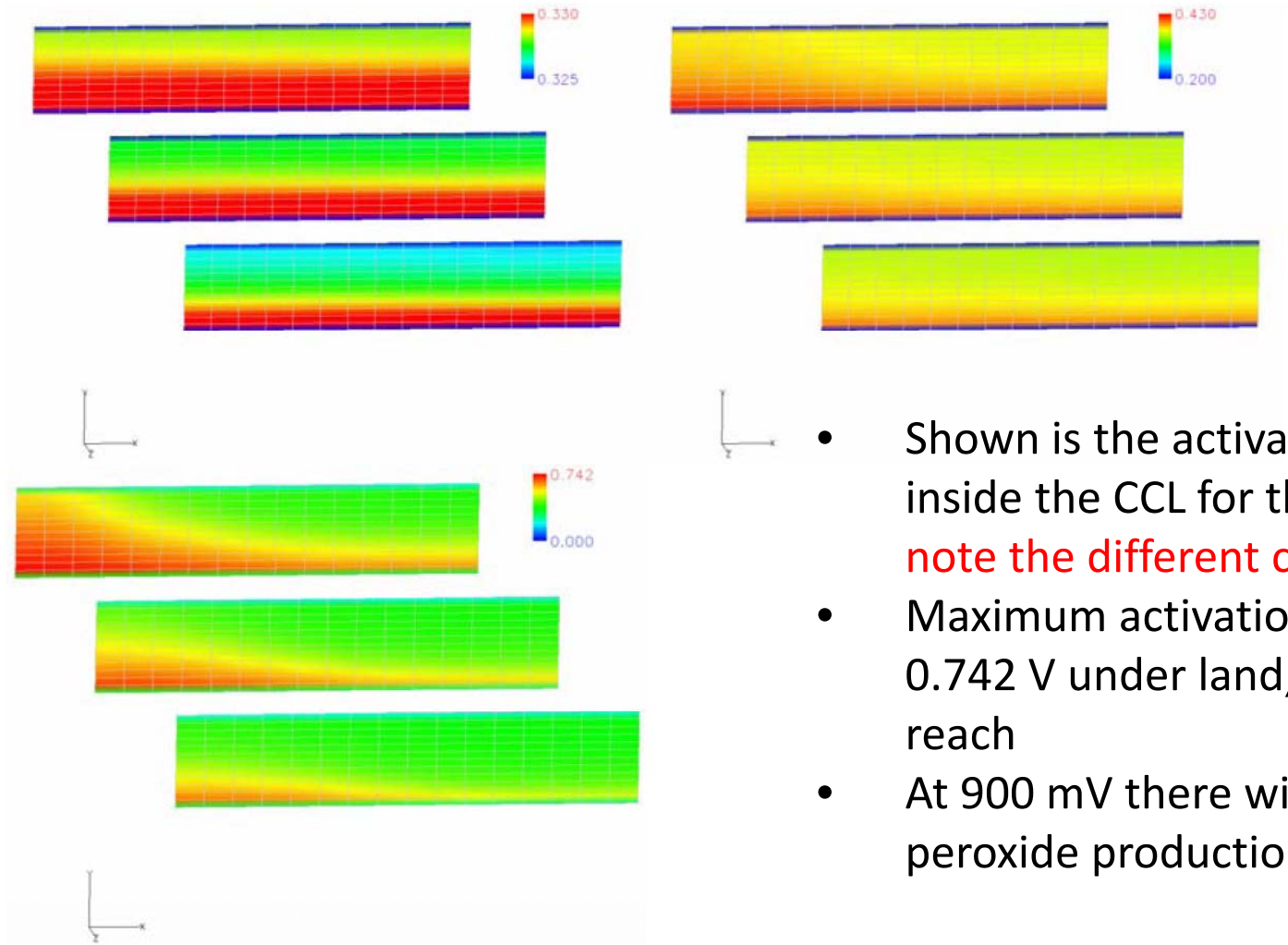


Sample results, Bang (AAU Dissertation), 2001



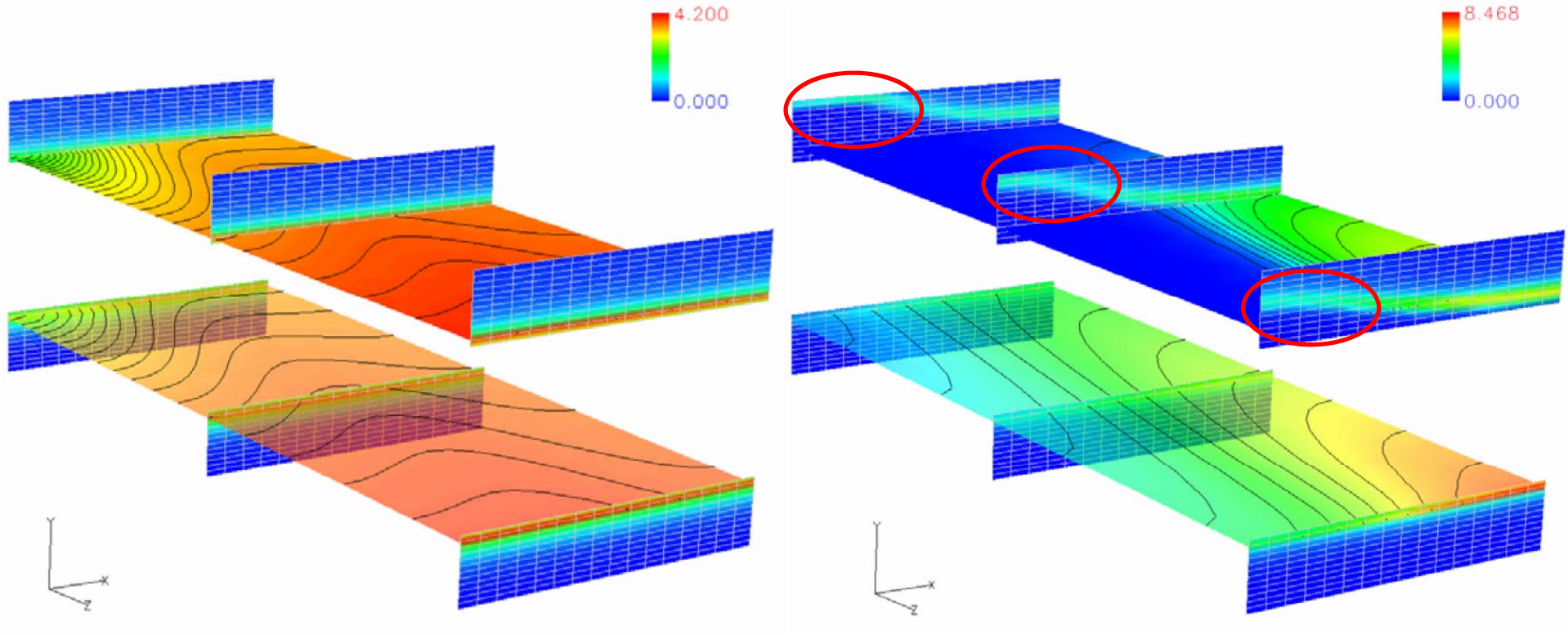
- Same three load cases showing the mass fraction of oxygen inside the cathode catalyst layer (CCL)
- Last case shows almost no oxygen inside CCL due to mass transport limitations,
- Predicted cell voltage was 0.03 V

Sample results, Bang (AAU Dissertation), 2001



- Shown is the activation overpotential inside the CCL for the three load cases, note the different color scales!
- Maximum activation overpotential is 0.742 V under land, where oxygen can not reach
- At 900 mV there will be hydrogen peroxide production (not predicted here)

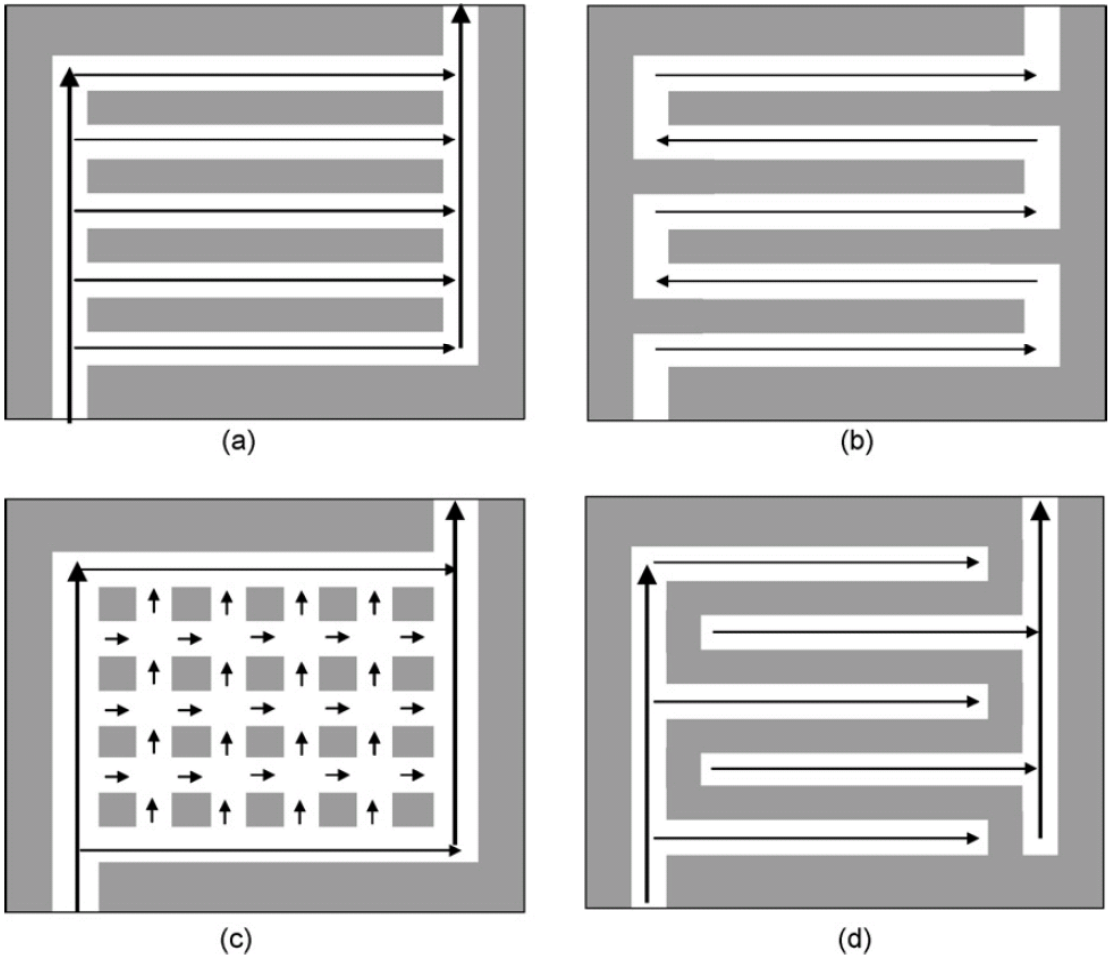
Sample results, Bang (AAU Dissertation), 2001



- Current density distribution for medium load case (left) and high load case (right)
- At high load current density moves away from the membrane due to mass transport limitations, giving rise to high activation overpotential and ohmic losses

General PEMFC question: Which flow field?

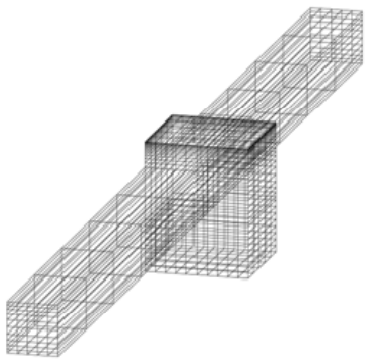
- Flow field options include parallel, serpentine, … and interdigitated.
- General consideration:
  - Pressure drop,
  - Reactant transport,
  - Contact resistance
  - Velocity, two-phase behaviour
- Ideal case for CFD if the model includes all major effects.



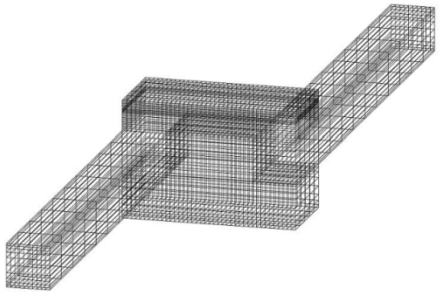
Source: Y. Wang et al., J. Power Sources 179, 2008

Use AAU multi-phase model to investigate two options

- New AAU PEMFC model with multi-phase capabilities, study published 2010.
- Modeling domain is cathode only, and in included:
  - three-dimensional catalyst layer (CL),
  - micro-porous layer (MPL)
  - gas diffusion layer (GDL)
  - gas channel (GC)
  - bipolar plate (BP)
- Active area is 1 mm long and discretized by 5 cells in flow direction to keep problem two-dimensional.



"conventional"



"interdigitated"

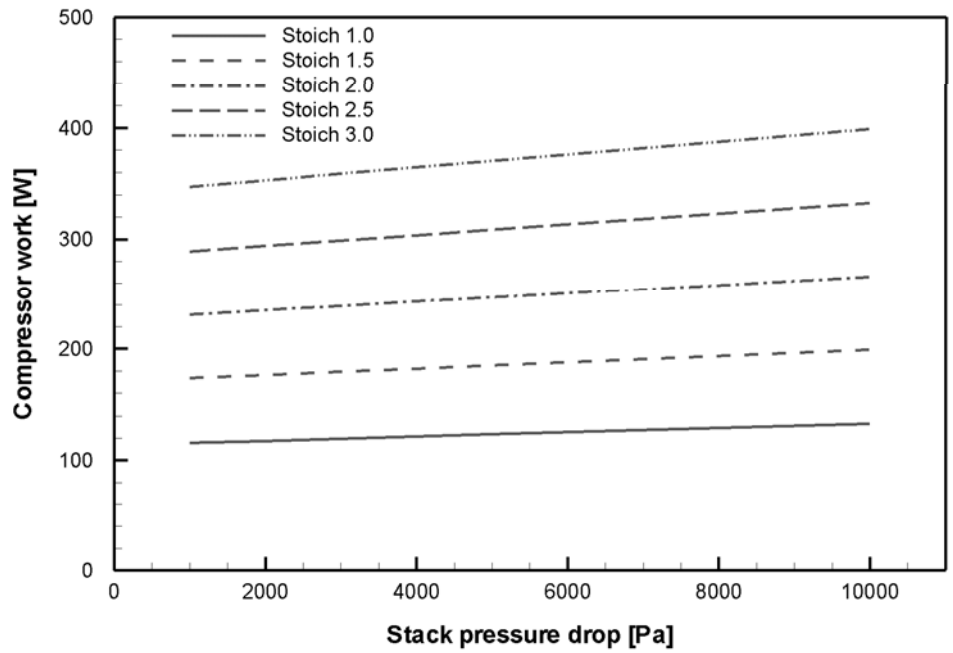
Source: Berning et al., J. Power Sources, 195, 2010.

Additional aspects of FC design: Compressor work

- The (air) compressor work is the highest parasitic load in a fuel cell system!
- Required compressor power depends on pressure drop and mass flow rate (stoich), but …
- Dependence on mass flow rate (stoich) is much stronger than on pressure drop (see right).

➢ The interdigitated flow field allows for low stoichiometry operation and hence may be advantageous over the conventional parallel flow field.

$$W_{compr} = 1004 \frac{J}{kg-K} \frac{293K}{\zeta_{compr}} \left[\left(\frac{1.5atm}{1.0atm} \right)^{0.286} - 1 \right] \dot{m}$$



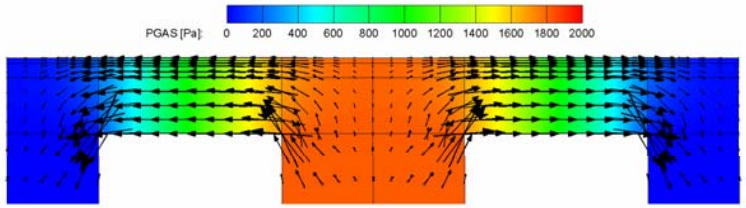
Back-of-envelope calculation for 5 kW stack

Source: Berning et al., J. Power Sources, 195, 2010.

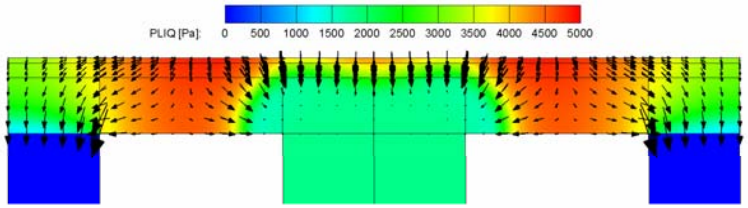
Sample CFD multi-phase results for interdigitated flow field

1.0 A/cm^2, RH_{in} 75 %, Stoich = 2.0

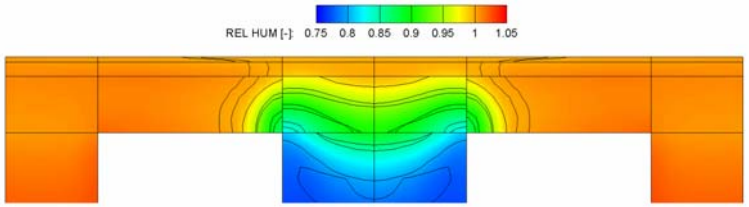
Gas phase pressure



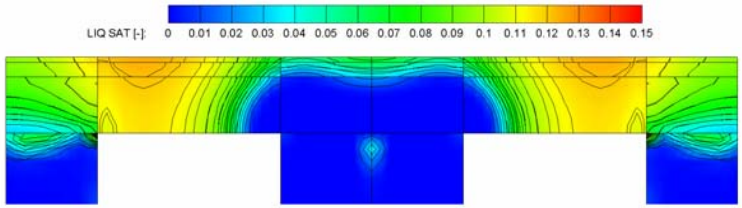
Liquid phase pressure



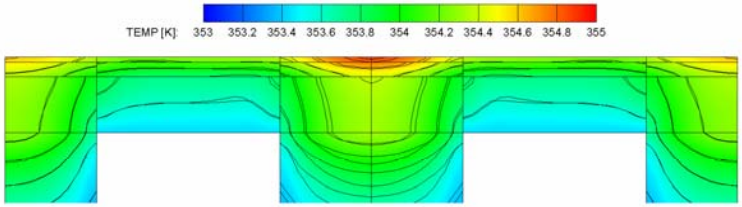
Relative Humidity



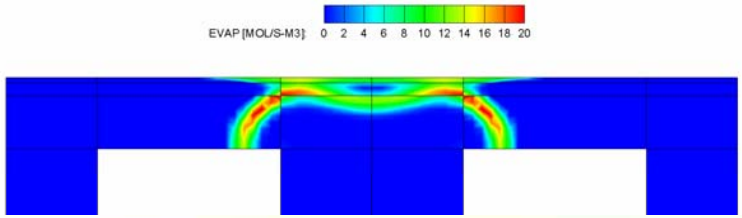
Liquid phase volume fraction



Temperature

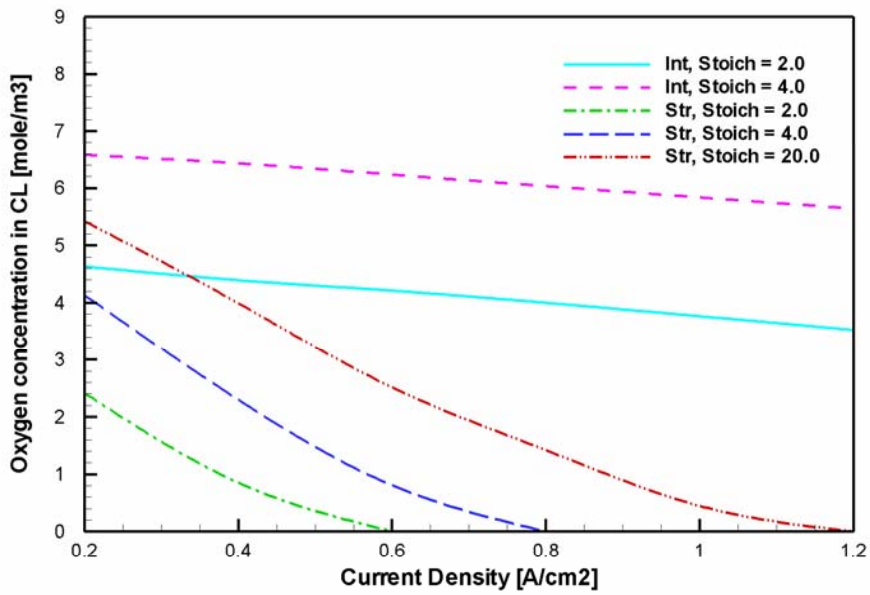


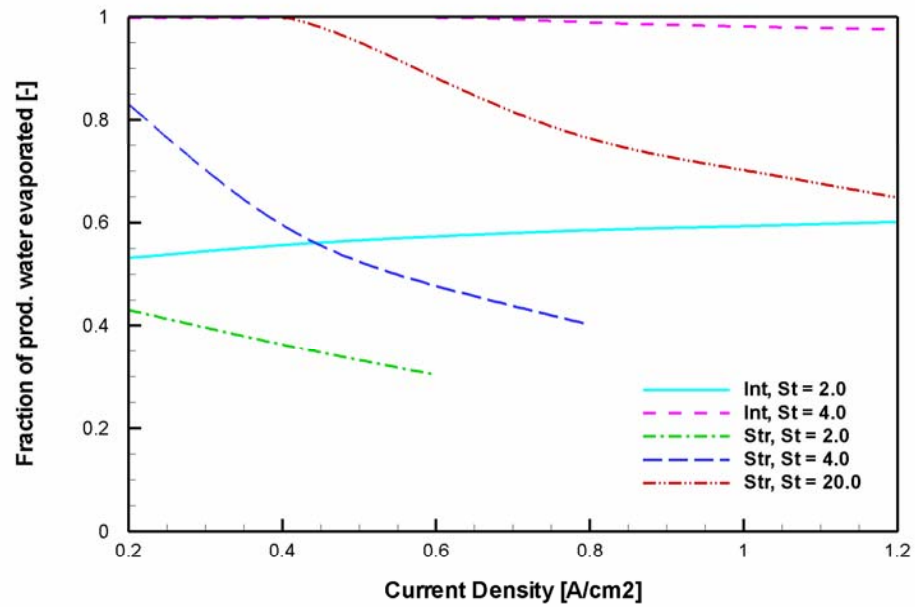
Rate of phase change



Source: Berning et al., J. Power Sources, 195, 2010.

Comparison betw. interdigitated and conventional flow field





- Compare two different flow fields at identical operating conditions, investigate two different stoichiometric flow ratios .
- Oxygen concentration in the interdigitated flow field does not drop off significantly with increasing current density.
- For increased inlet RH of 75 % more product water will leave the cell in the vapour phase for interdigitated flow field.

Source: Berning et al., J. Power Sources, 195, 2010.

Other notable publications

- Additonal publication of CFD models for fuel cells include:
  - Gurau
  - Djilali
  - Mazumder and Cole (CFD ACE)
  - … (MANY more)

Conclusions I

- CFD is a powerful tool for modeling three-dimensional, time dependent multi-phase and multi-species transport phenomena in flow channels and porous media that can:
  - ✓ Significantly reduce the number of experiments and hence safe cost and time and decrease the time to market of a new product
  - ✓ Significantly improve the fundamental understanding of transport phenomena as they occur e.g. in a fuel cell
  - ✓ Help to optimize the design and operating conditions of PEFC

Conclusions II

BUT

- Nearly all published CFD models of a fuel cell have insufficient physical models implemented because of a lack of fundamental understanding.
- A CFD model is only as good as its equations!
- There has been a bit of ”overselling” of (mostly commercial) fuel cell CFD models.
- There is the danger of conducting ”Colourful Fluid Dynamics”: It is easy to obtain a solution with today’s commercial CFD tools, and the user has to be very critical with his/her own results and ensure that this is the right solution to the problem.

➢ It is a very good practice to use a CFD model for the design of experiments: Try to identify a critical material parameter for fuel cell operation and help to design the right experiment in order to verify CFD finding.