Water management issues in PEMFC

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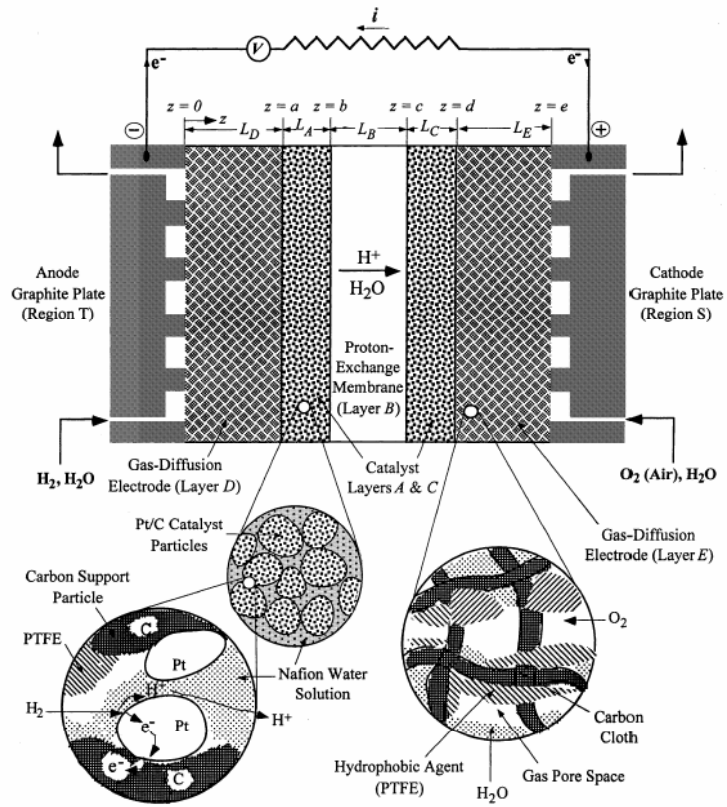
Outline

- Introduction to water management in PEFC
- Water transport issues in different PEFC regions/layers (and how to model it)
  - ❑ Flow channels/bipolar plates
  - ❑ GDL/MPL
  - ❑ CL/membrane
- What is ”flooding”
  - ❑ How can we detect it?
  - ❑ How can we avoid it?
- Calculating the dew point temperatures at the FC outlets
- Conclusions

INTRODUCTION TO WATER MANAGEMENT IN PEFC

Problems concerning water management

- In low temperature PEMFC we will typically encounter some liquid water.
- The membrane needs to be hydrated in order to stay proton conductive.
- Excessive liquid water may block the pores of the PTL and/or block the gas flow channels.
- What is the water balance between anode and cathode?
- What is the effect of the operating conditions on the occurrance of liquid water in a PEFC?
- Fundamental understanding of the water balance is required to model PEFC systems!

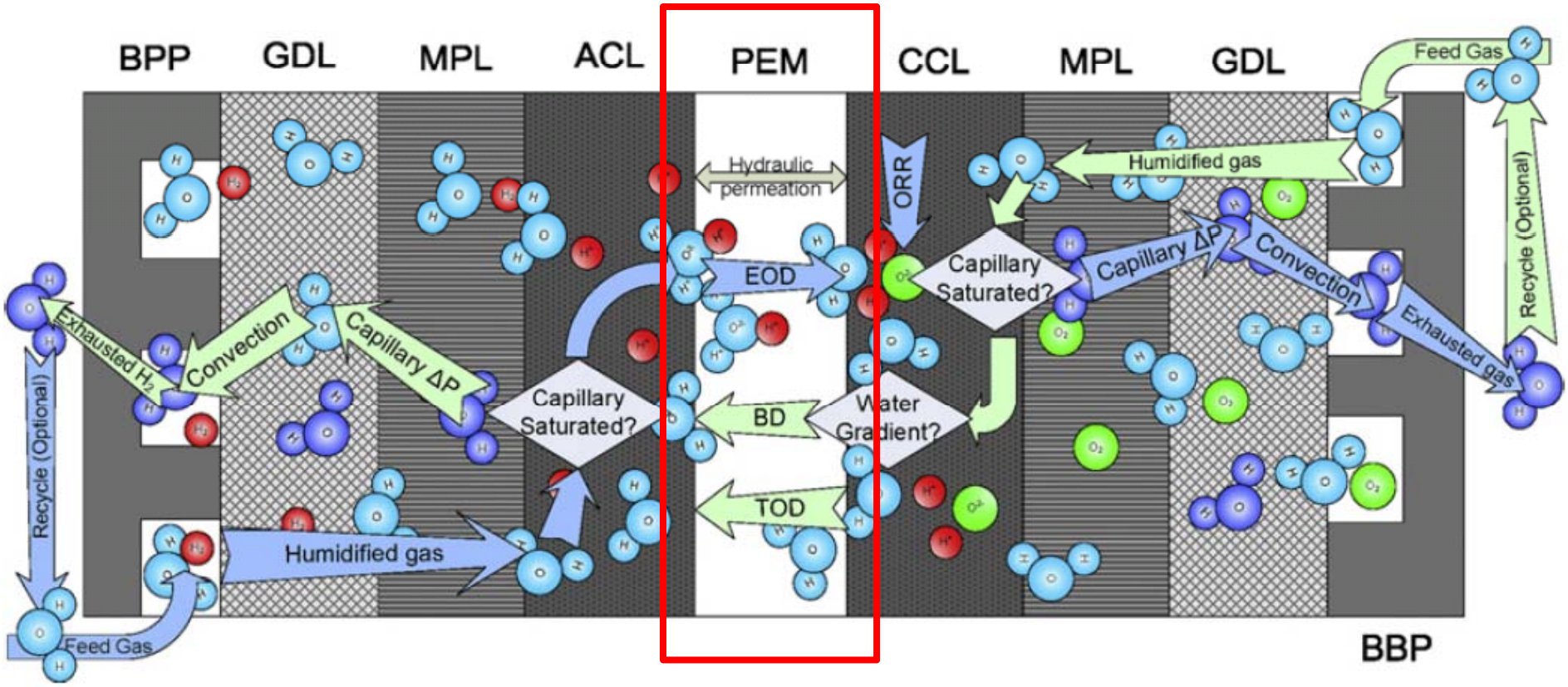


Source: Thampan, PEM Fuel Cell as a Membrane Reactor

Central questions concerning water management

- How much liquid water exists inside the porous media during operation?
- Under what conditions do we have a fully hydrated membrane and hence optimum performance?
- How can we quantify the detrimental effect of liquid water on the durability of the fuel cell?
- How does the water cross the membrane?
- How can we prevent the anode gas from drying out?

Water transport mechanisms in a PEMFC



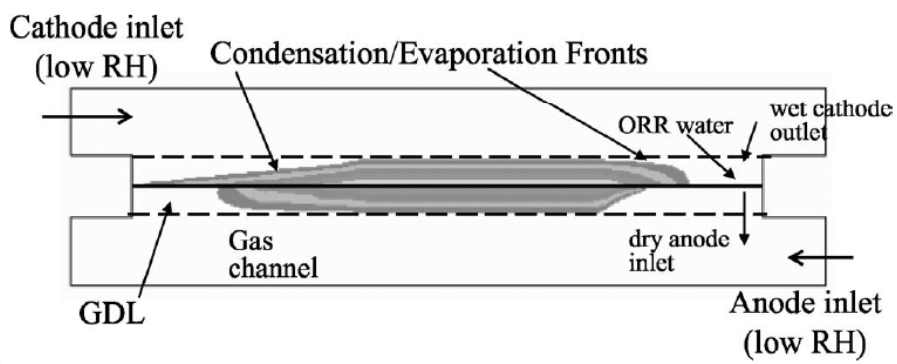
(Not fully correct!)

W. Dai et al., Int. J. Hydrogen Energy, 34, 9461-9478, 2009

WATER TRANSPORT ISSUES IN DIFFERENT PEFC REGIONS/LAYERS

Flow channels and bipolar plate

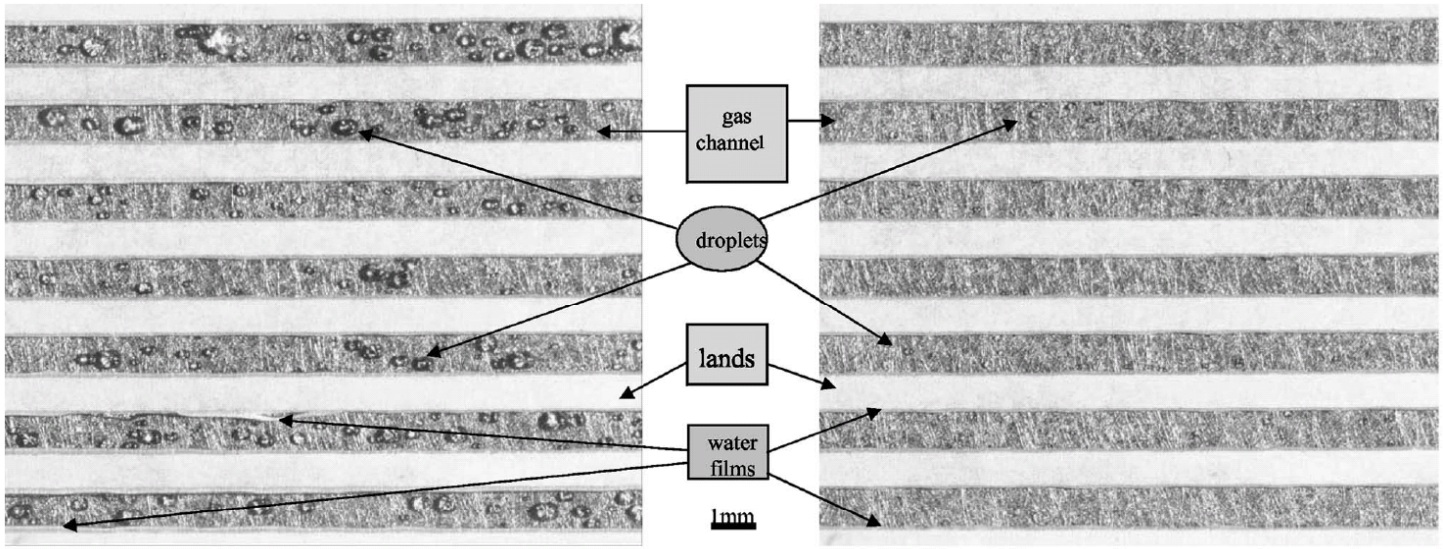
- Inside the flow channels the predominant transport mechanism is convection.
- Usually the inlet gases are pre-humidified (e.g. 50 % RH at 80 °C, …) adding cost and complexity to the system.
- Somewhere inside the cell the local RH will exceed 100 % and liquid water will occur.
- When local RH exceed 100 % there will be multiphase flow inside the channels.
- Liquid water can partially block some channels and lead to uneven reactant distribution and hence reduce durability.
  - ➢ It is very important to feed to reactants evenly and control the local temperature!



G. Luo, H. Ju & C.-Y. Wang, J. Electrochem. Soc. 154, 2007

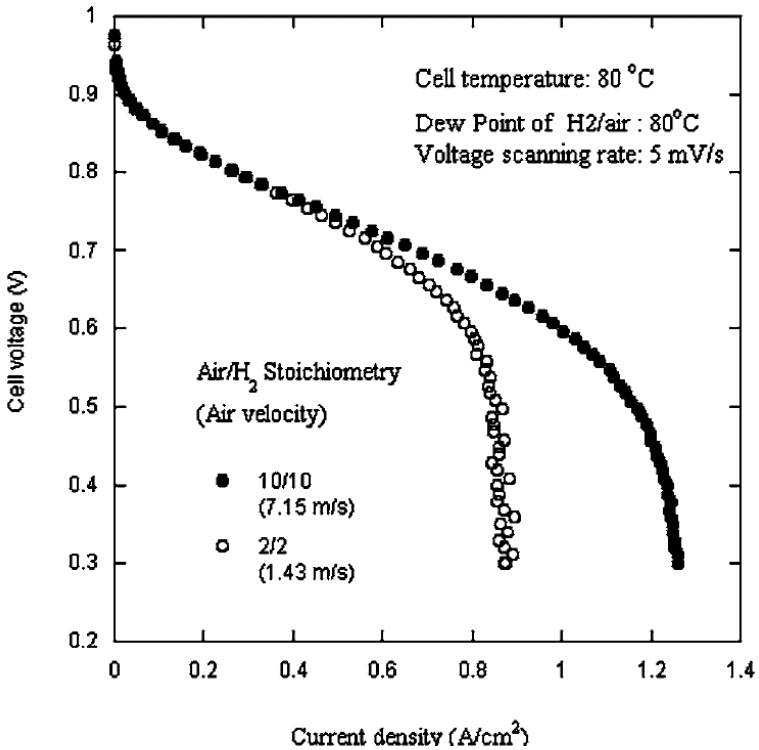
Flow channels and bipolar plate

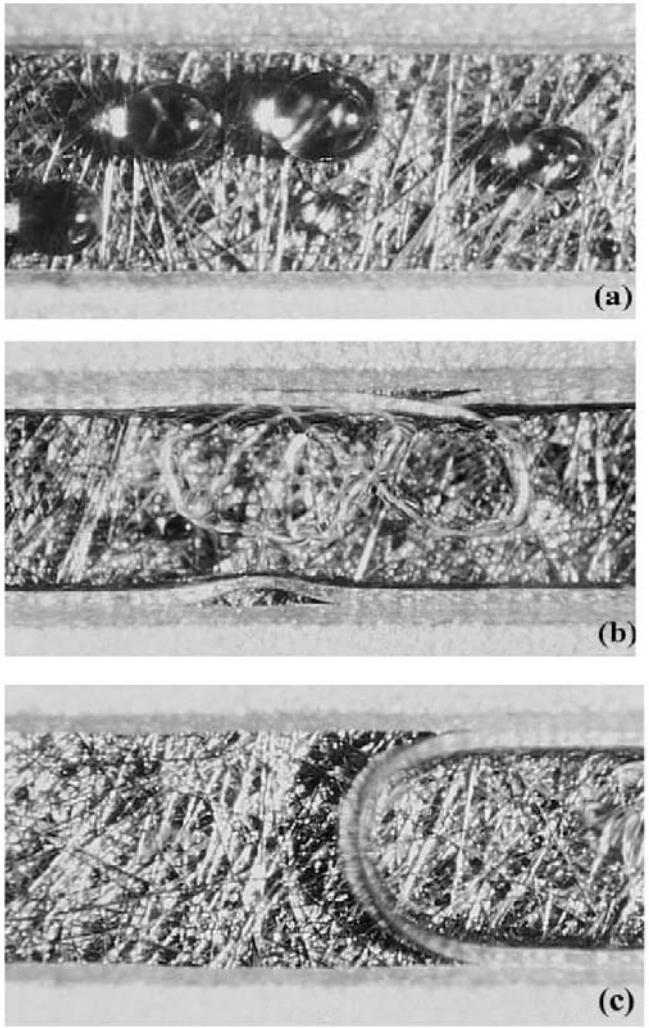
- When the local RH exceeds 100 % liquid water will enter the cathode channel coming from the cathode catalyst layer (CCL).
- Experimental observation: liquid water enters the channel periodically in form of droplets in certain ”preferred” locations.
- Droplet of a certain diameter will be sheared off by the main flow at a certain critical velocity.



F. Y. Zhang, X. G. Yang, C.-Y. Wang, J. Electrochem. Soc. 153, 2006

Flow channels and bipolar plate

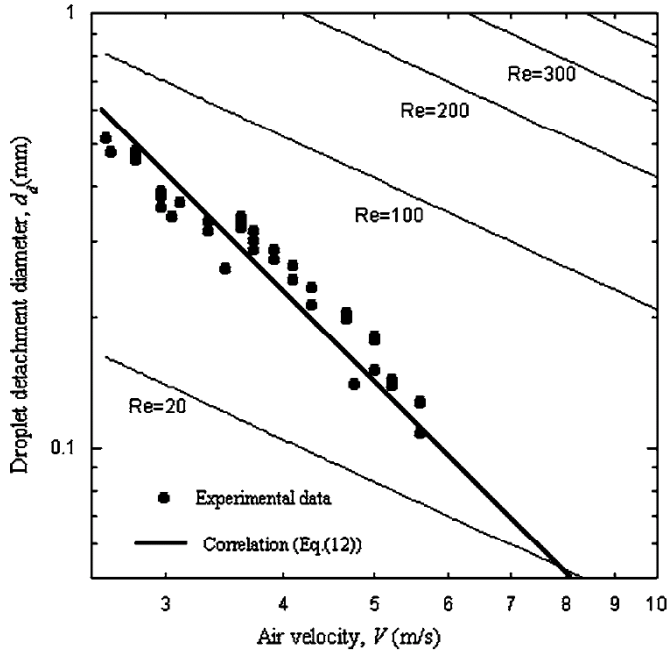


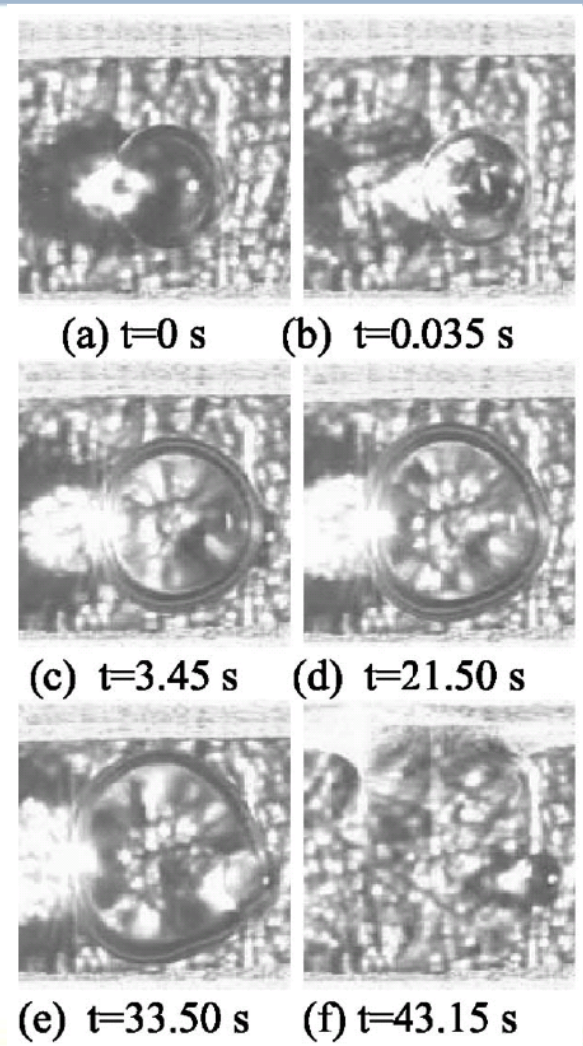


- Different channel velocities will lead to different flow regimes and cell performance.

F. Y. Zhang, X. G. Yang, C.-Y. Wang, J. Electrochem. Soc. 153, 2006

Flow channels and bipolar plate





Remedies:

- Increasing the flow velocity (higher compressor power) and/or using hydrophilic bipolar plates will reduce the partial channel blocking.
- Operate the cell dryer in order to avoid channel flooding.

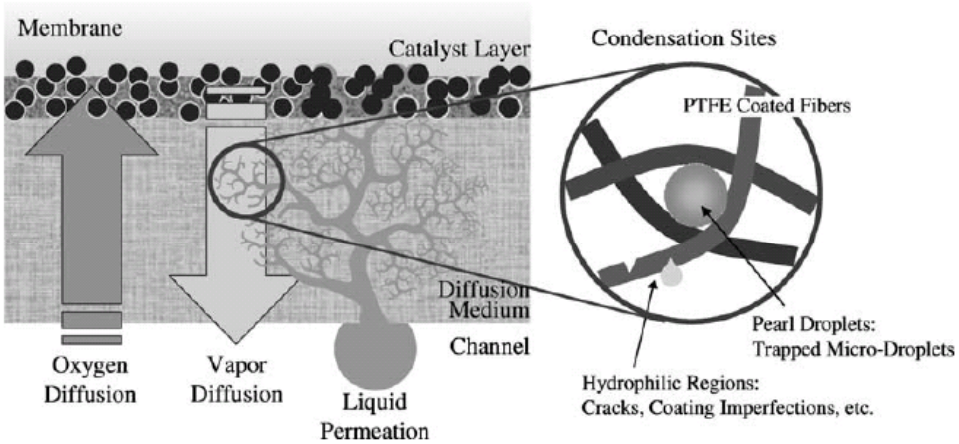
F. Y. Zhang, X. G. Yang, C.-Y. Wang, J. Electrochem. Soc. 153, 2006

Porous Layers: GDL, MPL and CL

- Inside the porous layers water can block the pores and prevent the reactants from reaching the CL.
- There will be liquid water if the local RH exceeds 100 %.
- The water transport inside the porous media is:
  - Gas phase: Diffusion and/or convection (e.g. interdigitated flow field)
  - Liquid phase: Capillary action

Questions:

- How much water will accumulate inside the porous layers during FC operation?
- Which material parameters play a dominant role and how can we thus modify the porous media?



Source: Nam and Kaviany, Int. J. Heat and Mass Transfer, 46, 2003.

First mode of mass transfer: Diffusion

- In general we talk about diffusion only in a multi-component system (i.e. oxygen, nitrogen and water vapor at the fuel cell cathode or hydrogen and water vapour at the anode).
- Fick's law of diffusion states that the rate of diffusion is proportional to the driving force and the diffusion coefficient, similar to Fourier's law of heat conduction:

"Proportionality coefficient":
Binary diffusion coefficient of species i and j,
[m^2/s]

$$J_i = -D_{i,j} \frac{\partial C_i}{\partial x}$$

Flux of species i,
[moles/(m^2-s)]

"Driving force":
Species concentration gradient,
[(moles/m^3)/m]

Diffusion in a porous medium

- Gas phase diffusion inside a porous medium (e.g. of oxygen) occurs through the open pores.
- The diffusivity is reduced by the fiber tortuosity ("windiness") and the presence of liquid water inside the open pores according to:

$$D_{O_2,air}^{eff} = D_{O_2,air}\left(\frac{\varepsilon}{\tau}\right)g(s)$$

Porosity of PTL

Specified function of liquid saturation (volume fraction)

e.g. $g(s)=(1-s)^{2.3}$

Effective diffusion coefficient inside porous medium

Binary diffusion coefficient (e.g. oxygen in air)

Tortuosity of PTL

Second mode of mass transfer: Convection

- Species convection is the movement of a species due to the bulk velocity $\vec{v}$
- Hence, the driving force for species convection is the pressure gradient

Bulk velocity, e.g. of gas phase
[m/s]

$$J_i = \vec{v} c_i$$

Flux of species i,
[moles/(m^2-s)]

Species concentration, [(mole/m^3)]

Convection in porous media

- Inside the porous media the momentum equations used to calculate the velocity profile reduce to Darcy's law, e.g.:

$$u_x = -\frac{k_x}{\mu}\frac{\partial p}{\partial x}$$

u_x:	*x-velocity of fluid*	*[m/s]*
k_x:	*hydraulic permeability of porous medium*	*[1/m²]*
μ:	*dynamic viscosity of fluid*	*[Pa/s]*
$\partial p/\partial x$:	*pressure drop of fluid*	*[Pa/m]*

Liquid transport in porous media – Capillary action

- To understand liquid water transport by capillary action we can start with Darcy's law of the liquid phase:

$$\vec{u}_l = -\frac{k_l}{\mu_l}\nabla p_l$$

- The definition of capillary pressure is:

$$p_c = p_{nw} - p_w = p_l - p_g$$

p_{nw}: *pressure of non-wetting phase (e.g. water in hydrophobic pores)*

p_w: *pressure of wetting phase (e.g. gas phase in hydrophobic pores)*

Liquid transport in porous media – Capillary action

- This yields: $$\vec{u}_l = -\frac{k_l}{\mu_l}\nabla p_g - \frac{k_l}{\mu_l}\nabla p_{cap}$$

- Also, for multi-phase convection in porous media we have relative permeabilities for each phase, e.g.:

$$\vec{u}_l = -\frac{k_{rel}K_{dry}}{\mu}\nabla p_g - \frac{k_{rel}K_{dry}}{\mu}\nabla p_{cap}$$

$$= -(1-s)^3\frac{K_{dry}}{\mu}\nabla p_g - s^3\frac{K_{dry}}{\mu}\nabla p_{cap}$$

s: *"liquid saturation",*
the fraction of open pore volume occupied by the liquid phase

K_{dry}: *dry permeability of the porous medium*

Liquid transport in porous media – Capillary action

- The definition of the capillary pressure inside the porous medium is:

$$p_{cap} = \sigma \cos\phi \left(\frac{\varepsilon}{K}\right)^{0.5} J(s)$$

σ: *Surface tension between gas and liquid phase, 6.25×10^{-2} N/m*
ϕ: *effective contact angle of hydrophobic pores ($\phi > 90°$)*
ε: *porosity of porous medium*
K: *dry permeability of porous medium, m^2*
J(s): *dependency on the saturation, frequently assumed cubic function of s, depends on pore-size distribution!*

Notes:

1. *The order of magnitude of the fuel cell porous media permeability is often around 10^{-12} m^2, and this is called 1 Darcy.*
2. *The square-root of porosity ε divided by permeability K has the unit of 1/m, and this is the characteristic pore size of the porous medium $1/r_c$.*

Liquid transport in porous media – Capillary action

- Combining the last equations yields for the flow in porous media:

$$\vec{u}_l = -(1-s)^3 \frac{K_{dry}}{\mu_l} \nabla p_g - s^3 \frac{K_{dry}}{\mu_l} \nabla p_{cap}$$

$$= -(1-s)^3 \frac{K_{dry}}{\mu_l} \nabla p_g \underbrace{- s^3 \frac{K_{dry}}{\mu_l} \frac{\partial p_{cap}(s)}{\partial s}}_{\text{"Capillary diffusivity" } [m^2/s]} \nabla s$$

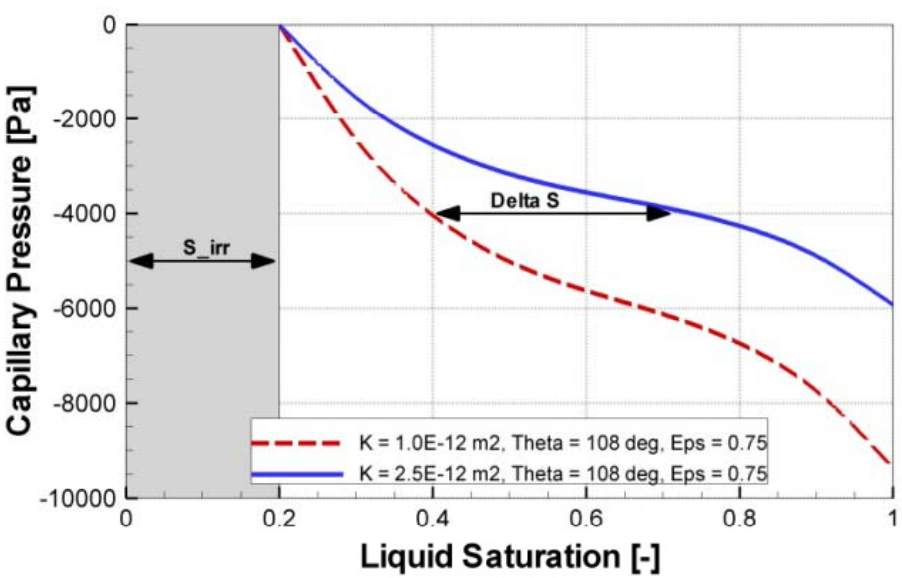
- The nature of capillary transport is similar to diffusion: from regions of high saturation to regions of low saturations.
- The functional dependency between the capillary pressure and the saturation $p_{cap}(s)$ is frequently described by the Leverett function.

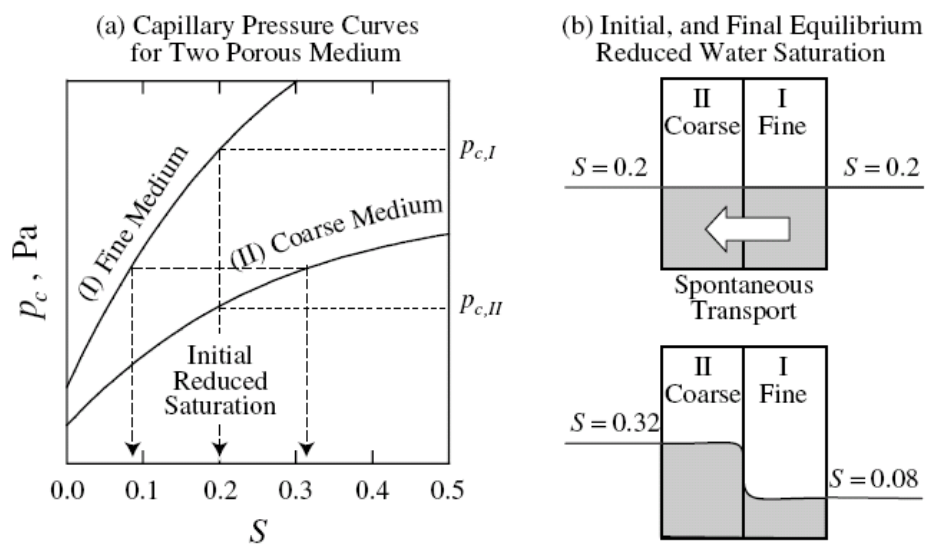
The capillary pressure as function of liquid saturation *S*

- Shape curve of Leverett equation J(s), written as function of <u>reduced saturation</u>:

$$J(S)=\begin{cases}1.417(1-S)-2.120(1-S)^2+1.263(1-S)^3;\theta<90^\circ\\ 1.417S-2.120S^2+1.263S^3;\theta>90^\circ\end{cases}\qquad S=\frac{s-s_{irr}}{1-s_{irr}}$$

- The irreducable saturation s_{irr} does not contribute to the capillary transport.
- The capillary transport of the water is through the hydrophobic pores!

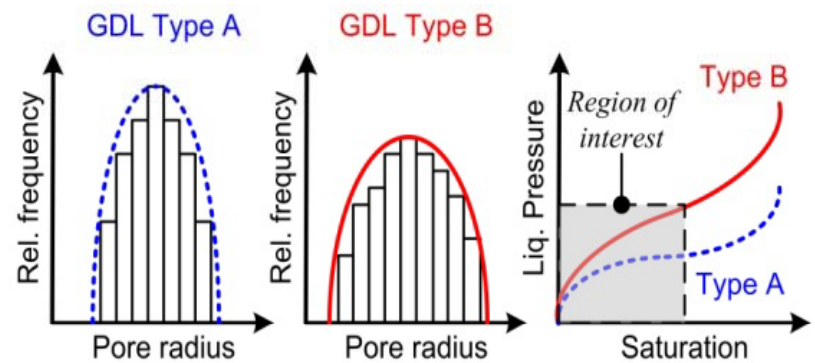




Nam & Kaviany, Int. J. Heat Mass Transfer, 2003.

Importance of pore size distribution – A theory

- Consider two different porous media
  - Blue: narrow pore-size distribution (PSD)
  - Red: wider pore-size distribution (PSD)



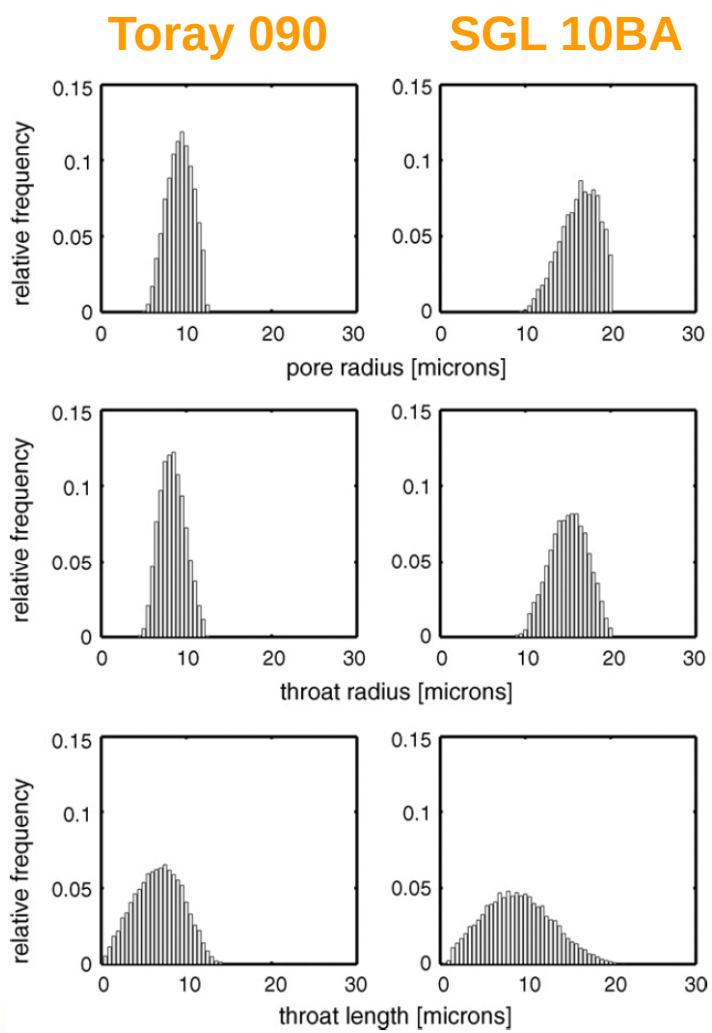
- Young-Laplace Eq.: $$P_{cap} = \frac{2\sigma\cos\theta}{r}$$
- Resulting Leverett functions, qualitatively:
  - As the PSD is narrow for the blue case, there is a smaller driving force for the liquid phase inside GDL.

- Thought experiment: Imagine a porous medium where all pores have exactly the same size and shape.
  - ➢ The capillary pressure is uniform everywhere and no function of the saturation, so there would be no driving force for the liquid phase, the porous medium would become flooded!

Source: Berning et al., J. Electrochem. Soc., 2009

GDL Characterization: Pore Size Distribution

- Different types of porous media of different material characteristics and different water management behaviour.
- A central question is, how the different material properties affect the cell performance and the water management.
- Two very commonly used types are Toray 060/090 or SGL type which may vary in thickness.
- SGL has a more irregular structure with a wider pore size distribution (”Type B”).



J. T. Gostick et al., J. Power Sources 173, 277-290, 2007

Neutron Radiography (NR) to detect liquid water

- With NR the amount of water inside the operating fuel cell can be detected and the film thickness quantified.
- Result is typically given in ”water mass per cm^2”, postprocessing required.
- Only 2D information available, but through-plane and in-plane measurements are possible.

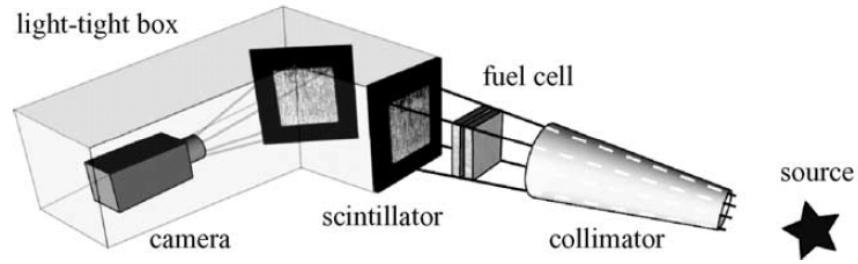
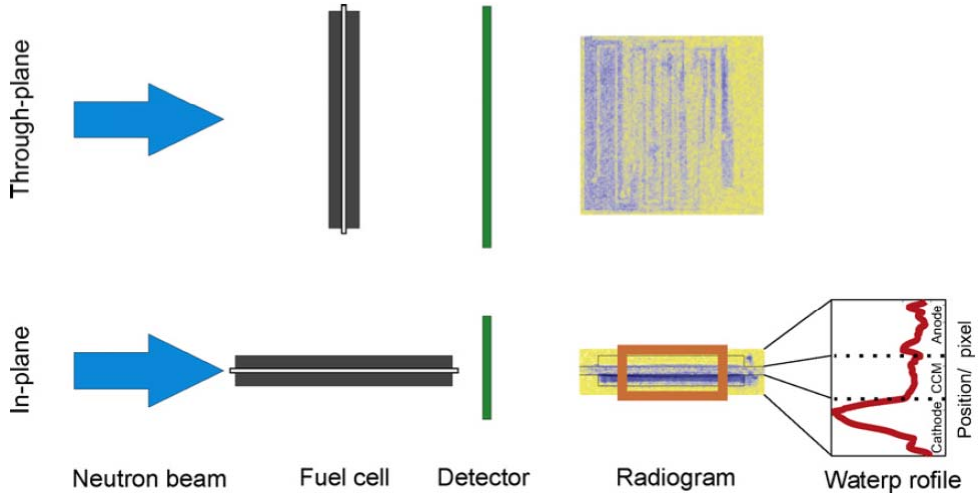


Fig. 1. Schematic drawing of the experimental setup for neutron radiography.

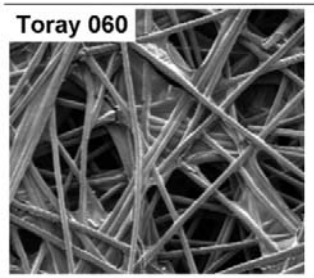
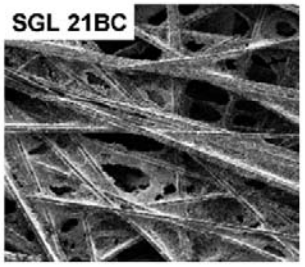
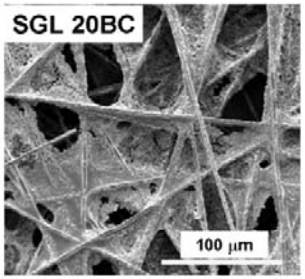
Kramer et al., Electrochim. Acta 50, 2005



Seyfang et al., Electrochim. Acta 55, 2010

Experimental study of GDL impact

Table 1
Physical properties of gas diffusion layers

	Thickness (μm)	MPL	Porosity (%)	Substrate PTFE (mass%)	In-plane gas permeability[a,b]		Through-plane thermal resistance[c] (m^2 K/W)
					(μm^2)	(darcy)	
Toray 060 	190	No	78	7	5.25	5.32	$1.12E-04$
SGL 21BC 	260	Yes	79	5	3.16	3.20	$5.13E-04$
SGL 20BC 	260	Yes	76	5	1.10	1.11	$3.98E-04$

J. P. Owejan et al., Int. J. Hydrogen Energy 32, 4489-4502, 2007

Experimental study of GDL impact

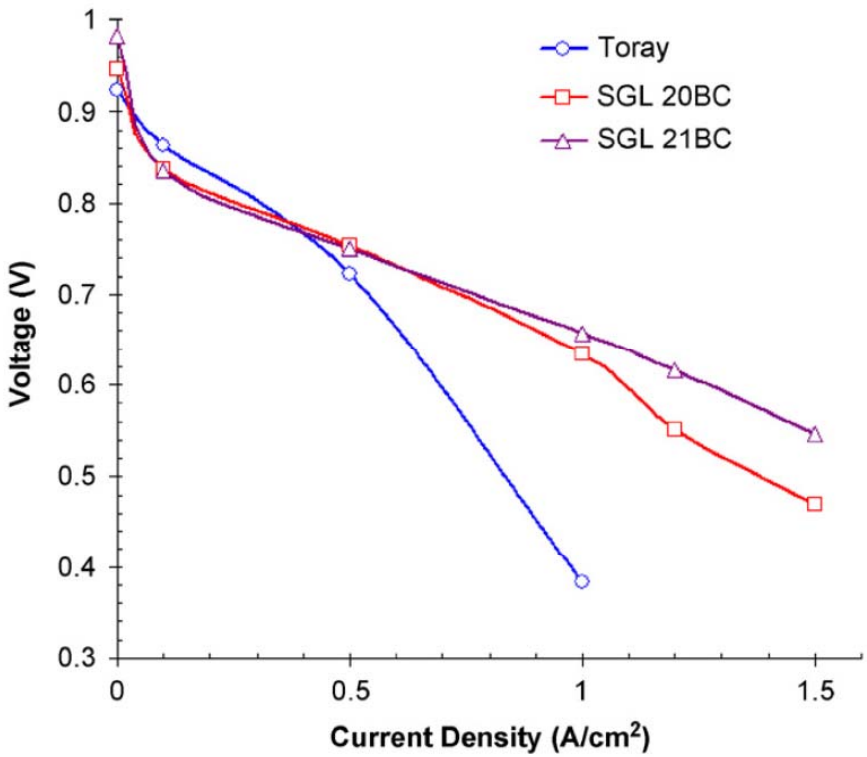


Fig. 4. Performance comparison among GDL materials.

- Example: Performance under "wet" operating conditions show that SGL is typically better than Toray.

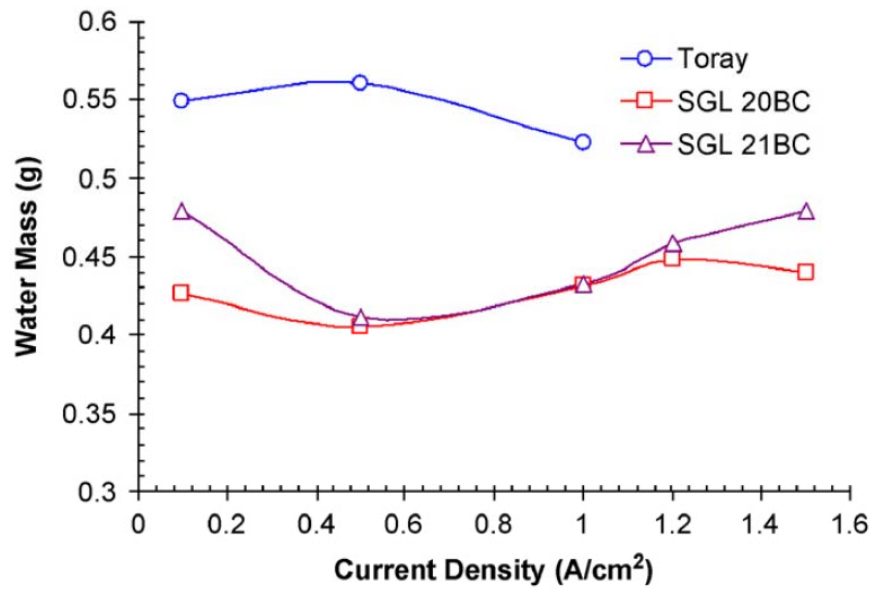


Fig. 7. Total water mass variation with current density.

- One likely reason for the worse cell performance is that the cell contains much more liquid water in the case of Toray paper.

J. P. Owejan et al., Int. J. Hydrogen Energy 32, 4489-4502, 2007

Experimental study of GDL impact

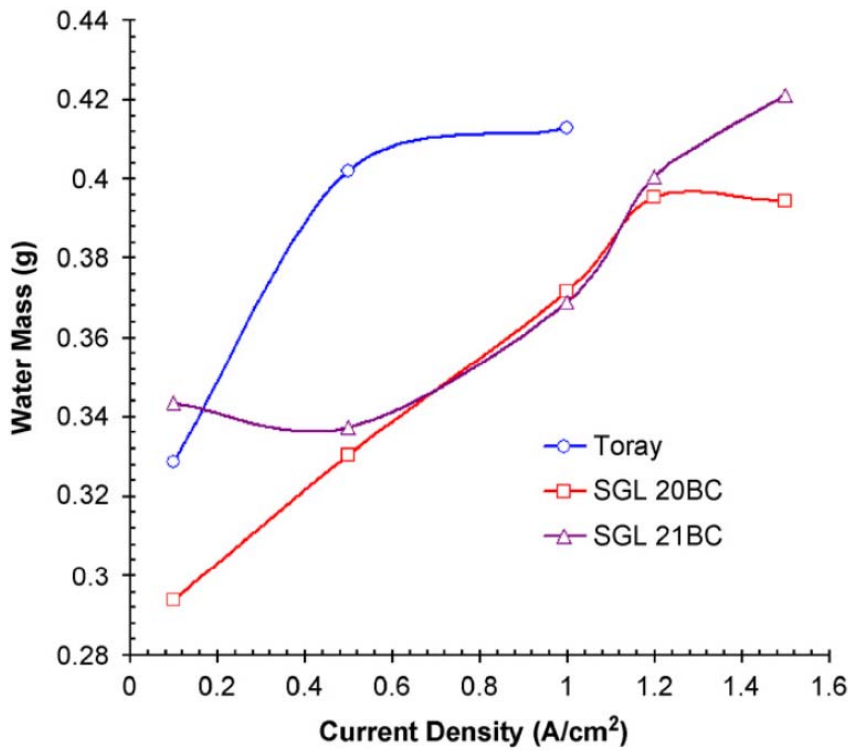


Fig. 10. Water mass in softgoods only, resulting from water separation procedure.

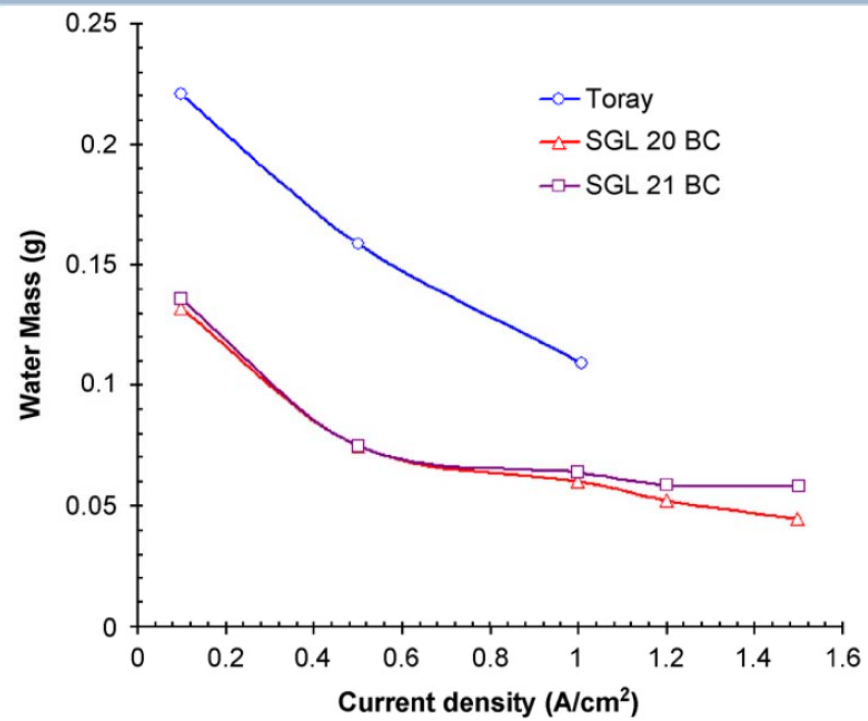


Fig. 11. Water mass in channels only, resulting from water separation procedure.

- Water mass inside the "softgoods" is higher for Toray paper.
- Water mass inside the channels is also higher for Toray, but decreases with increasing current density.

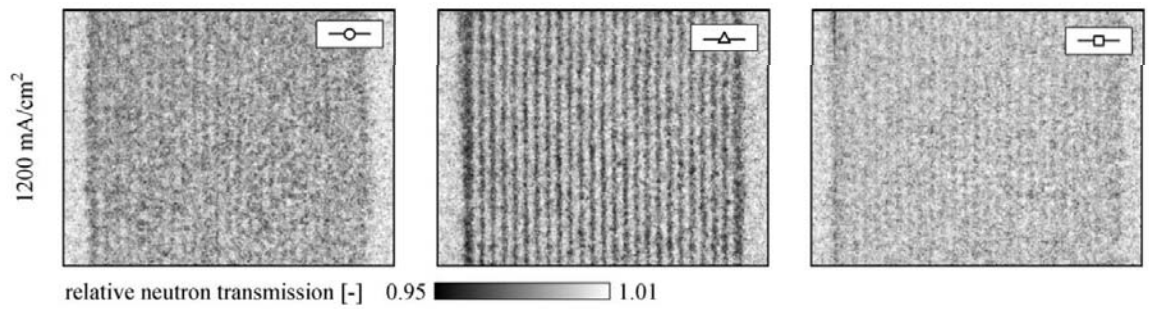
J. P. Owejan et al., Int. J. Hydrogen Energy 32, 4489-4502, 2007

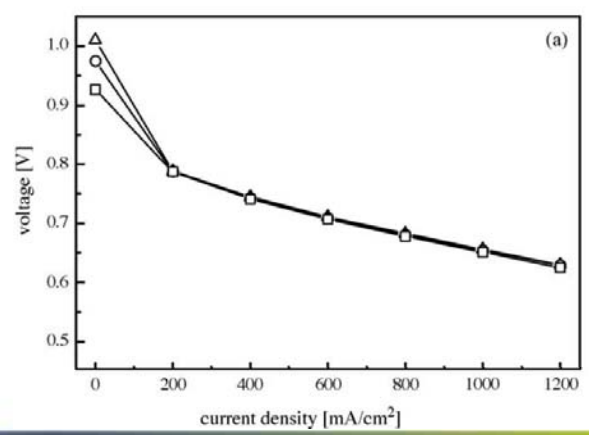
Neutron Radiography (NR) to detect liquid water

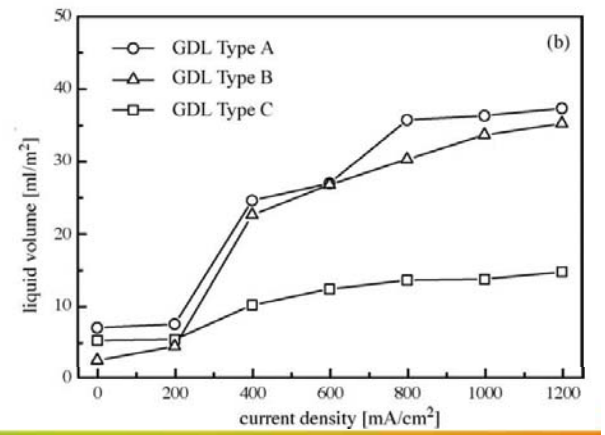
Table 1
Properties of investigated GDL materials

Property	Type A	Type B	Type C
Substrate	Paper	Paper	Cloth
Thickness (uncompressed) (μm)	300	300	400
Porosity (uncompressed) (%)	68	75	78
PTFE-content GDL (%)	17	5	0
PTFE-content MPL (%)	31	23	38

- Three different types of porous media studied.
- Strong land-channel variation in water thickness measured.
- No effect on fuel cell performance visible, but
- Effect on durability not understood.







J. Zhang et al., Electrochimica Acta 51, 2715-2727, 2006

Effect of GDL on liquid water and performance

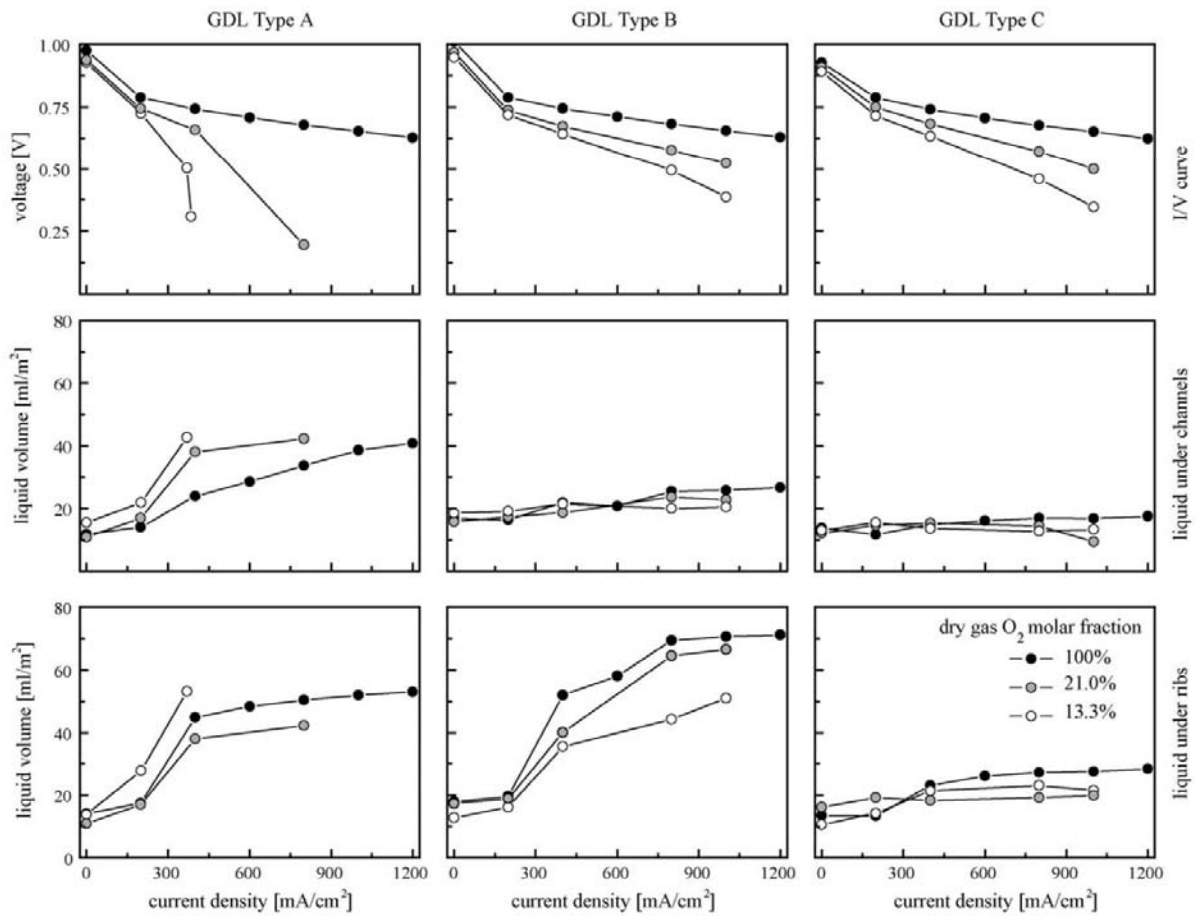


Fig. 8. Influence of oxygen molar fraction on liquid content, separated into rib (lower row) and channel area (middle row), and electrochemical performance (upper row) for different GDL materials applied at the cathode; the cell temperature is 70 °C; the relative humidity of anodic and cathodic gas feed is 80%, the anodic flow rate according to a stoichiometry of 18 for oxygen and air operation and 7 for diluted air; the cathodic flow rate corresponds to a stoichiometry of 150 for oxygen, 30 for air and 19 for diluted air; the exposure time is 10 s.

J. Zhang et al., Electrochimica Acta 51, 2715-2727, 2006

Measurements of liquid water distribution

LASER-PERFORATED FUEL CELL DIFFUSION MEDIA
PART I: RELATED CHANGES IN PERFORMANCE AND WATER CONTENT

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Under Review for publication

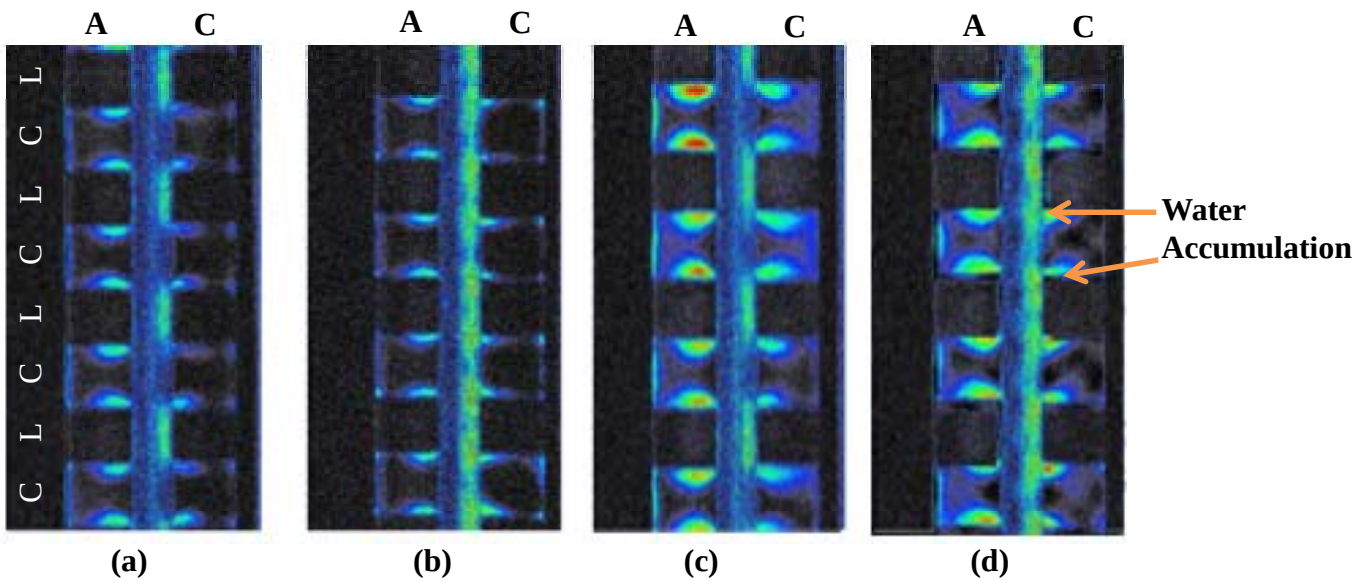


Figure 7. Neutron images from high humidity (100% inlet RH anode and cathode) testing showing (a) high current (1.2 A cm^{-2}) virgin DM, (b) high current perforated DM, (c) low current (0.2 A cm^{-2}) virgin DM, and (d) low current perforated DM. In each image, the right-hand-side is the cathode.

Courtesy of Prof. Matthew M. Mench, Pennsylvania State University

Summary

- In PEMFC we are likely to encounter liquid water inside the porous layers (Catalyst layer, micro-porous layer and “gas diffusion layer“ or “porous transport layer”).
- When the GDL is not treated with Teflon (PTFL), this liquid water will block the pores and prevent the reactants fom reaching the CL and so reducing fuel cell performance.
- In PTFL treated porous media the liquid water will travel through the hydrophobic pores via capillary action, this transport mechanism can me captured with a CFD code.

- Liquid water will also occur inside the flow channels due to local condensation, but this is typically not captured with a CFD code.

HOW DOES THE WATER CROSS THE MEMBRANE?

Water balance in a PEMFC

- Traditional thinking: Four different fundamental mechanisms of water transport through the membrane:
  - Electro-osmotic drag (EOD), always from anode to cathode
  - Back diffusion (BD) from cathode to anode
  - Hydraulic permeation (pressure driven), mostly from cathode to anode, often negligible compared to EOD and BD
  - ~~Thermo-osmotic drag (TOD), typically small due to small temperature gradients across membrane~~

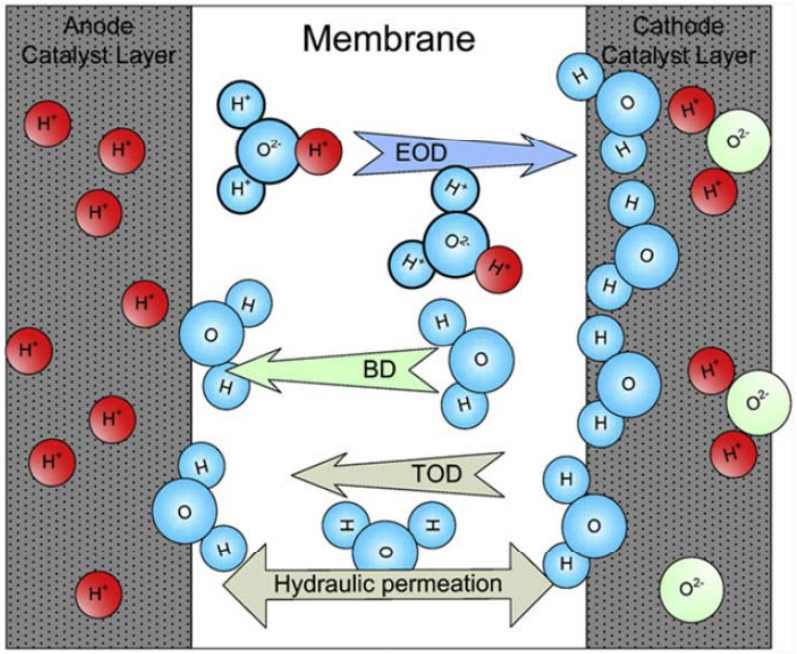
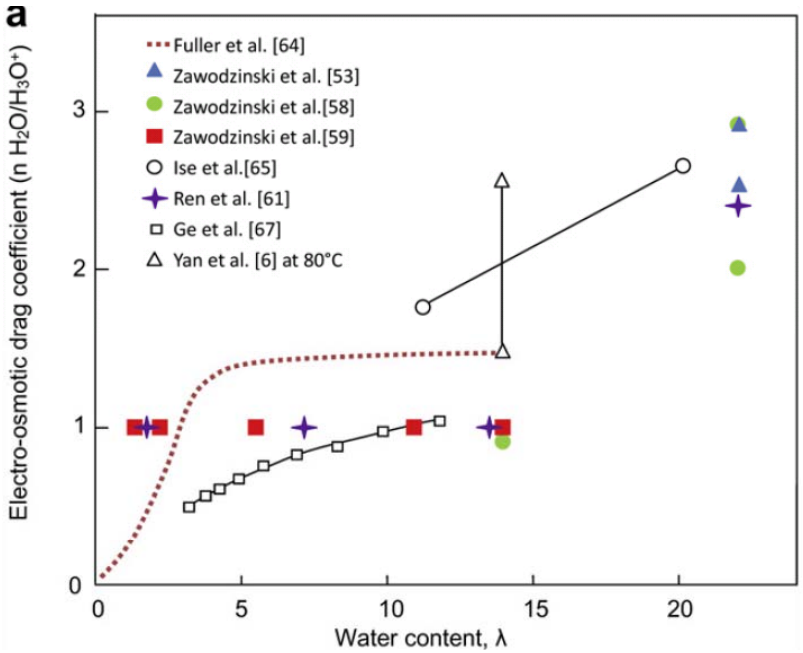


Fig. 4 – Water transport mechanism in proton exchange membrane (PEM).

W. Dai et al., Int. J. Hydrogen Energy, 34, 9461-9478, 2009

Electro-osmotic drag (EOD)

- Protons migrating through the membrane drag along water.
- Amount of water is significant, EOD coefficients of at least 1.0 and up to 2.5 have been determined.
- Note: Very credible groups have determined a constant EOD coefficient of 1 for a wide range of membrane hydration conditions!



- An EOD coefficient of 1 means that twice the amount of product water is dragged from anode to cathode!
- Drying out of the anode has to be prevented by allowing for sufficient back diffusion.

W. Dai et al., Int. J. Hydrogen Energy, 34, 9461-9478, 2009

Diffusion of water inside the membrane

- Driven by water concentration gradient (inside membrane).
- Diffusion coefficient depends on temperature and wetting state of the membrane (dimensionless membrane water content λ).
- Most research groups have determined a diffusion coefficient in the range of 10^{-6} cm^2/s.

➢ It can be shown that when only considering "EOD versus back diffusion" the effective (net) drag of water must be positive, i.e. from anode to cathode, back diffusion can not balance EOD!

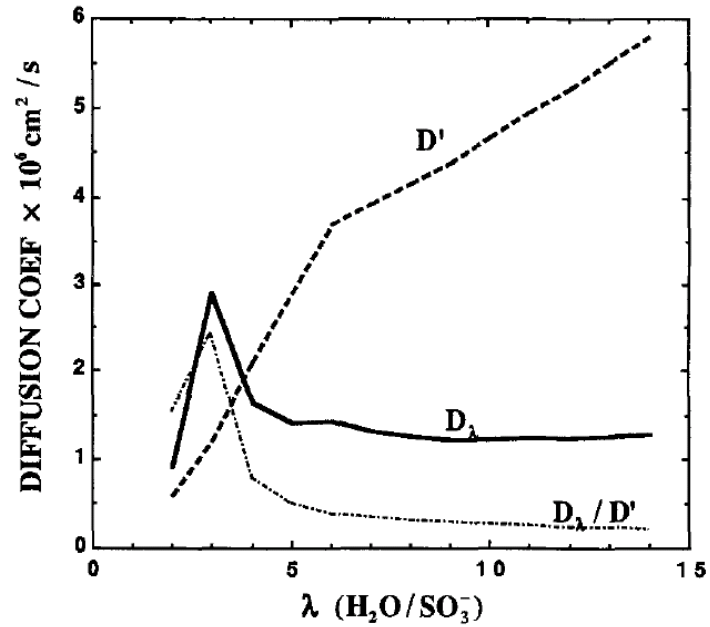
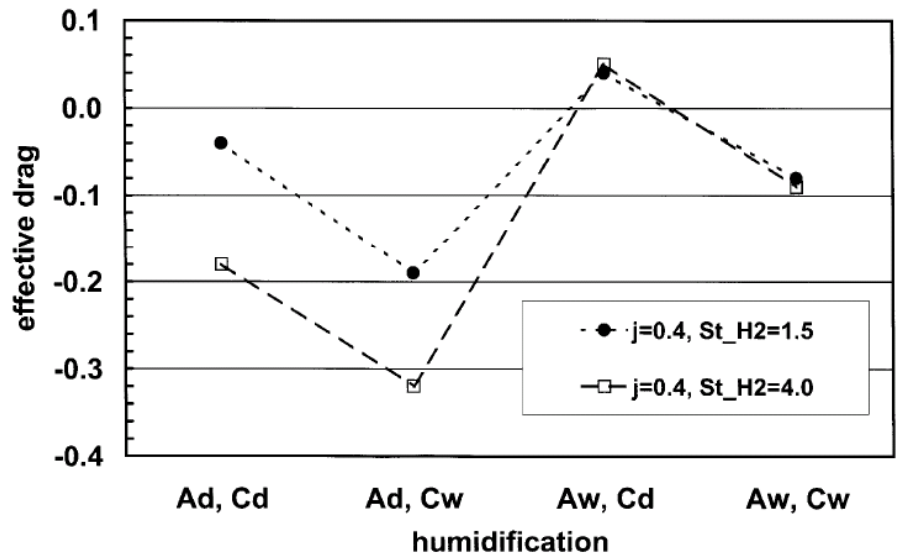


Fig. 3. Measured intradiffusion coefficient, D', at 30°C, the corrected diffusion coefficient, D_λ, and the correction factor, D_λ/D', calculated from measured activity and swelling, plotted against water content per charge site for Nafion 117.

Springer et al.,
J. Electrochem. Soc., 138, No. 8, 1991.

Net drag measurements

- Net drag can be either positive (anode to cathode) or negative, depending on operating conditions and materials.
- These experimental results can not be explained with the traditional theory!
- The traditional thinking that the predominant terms governing water transport through the membrane: EOD and ”back” diffusion, can not be correct.
- (Hydraulic permeation is small and can be neglected).



Janssen & Overvelde,
J. Power Sources 101, 117-125, 2001

➢ So how then does the water cross the membrane?

Water sorption/desorption kinetics

- More recent evidence indicates that overall amount of water transported across membrane is limited by sorption-desorption kinetics (not by diffusion), the detailed steps are:
  1. Absorption from gas/liquid to membrane
  2. Diffusion of water through the membrane
  3. Desorption from membrane to gas/liquid

- Absorption is slower than desorption and might be rate determining for thin membrane (< 100 μm).
- Overall absorption rate depends on the available surface area of electrolyte inside the CL.

➢ Specific electrolyte surface area (and CL thickness) are important parameters for overall water balance!

Ge et al., J. Electrochem. Soc., 153, A1443-A1450, 2006
Monroe et al., J. Mem. Sci., 324, 1-6, 2008

Transport of dissolved water inside membrane

- Conservation equation for dissolved water in CL and membrane:

$$\frac{\rho^{mem}}{EW} M_W \nabla \cdot \left(\underbrace{D_W^{mem}}_{\text{Diffusion coefficient}} \nabla \underbrace{\lambda}_{\text{Membrane water content}} \right) = \cancel{S_{\lambda(sorp/desorp)}} + \cancel{\nabla \cdot \left(n_d \frac{I}{F} \right) M_W}$$

- Sorption/desorption source terms only exist in catalyst layer
- Drag coefficient n_d is constant
  - ➢ last term vanishes inside membrane
- Pure diffusion of water inside electrolyte membrane phase
  - ➢ membrane is locally dryer at the side where the water diffuses to (mostly cathode side), <u>depends entirely on net drag coefficient!</u>

Water sorption/desorption term in CL

$$S_{\lambda(sorp/desorp)} = \alpha \times k_{abs/des}(T) \times \frac{\rho^{mem}}{EW} M_W \left\{ \lambda_{W,equil} - \lambda_W \right\}$$

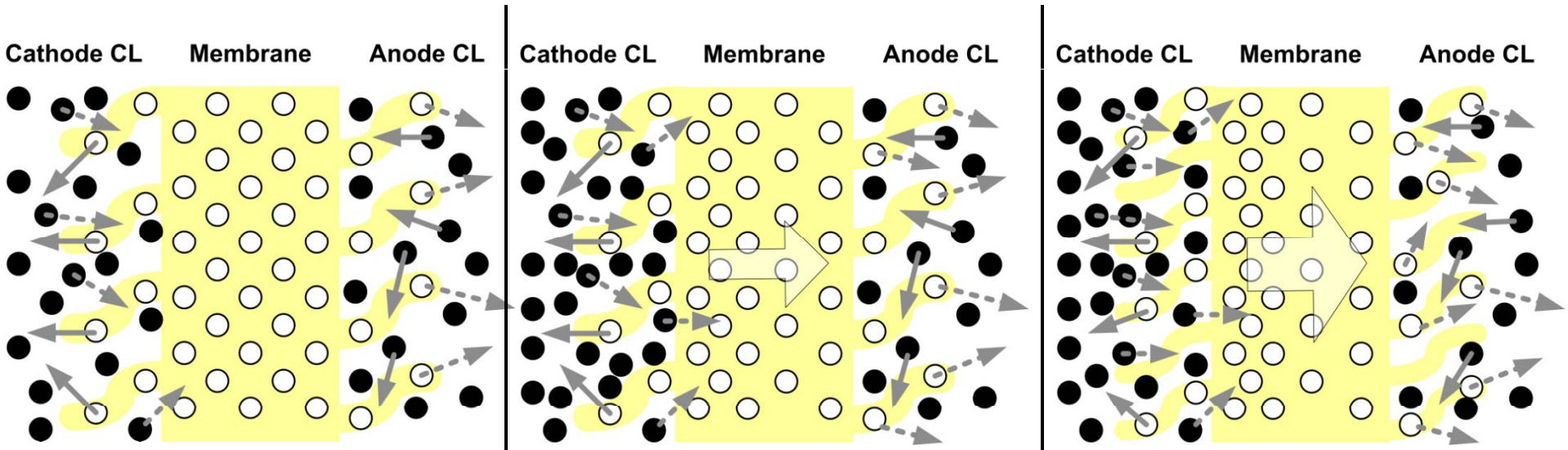
α:	specific surface area of electrolyte phase in CL	[m^2/m^3]
$k_{abs/des}$:	absorption/desorption kinetic coefficient	[m/s]
$\lambda_{w,equil}$:	equilibrium water content in electrolyte phase	[-]
λ_w:	water content in electrolyte phase	[-]
M_W:	molecular mass of water	[kg/mole]

- Specific surface area of electrolyte phase in CL α is adjustable and can in practice be easily changed by varying electrolyte loading close to the membrane.
- Absorption/desorption enthalpy needs to be accounted for in a model.
- Absorption is slower than desorption and hence rate-determining.

Berning et al., J. Power Sources 196, 6305-6317, August 2011

Picturing water transport through the MEA

$$-\frac{\rho^{mem}}{EW}\nabla\cdot\left(D_W^{mem}\nabla\lambda_w\right)=\alpha\times k_a\times\frac{\rho^{mem}}{EW}\left(\lambda_{w,equil}-\lambda_w\right)-\nabla\cdot\left(n_d\frac{I}{F}\right)$$



Case 1:

No net transport

Case 2:

Back diffusion

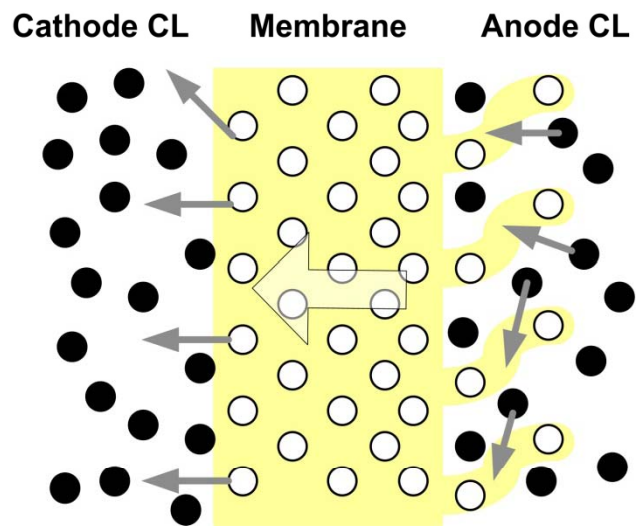
Case 3:

Back diffusion and WUL

Berning, Int. J. Hydrogen Energy (2011)

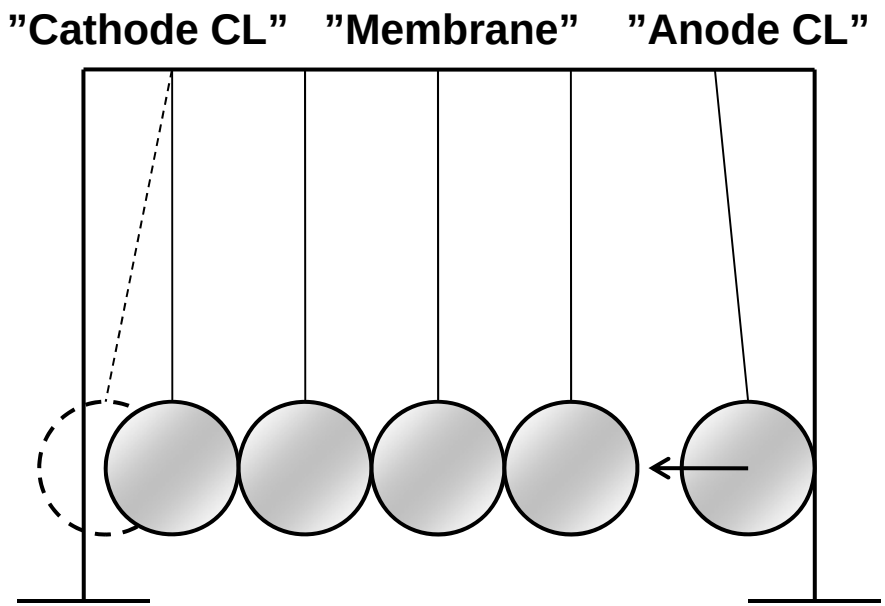
In situ experiment to measure EOD coefficient

- We can see from the transport equation that when the specific surface area α is sufficiently low we can measure the EOD coefficient n_d directly with *in situ* experiments.
- Results for the net drag should be completely independent of cathode side RH, but sufficient water at anode side has to be provided to sustain EOD.
- Low-temperature experiments may be preferred, because the kinetic absorption coefficient *k* is strongly temperature dependent.



Case 4: *In Situ* determination of EOD coefficient

A picture of the effect of the EOD: ”Newton’s Cradle”



$$\nabla \cdot \left(n_d \frac{I}{F} \right) < 0 \qquad \nabla \cdot \left(n_d \frac{I}{F} \right) = 0 \qquad \nabla \cdot \left(n_d \frac{I}{F} \right) > 0$$

- Effect of EOD only noticeable in CL’s
- Protons travel through PEM via ”*Grotthus Hopping Mechanism*”

Berning, Int. J. Hydrogen Energy 36, 9341-9344, 2011

WHAT IS THE EFFECT OF THE OPERATING CONDITIONS ON THE FUEL CELL WATER CONTENT?

General observations

- A fuel cell that operates at elevated pressure shows a higher water content than a cell operating at atmospheric pressure.
- A fuel cell that operates at low stoichiometric flow ratios is ”wetter” than a cell that operates at high stoichiometric flow ratios.

➢ How can we fundamentally understand the role of the fuel cell operating conditions on the expected water level?

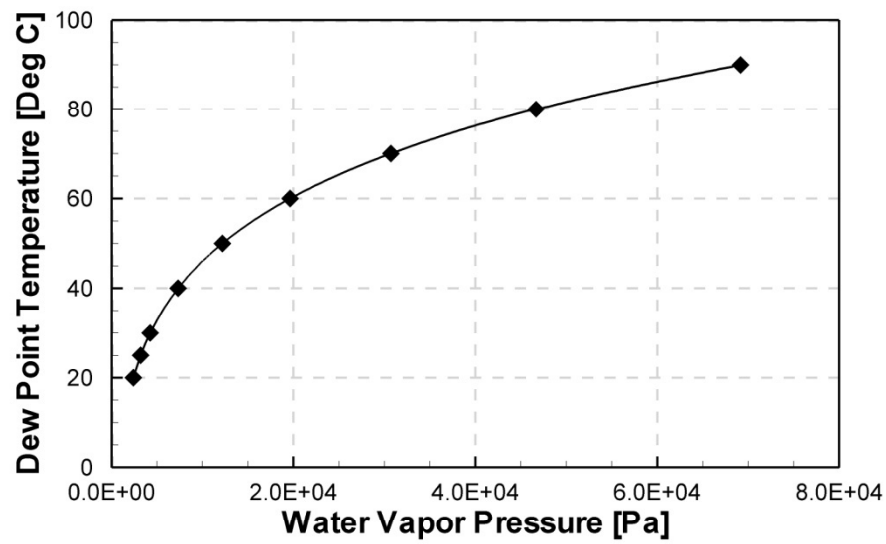
➢ An answer to this question can be found when calculating the Dew point temperature of the gas streams leaving the fuel cell!

What is the dew point temperature?

- The dew point temperature is the temperature at which water will start to condense when a gas stream is cooled down at a constant pressure.
- It is the temperature at which the relative humidity (RH) of the gas phase is exactly 100 %.
- It is the reciprocal of the saturation pressure as function of temperature and a reasonable curve fit equation is:

$$T_{dew}(°C) = -2.581E^{-18} \times \left(p_{H_2O}\right)^4 + 6.4056E^{-13} \times \left(p_{H_2O}\right)^3 - 5.8916E^{-8} \times \left(p_{H_2O}\right)^2 + 2.8427E^{-3} \times \left(p_{H_2O}\right) + 2.2455E^{+1}$$

Partial pressure of water vapor, [Pa]



Berning, Int. J. Hydrogen Energy 37, 10265-10275, 2012

Anode side dew point temperature

- In order to calculate the dew point temperature at the anode outlet we need to determine the partial pressure of water at the anode outlet:

$$p_{H_2O,out} = x_{H_2O,out} \times p_{an,out} = \dot{N}_{H_2O,out} \big/ \dot{N}_{total,out} \times p_{an,out}$$

- Introducing the effective drag coefficient r_d, the molar flow rate of water at the anode outlet can be written as:

$$\dot{N}_{H_2O,out} = \dot{N}_{H_2O,in} - \dot{N}_{H_2O,drag} = \dot{N}_{H_2O,in} - r_d \times I/F$$

- And it can be shown that:

$$\dot{N}_{H_2O,in} = x_{H_2O,in} \big/ \left(1 - x_{H_2O,in}\right) \times \xi_{an}\, I/2F$$

- With:

$$x_{H_2O,in} = \dot{N}_{H_2O,in} \big/ \dot{N}_{total,in} = RH_{in} \times p_{sat}\left(T_{in}\right) \big/ p_{total,in}$$

Anode side dew point temperature

- The molar stream of hydrogen leaving the anode is:

$$\dot{N}_{H_2,out} = (\xi_{an} - 1)\dot{N}_{H_2,cons} = (\xi_{an} - 1) \times I/2F$$

- And the total molar stream leaving the anode is:

$$\begin{aligned}\dot{N}_{total,out} &= \dot{N}_{H_2O,out} + \dot{N}_{H_2,out} \\ &= x_{H_2O,in} \times (1 - x_{H_2O,in}) \times \xi_{an}\, I/2F - r_d\, I/F + (\xi_{an} - 1) I/2F\end{aligned}$$

- If the incoming gas stream at the anode is comletely dry, e.g. pure hydrogen enters, the molar fraction of water vapour at the anode outlet is:

$$\boxed{x_{H_2O,out} = \frac{\dot{N}_{H_2O,out}}{\dot{N}_{total,out}} = \frac{-r_d (I/F)}{(\xi_{an} - 1)(I/2F) - r_d (I/F)} = \frac{2r_d}{2r_d - (\xi_{an} - 1)}}$$

- And multiplying this value with the outlet pressure yields the partial pressure of water vapour at the anode outlet.

Cathode side dew point temperature

- Likewise, it can be shown that the molar fraction of water vapour at the cathode outlet is:

$$\boxed{x_{H_2O,out} = \frac{\dot{N}_{H_2O,out}}{\dot{N}_{air,out} + \dot{N}_{H_2O,out}} = \ldots = \frac{2\times(1+2r_d)}{2\times(1+2r_d)+4.76\times\xi_{Ca}-1}}$$

- This assumes that dry air enters the cell that consists of 79 % nitrogen and 21 % oxygen.

- The derivation of this is left to the students as homework ☺

Notes on dew point temperature

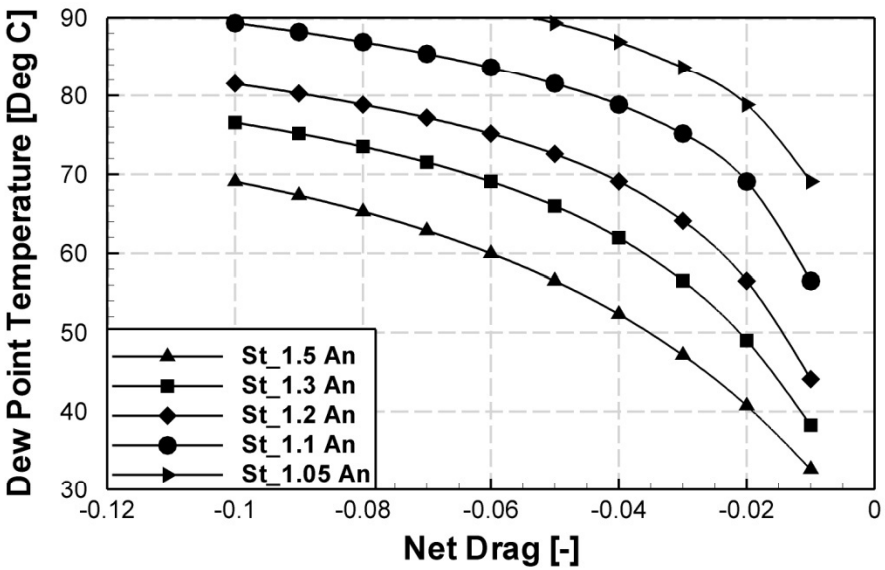
It can be seen from the previous derivations that:

1. The dew point temperatures do NOT depend on the current density! The cell current density cancelled out during the derivation.
2. The dew point temperatures do NOT depend on the cell geometry, co-flow or counter-flow, choice of materials, …
3. The dew point temperatures depend STRONGLY on the stoichiometric flow ratios.
4. The dew point temperatures depend STRONGLY on the operating pressure.
5. The dew point temperatures depend on the effective drag coefficient r_d, which in turn varies with current density, cell geometry, materials, …

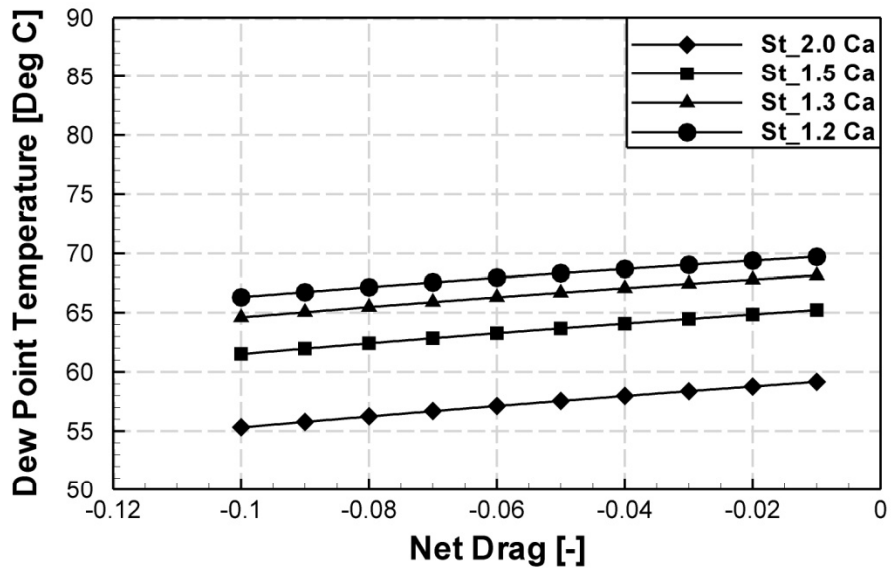
Because r_d is unknown *a priori*, the anode and cathode dew point temperatures can not be directly calculated. But we can construct Dew Point Diagrams that show the dew point temperatures as function of r_d!

Dew point diagrams for p = 1.0 atm

Anode



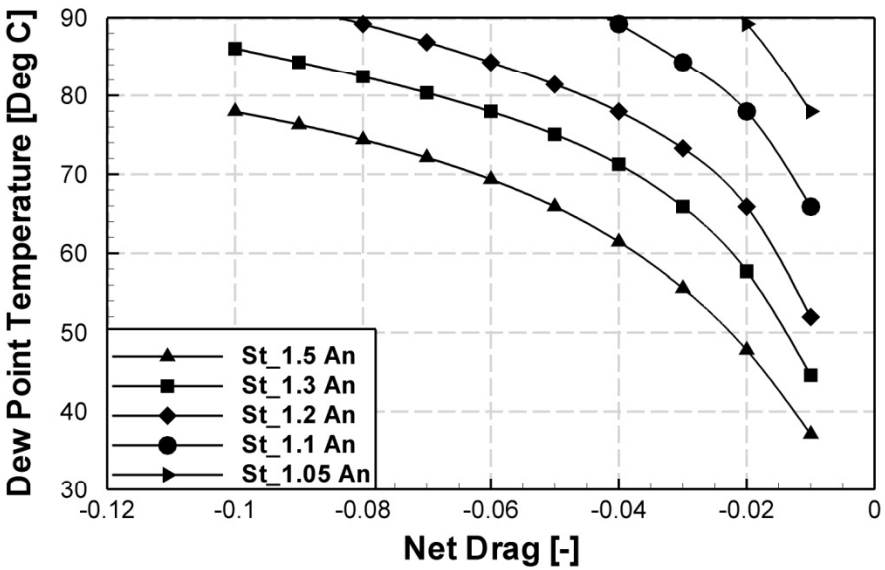
Cathode



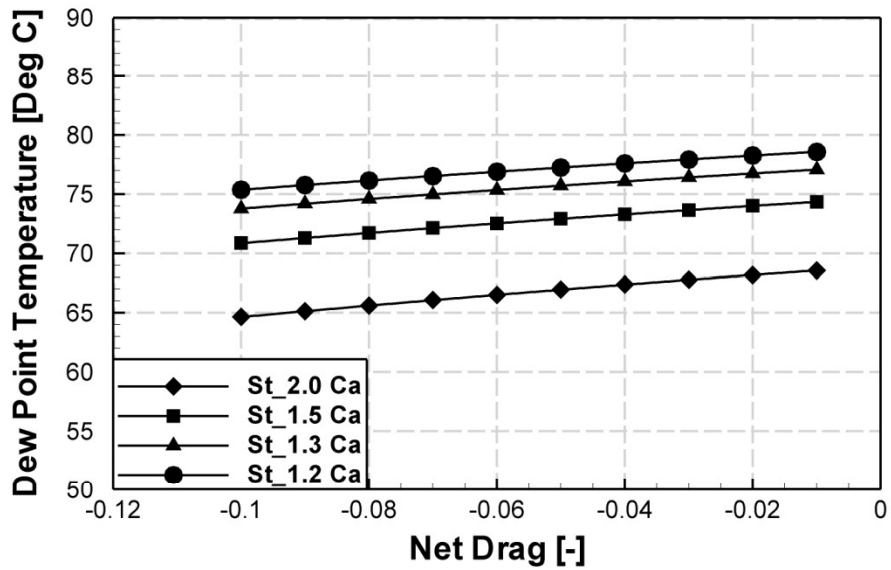
- These dew point diagrams are for completely dry inlet gases.
- Note the strong dependency on the stoichiometric flow ratio.
- At atmospheric pressures the cathode side dew point temperatures are quite low, especially at higher stoichs we need to humidify the inlet gas stream.

Dew point diagrams for p = 1.5 atm

Anode

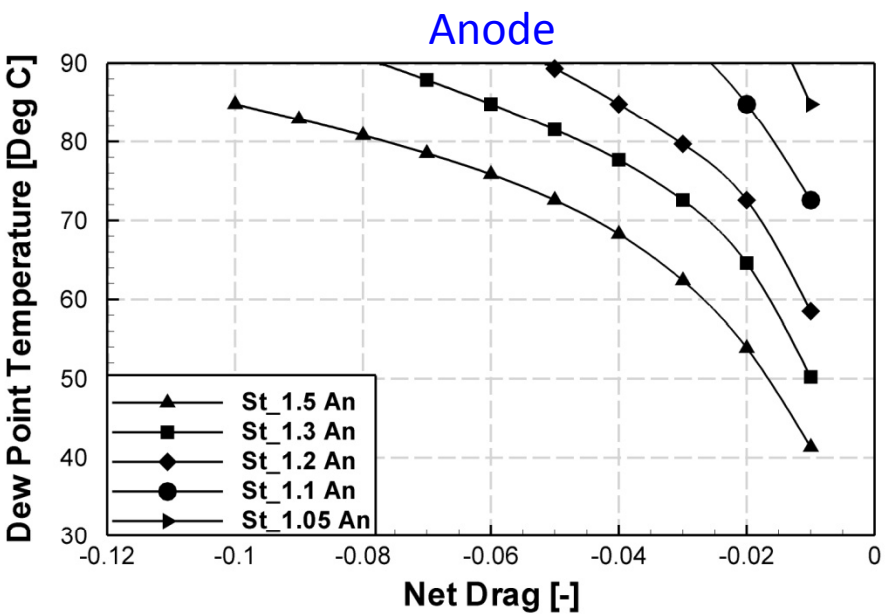


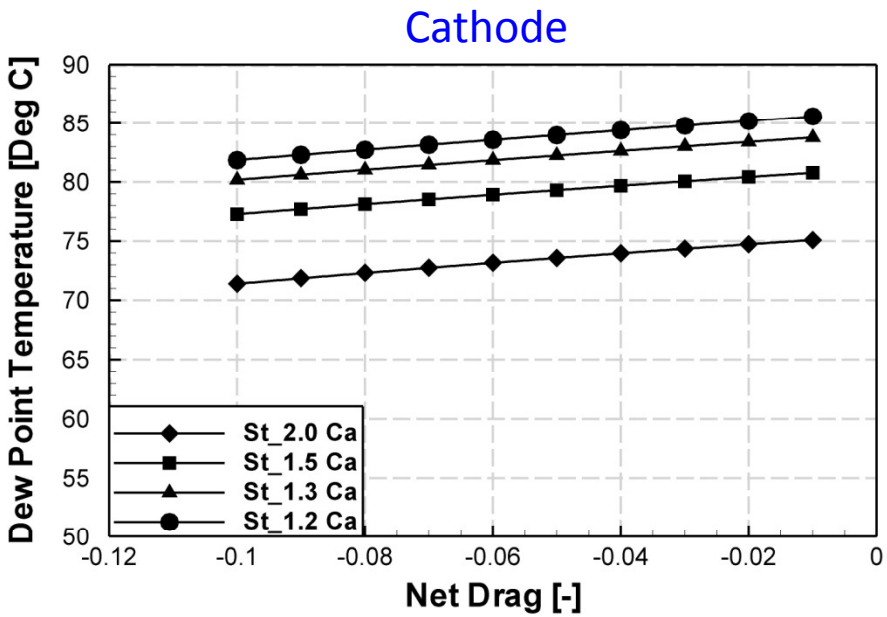
Cathode



- Increasing the pressure raises the dew point temperatures, as expected
- Anode dew point temperatures are higher than cathode dew point temperatures
- But: Anode and cathode do not need to operate at the same pressure!

Dew point diagrams for p = 2.0 atm





- If the anode should operate at a low stoich (to allow for steady-state operation), 2.0 atm may be too high because the dew point temperatures are very high.
- Cathode side appears comfortable at 2.0 atm, T_{dew} is around 75 – 85 °C.
- In general, we want to operate the cell at a temperature as high as possible.

Summary: Dew point diagrams

- Dew point diagrams are a fundamentally derived tool that can help to understand the effect of the fuel cell operating conditions on the cell hydration status
- The dew point temperature only depends on the stoichiometric flow ratio, the pressure and the net drag coefficient r_d
- The dependency of the cathode dew point temperature on r_d is relatively weak, and r_d can be estimated with sufficient accuracy to give a very good estimation of the cathode T_{dew}.
- The dependency of the anode dew point temperature on r_d is very strong, and the anode T_{dew} tends to be higher than the cathode T_{dew}.
- Because r_d is non-dimensional and just denotes the molar flow of water through the membrane, anode and cathode dew point diagrams at different pressures (or stoichs) can be mixed and matched.

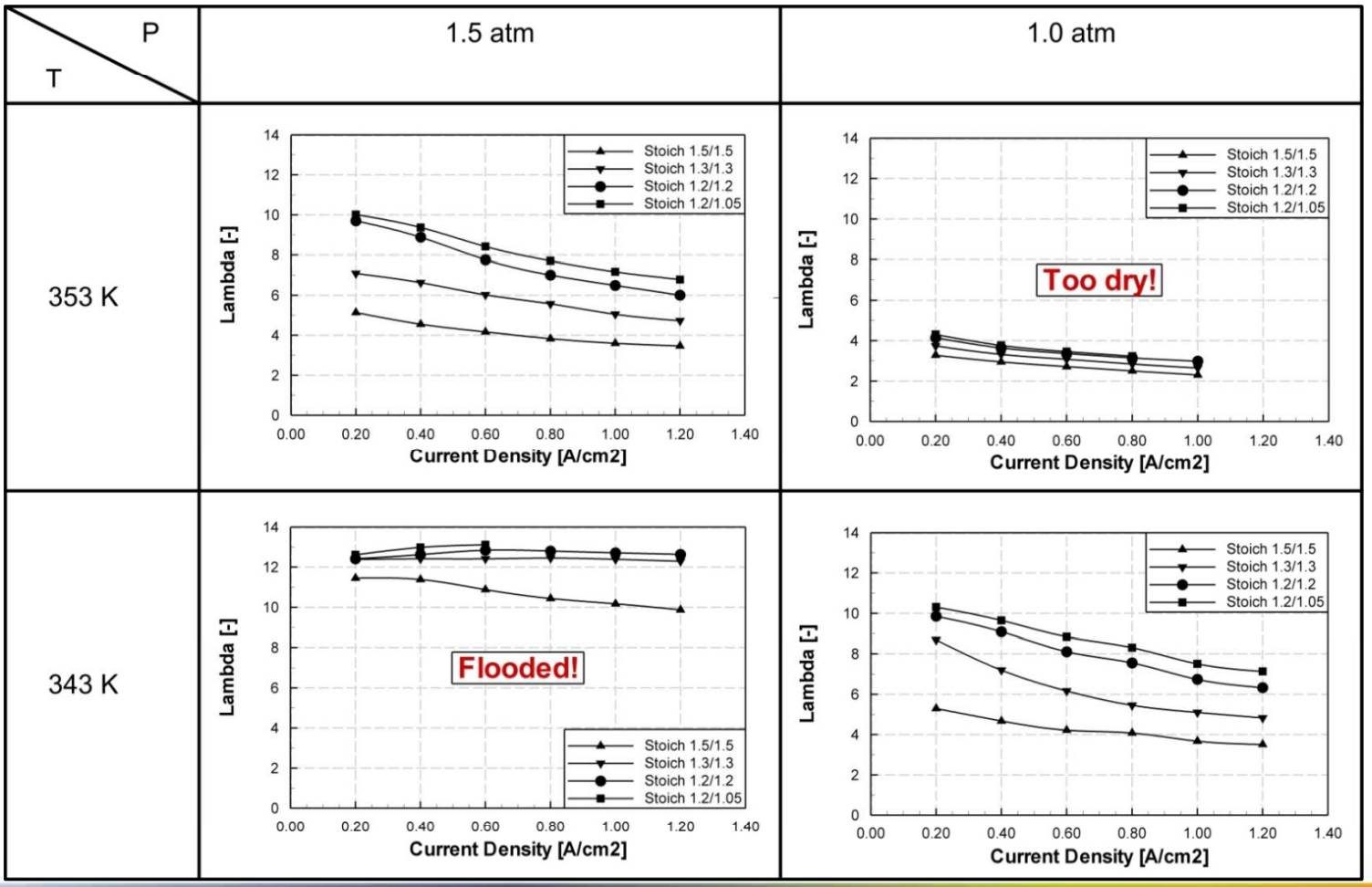
A case study using a CFD model

	P = 1.0 atm	P = 1.5 atm
T = 353 K	CASE 2	CASE 1
T = 343 K	CASE 3	CASE 4

- Calculate current densities between 0.2 A/cm^2 and 1.2 A/cm^2
- Investigate stoichiometric flow ratios ξ_c/ξ_a of:
  - 1.5/1.5
  - 1.3/1.3
  - 1.2/1.2
  - 1.2/1.05
- Focus of analysis is on water balance/feasibility to operate, and predicted membrane water content

Modeling results

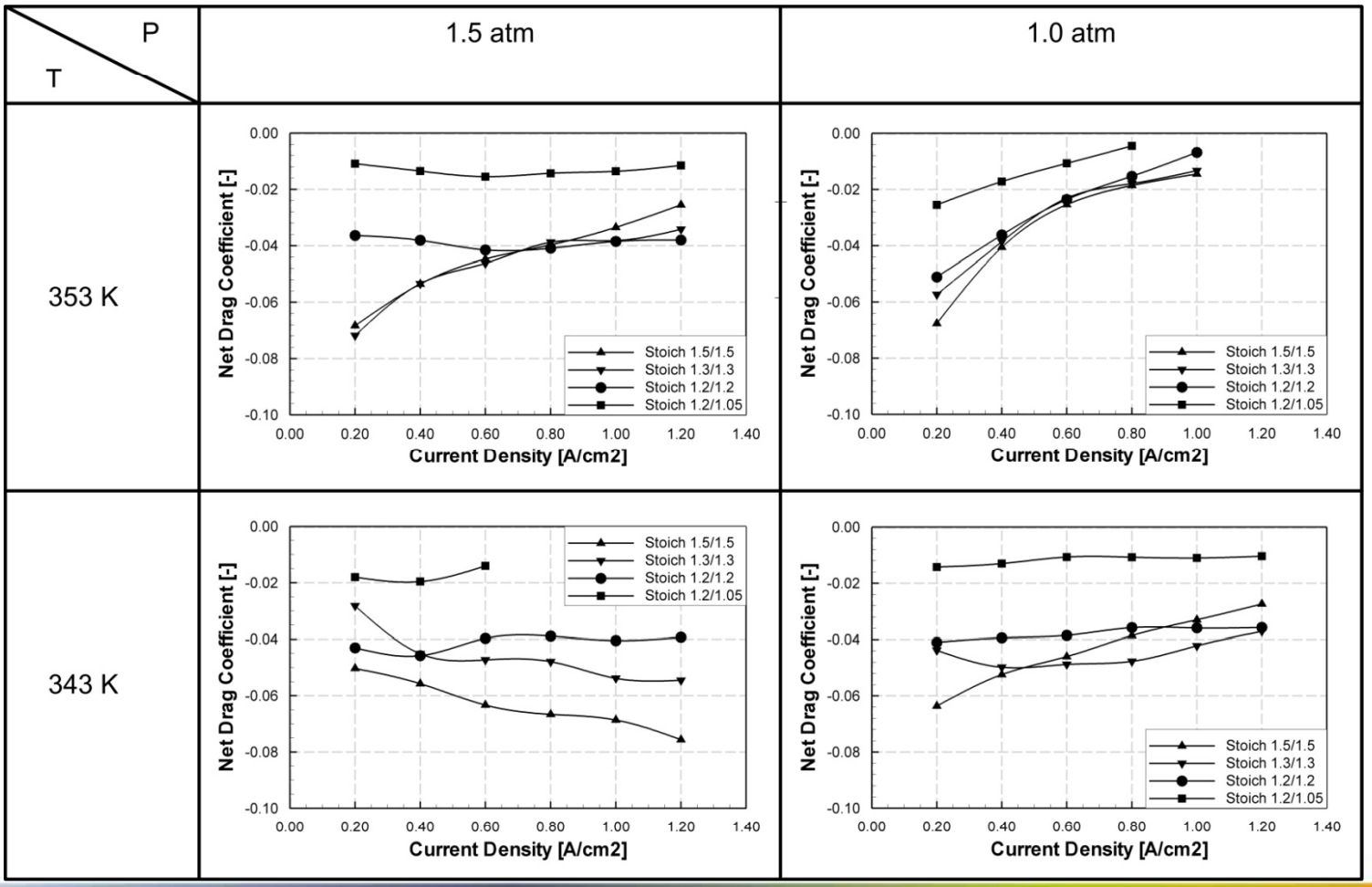
Predicted membrane water content



Berning & Kær, Int. J. Hydrogen Energy 37, 2012

Modeling results

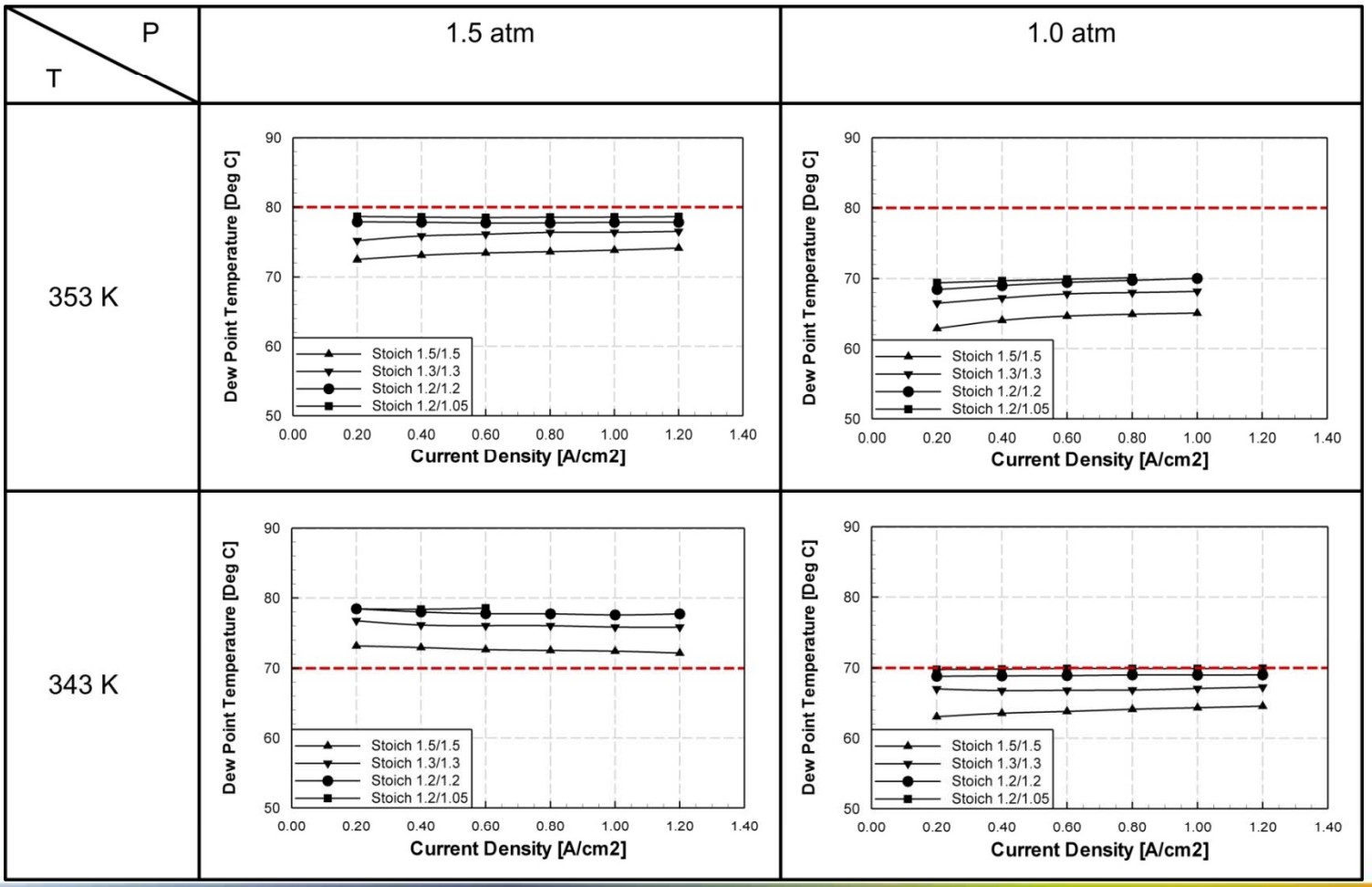
Predicted net drag coefficient r_d



Berning & Kær, Int. J. Hydrogen Energy 37, 2012

Cathode side dew point temperatures

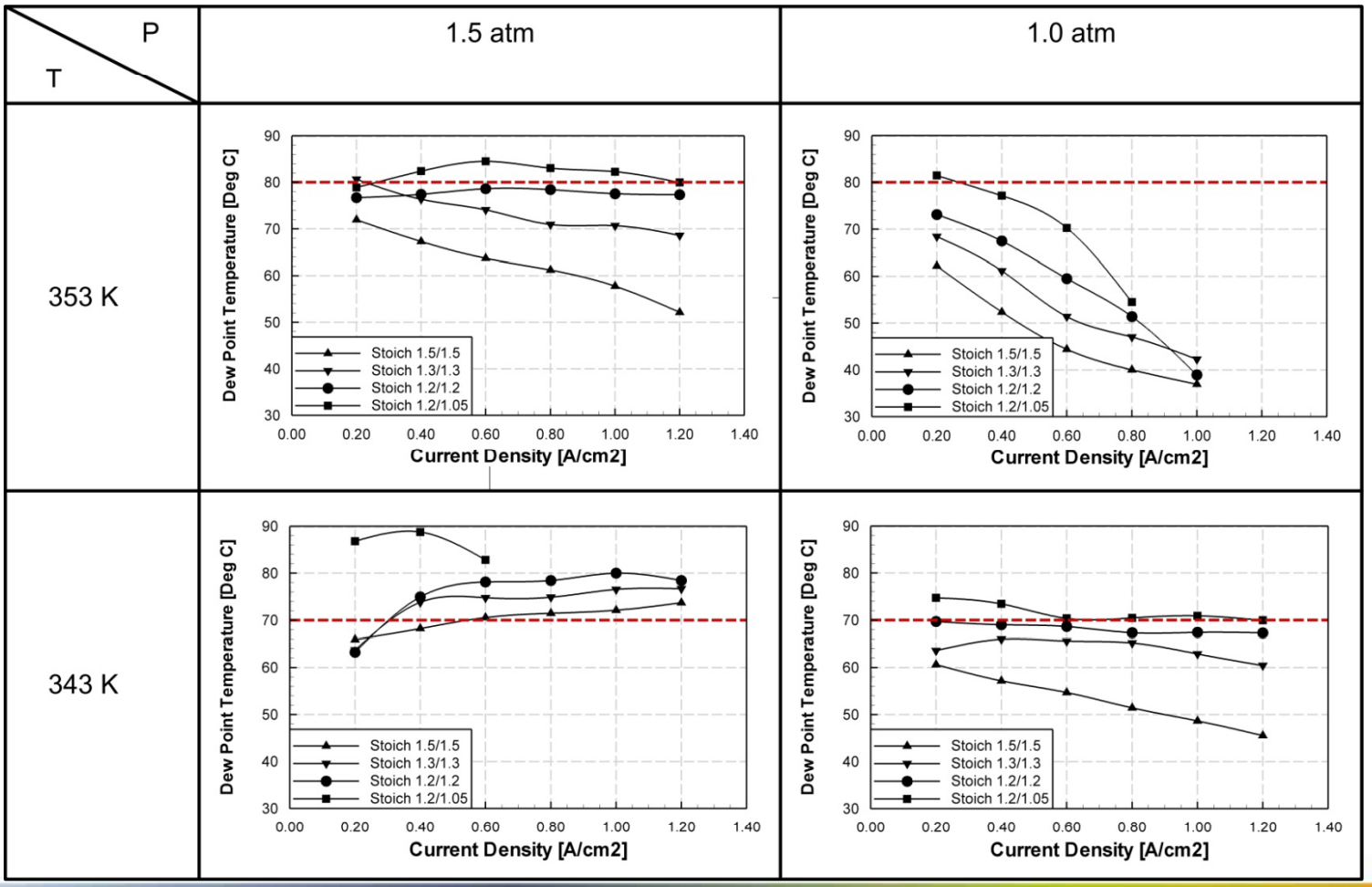
Calculated out of the predicted net drag coefficient r_d



Berning, Int. J. Hydrogen Energy 37, 2012

Cathode side dew point temperatures

Calculated out of the predicted net drag coefficient r_d



Berning, Int. J. Hydrogen Energy 37, 2012

Summary: Modeling results

- Cathode dew point temperatures show a weak dependency of the net drag coefficient.
- The predicted membrane water content shows a strong correlation to the cathode dew point temperature.
- Anode dew point temperature appears to cling to the operating temperature, anode gas phase ”tries” to stay at 100 % RH, when possible.

➢ The membrane water content can apparently be controlled by operating the cell close to the cathode dew point temperature!

➢ But are these modeling results physical? Validation is still required!

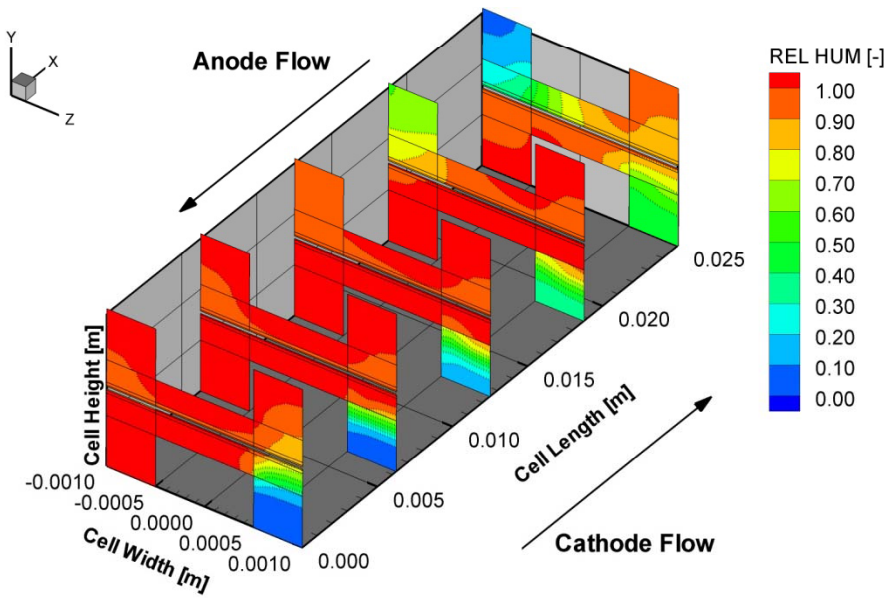
Verification of modeling results

- CASE 4 was the ”wet case” at T_{cell} = 70 °C and p_{cell} = 1.5 bar
- The dew point calculations show that the cathode side the dew point temperature of the outlet gas stream is above the cell temperature for all data point calculated: the model has to predict an RH above 100 % (and multi-phase flow)

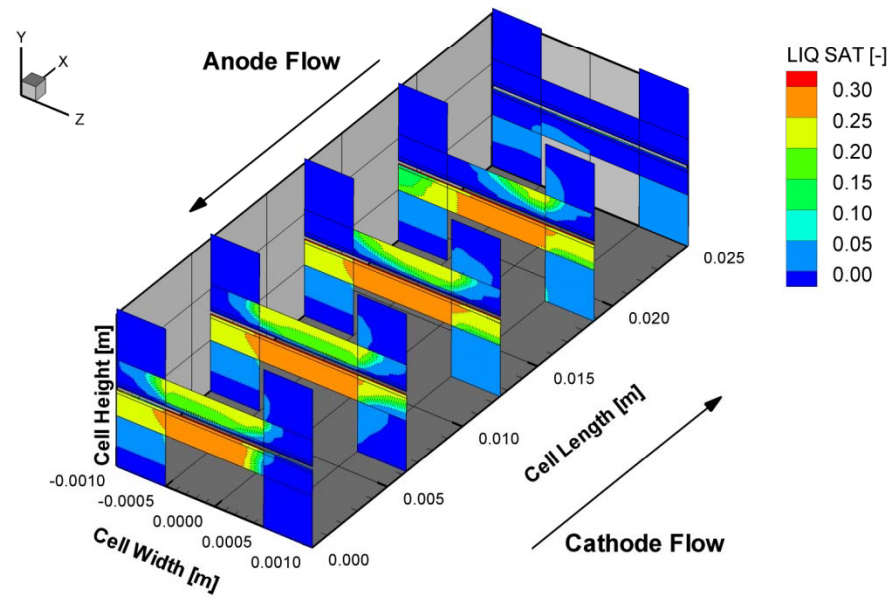
Note: Despite the fact that the gases may enter the cell at 0 % RH, the cell can still be as wet as we like if we keep the operating temperature substantially below the dew point temperatures of the utlet gases, i.e. by adjusting the cell pressure and the stoichiometric flow ratio we can control the general hydration status of the cell.

CASE 4 for at 1.0 A/cm^2 and ξ_a/ξ_c = 1.2/1.2

Relative humidity distribution



Liquid water volume fraction ("saturation")



- Both outlet channels show an RH of over 100 %, continuous condensation would occur (not implemented in the model).
- Any computational model MUST predict an RH > 100% because the results MUST agree with (fundamentally derived) dew point temperaures!

Berning & Kær, Int. J. Hydrogen Energy 37, 2012

Summary: Dew point temperature

- Dew point temperatures depend only on stoichiometric flow ratio, pressure and the effective drag coefficient r_d.
- Allow for the construction of Dew Point Diagrams, which in turn give information with respect to suitable operating temperatures.
- If the outlet temperature at the anode side and the cathode side are both equal to the dew point temperatures, the gases would leave the cell at exactly 100 % RH.

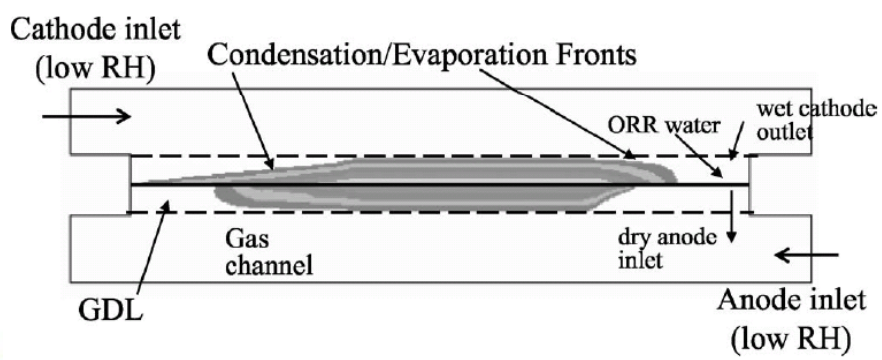
➢ It is possible to employ Dew Point Diagrams in order to identify an operating point where both gases leaving the cell at exactly 100 % RH while entering the cell completely dry.

➢ Finally, these considerations may allow us to define the term ”flooding”: Operating the fuel cell at a temperature substantially below the anode/cathode dew point temperatures so that continuous condensation inside the cell occurs.

CFD SIMULATIONS OF MULTI-PHASE FLOW IN PEMFC

Modeling approaches

1. Multiphase mixture model:
   - CFD solver solves one set of conservation equations that includes both phases (gas and liquid);
   - amount of liquid water in porous media determined in a post-iterative step;
   - Mathematically equivalent to two-fluid model with few exceptions, but implementation is difficult
   - Frequently applied in commercial CFD codes like Fluent, Star CD and CFD-ACE
2. Two-fluid model ("Eulerian model"):
   - CFD solver solves two sets of conservation equations, one for each phase, including exchange terms between the phases
   - Physically more complete than multiphase mixture model and straight-forward to implement
   - Computationally expensive and requires full multi-phase solver (e.g. CFX-4)

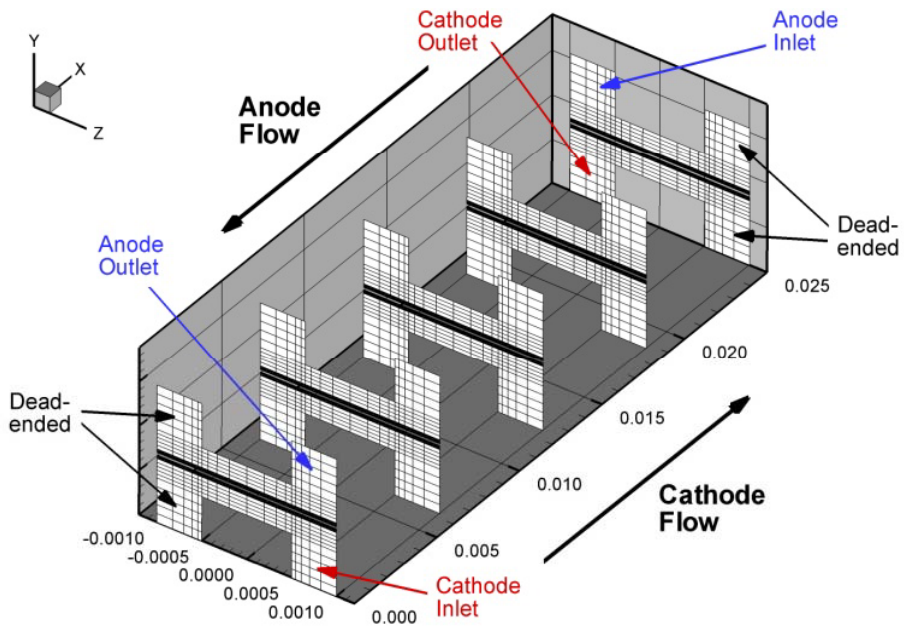


Source: Luo, Ju and Wang, J. Electrochem. Soc., 154, 3, 2007

The ET-AAU fuel cell model based on CFX-4

- Employs Eulerian approach: two full sets of transport equations solved for optimum physical representation
- Includes all major domains in a fuel cell: membrane, catalyst layer, micro-porous layer, gas diffusion layer, flow channels and bipolar plates
- Only small computational grid affordable (no parallel solver), can simulate one ”repeat unit”.
- First publication of full multi-phase simulations employing the so-called interdigitated flow field
- Model accounts for three-dimensional, non-isothermal multi-phase (gas and liquid with porous solid phase), multi-species (oxygen, hydrogen, water with nitrogen as ”background fluid”) transport including phases change, chemical reactions, capillary water transport through the porous layers and water transport through the polymer electrolyte membrane

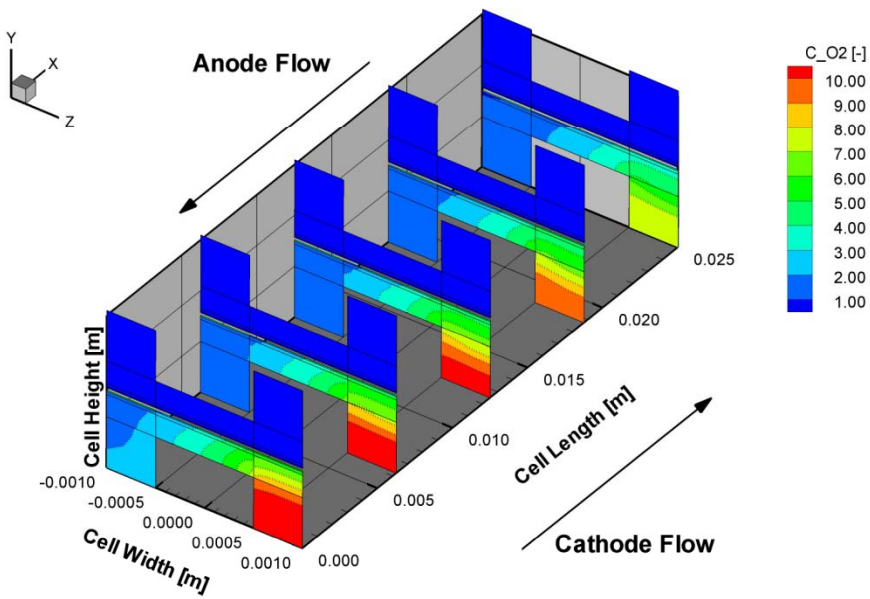
Computational domain and numerical grid

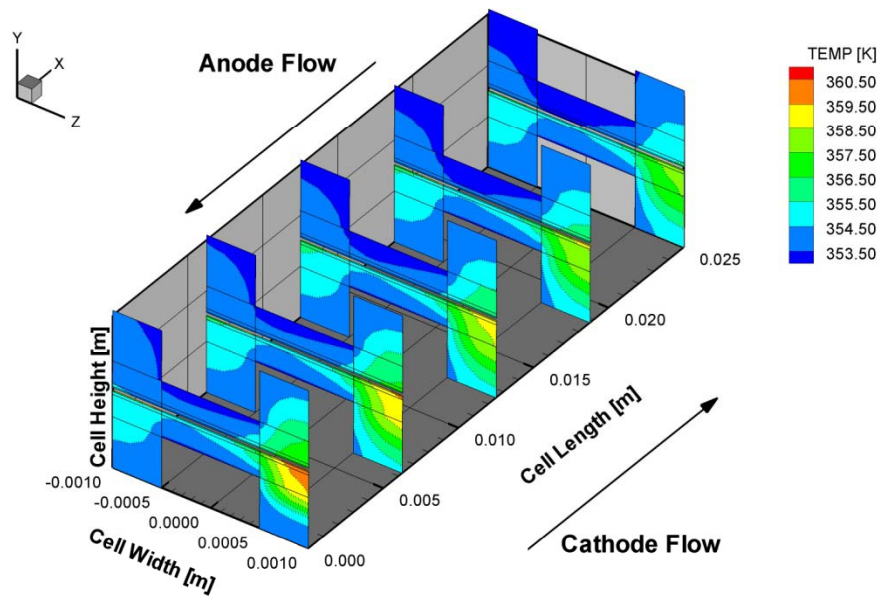


- Dry air enters at lower right, dry hydrogen at upper left, in counter-flow arrangement
- In the interdigitated flow field the flow is forced from the inlet section to the outlet section through the porous media, hence improving mass transport to the CL at the cost of a slightly increased pressure drop

Sample results

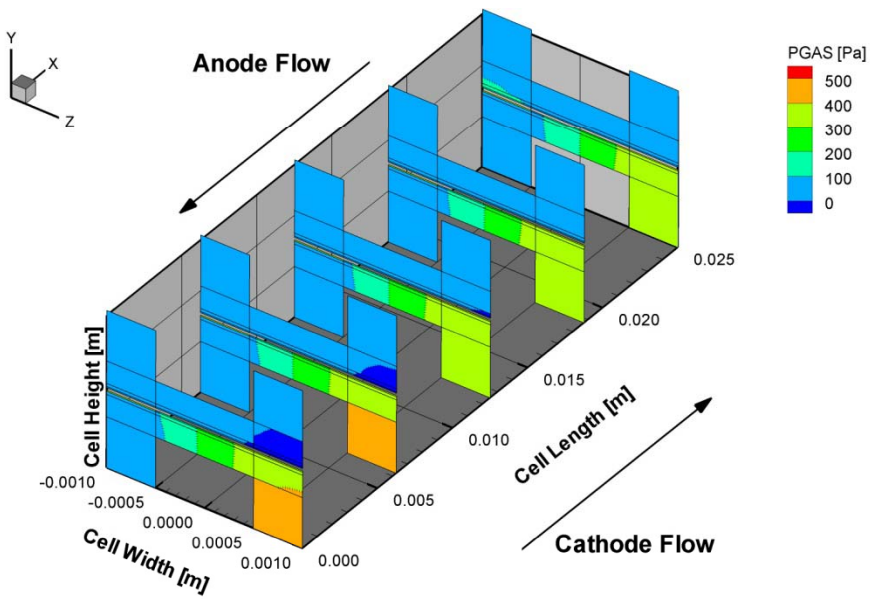
- The goal of this study was to investigate the possibility of operating a fuel cell at a low stoichiometric flow ratio to increase system performance without the need of external humidification
- Stoichiometry was as low as 1.2 at air side and 1.05 at hydrogen side
- Different cell temperatures and pressures were investigated to better understand the effect of the operating conditions

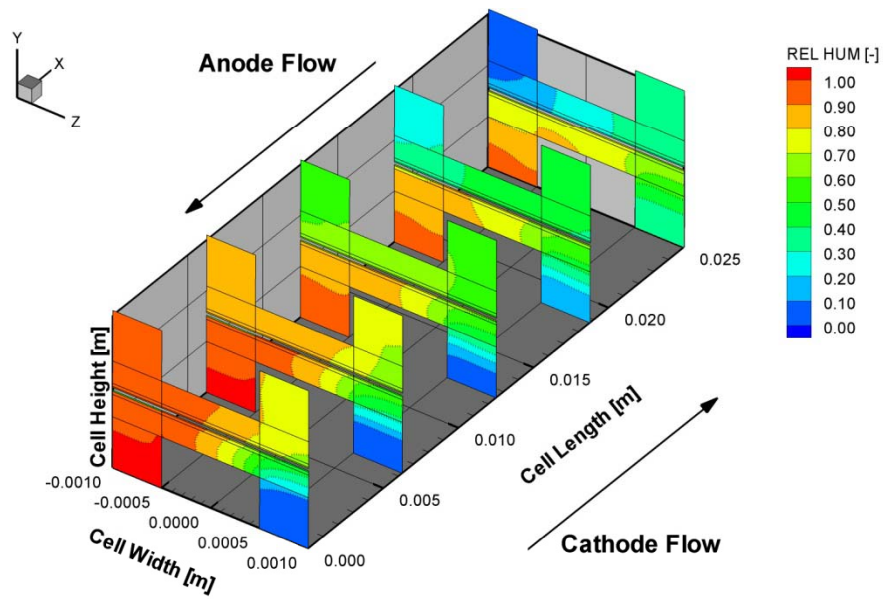




Sample results – ET-AAU fuel cell model

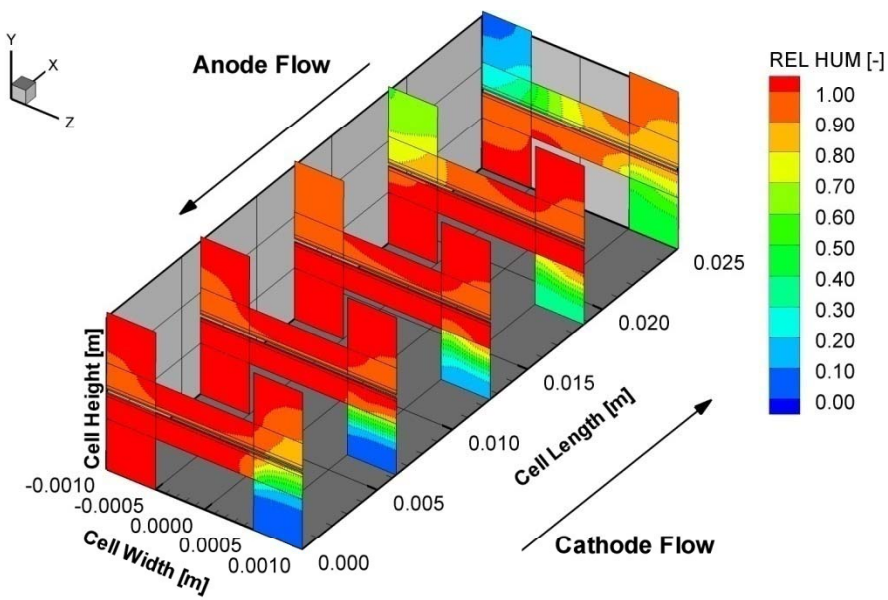
- Predicted pressure drop was surprisingly low, owing to the fact that cell operates at low stoich (low mass flow rates) and air enters completely dry. Depends strongly on hydraulic permeability of the PTL
- Relative humidity in the cell exceeds 100 %, although the gases enter completely dry => membrane may be sufficiently hydrated and allow dry FC operation

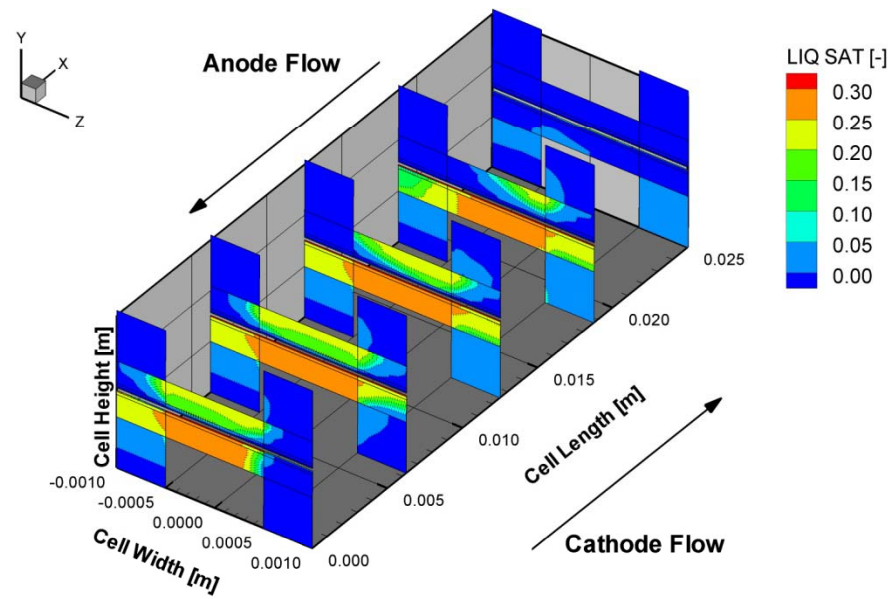




Sample results – ET-AAU fuel cell model

- When the pressure is increased to 1.5 atm and the operating temperature is decreased to 70 °C, the cell is much ”wetter” and substantial amounts of liquid water are predicted at both anode and cathode side
- Note how nicely the interface between the two-phase region and the single-phase region has come out using CFD!



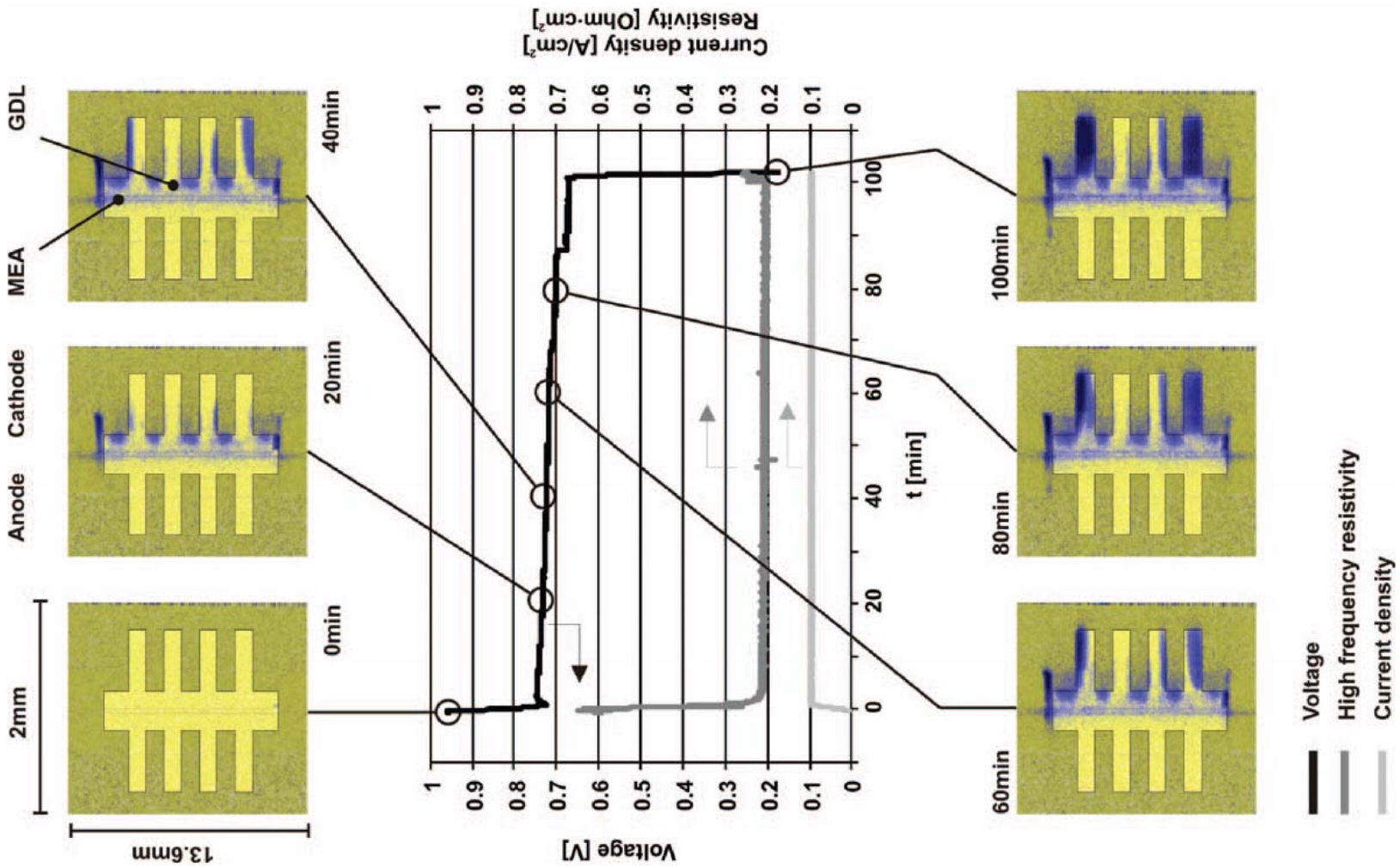


Important aspect: Model validation

- **Model validation** is a very important part of our work. A general rule is:
  - when an experimentalist gives a presentation, EVERYBODY in the room believes that data - except for the presenter
  - when a modeler gives a presentation, NOBODY in the room believes that data - except for the presenter

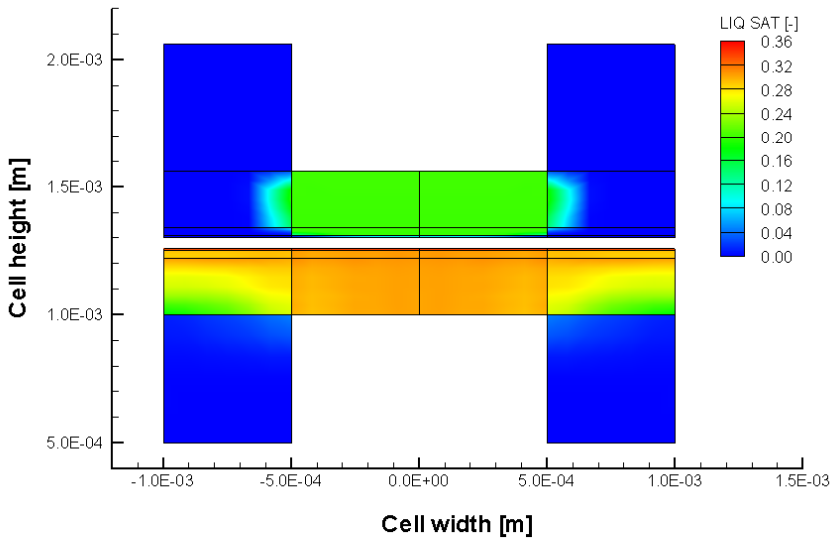
- Good qualitative agreement between our modeling results and water content mesurements using *"Neutron Radiography"* exists (next slide)
  - ✓ Liquid water is present predominantly at the cathode side under land
  - ✓ The amount of liquid saturation is relatively constant
  - ✓ no liquid saturation shown at anode side, but this can be "switched off" in our code by changing a single parameter

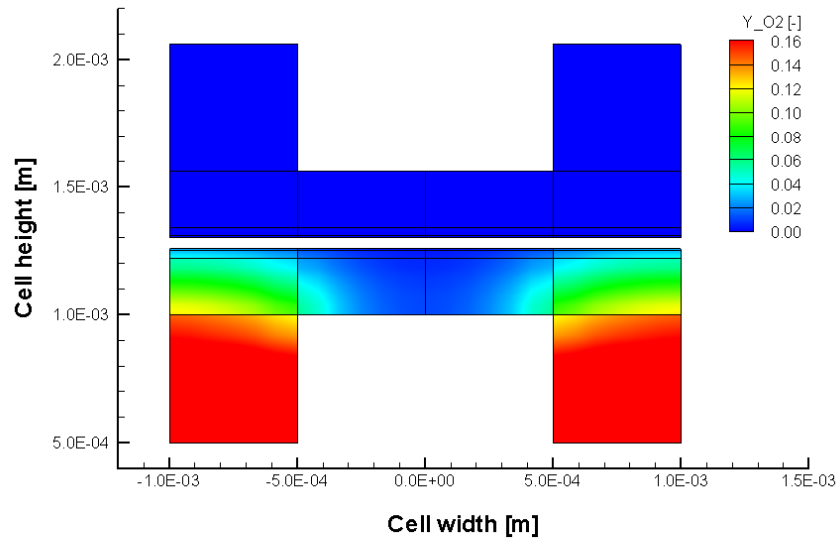
Neutron Radiography data by Oberholzer et al.



Source: Oberholzer, et al., J. Electrochem. Soc., 159 (2), 2012

Liquid water inside the porous media





- Liquid water inside porous media is predominantly predicted at the cathode side (with AAU model), only in exceptional cases predicted at anode side as well
- Liquid water blocks pores and leads to oxygen starvation under the cathode land areas; limits current density
- Level of liquid water saturation depends strongly on the irreducible saturation, i.e. fraction of hydrophilic pores