

# Non-Equilibrium Thermodynamics: Foundations and Applications.

## Lecture 9: Modelling the polymer electrolyte fuel cell

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**and**

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**<http://www.chem.ntnu.no/nonequilibrium-thermodynamics/>**

# Non-Equilibrium Thermodynamics: Foundations and Applications

	Tuesday, Sept. 7	Wednesday, Sept. 8	Thursday, Sept.9	Friday, Sept.10
9:00-10:30	Why non-equilibrium thermodynamics?	Transport of heat and mass	Transport of heat and charge	Entropy production minimization theory
11:00-12:30	Entropy production for a homogeneous phase	Multi-component heat and mass diffusion	Transport of mass and charge	Entropy production minimization. Examples.
16:00-17:00	Flux equations and Onsager relations	Power from regular and thermal osmosis	Modeling the polymer electrolyte fuel cell	

# Non-Equilibrium Thermodynamics: Foundations and Applications

## Lecture 9. Transport heat, mass and charge in fuel cells

### Chapter 19



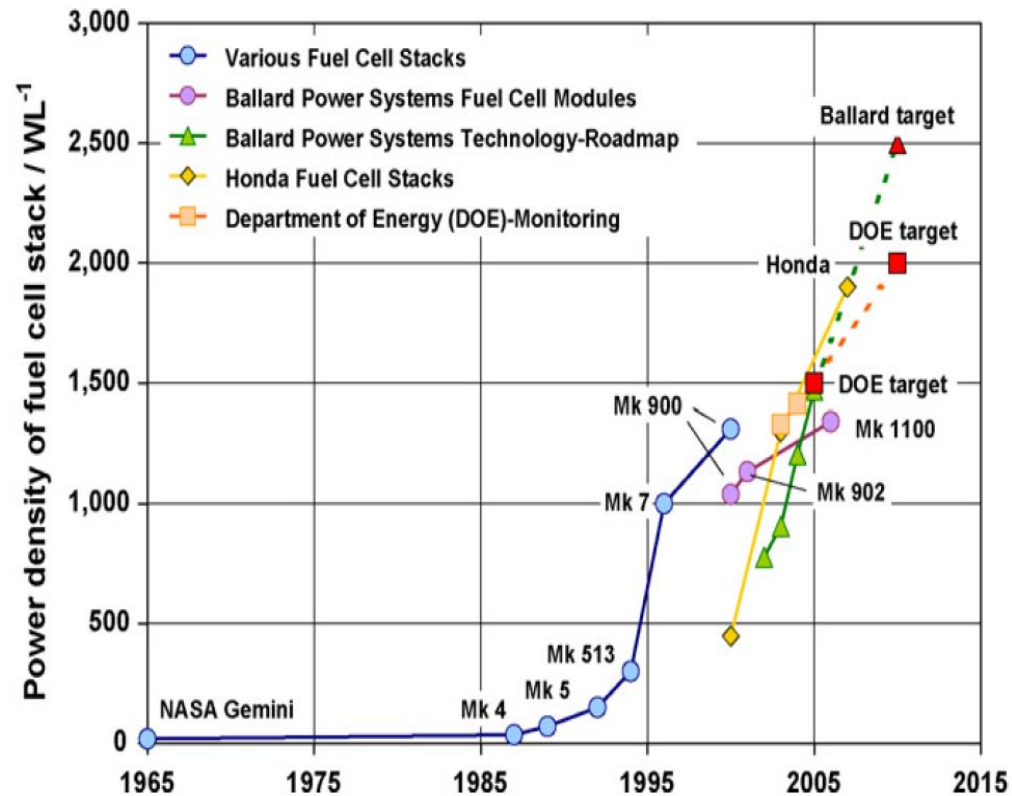
### Lecture aims

**Scetch solution procedure for one-dimensional model and present some results**

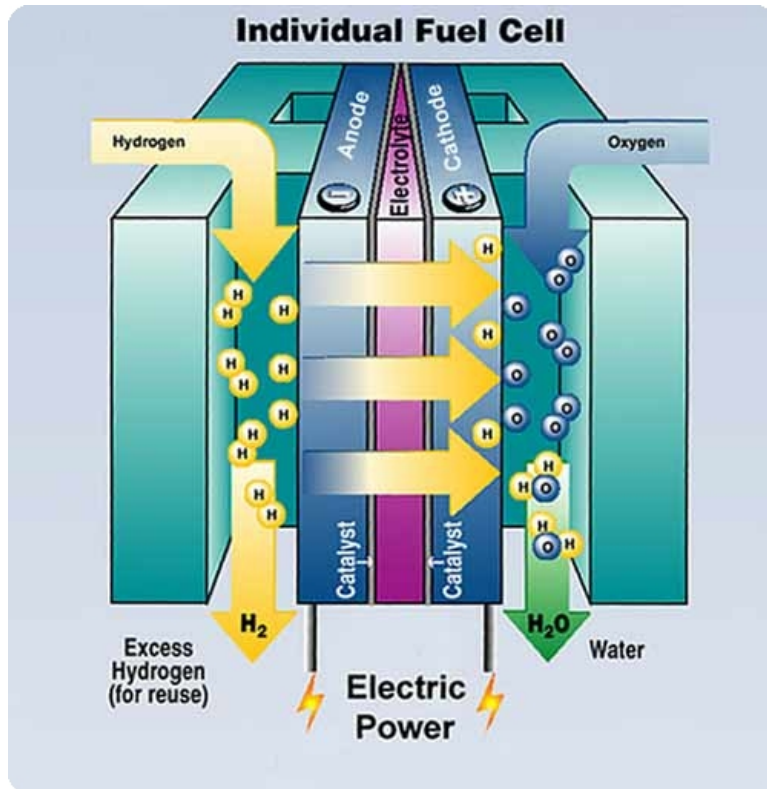
**Present an idea for more energy- and material-efficient design**

# PEM fuel cell challenges

- Too expensive
- Lifetime lower than competing technology
- Efficiency high, but can be higher

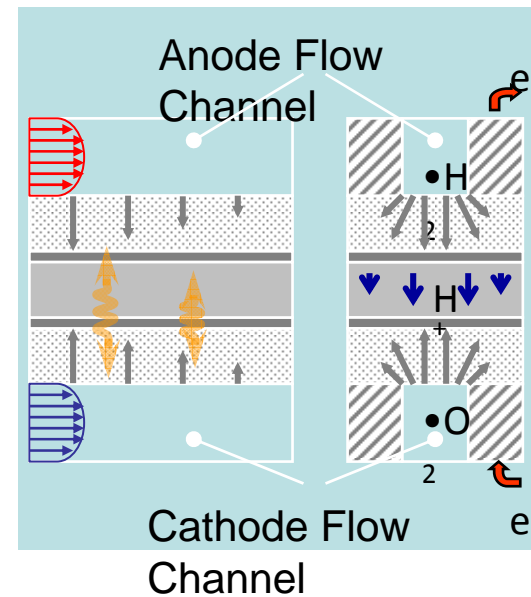


# PEMFC Description



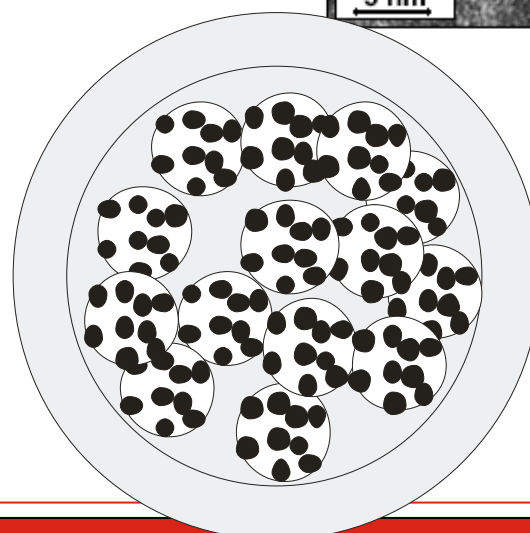
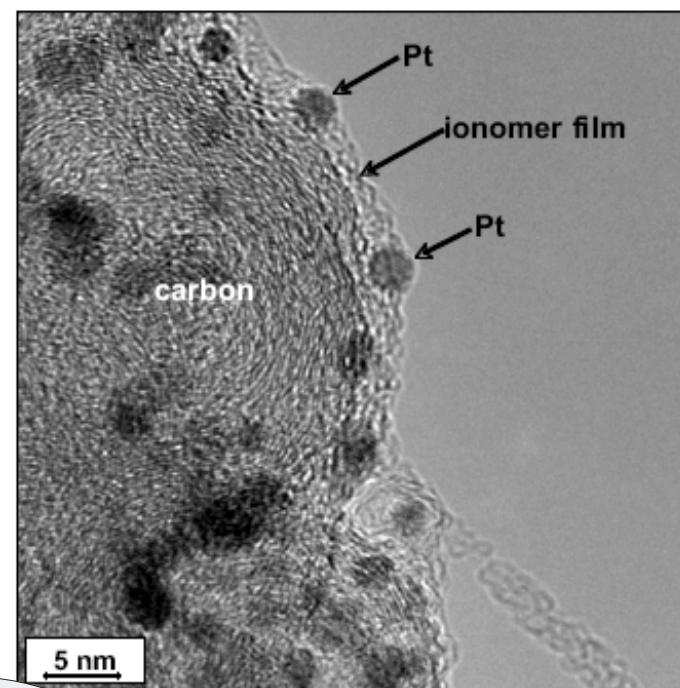
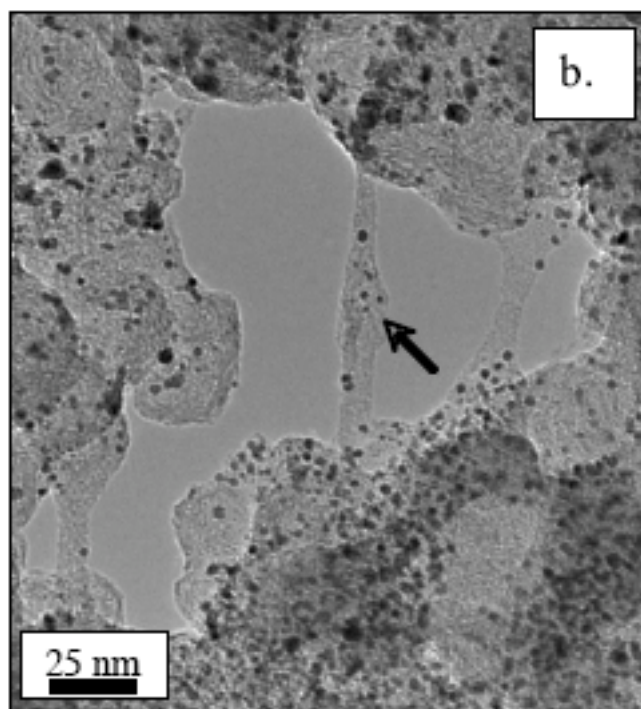
- Fuel cell models must consider
  - Heat transport
  - Electron production
  - Proton and water transport
  - Gas access
  - Water removal

- Design must consider
  - Catalyst nanoporous layer
  - Microporous support layer
  - Gas supply system
  - Water removal system



# PEMFC Description

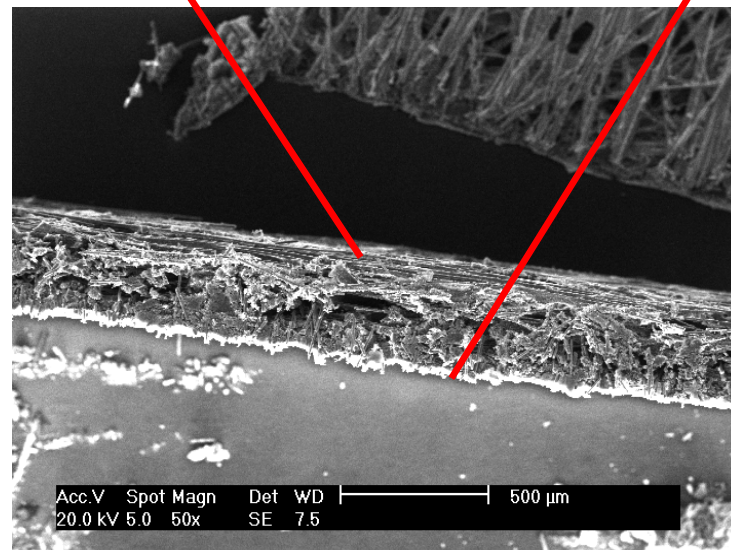
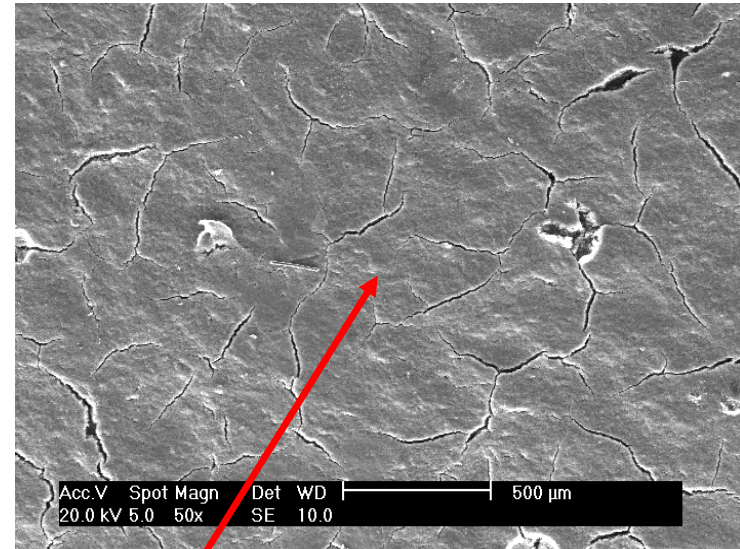
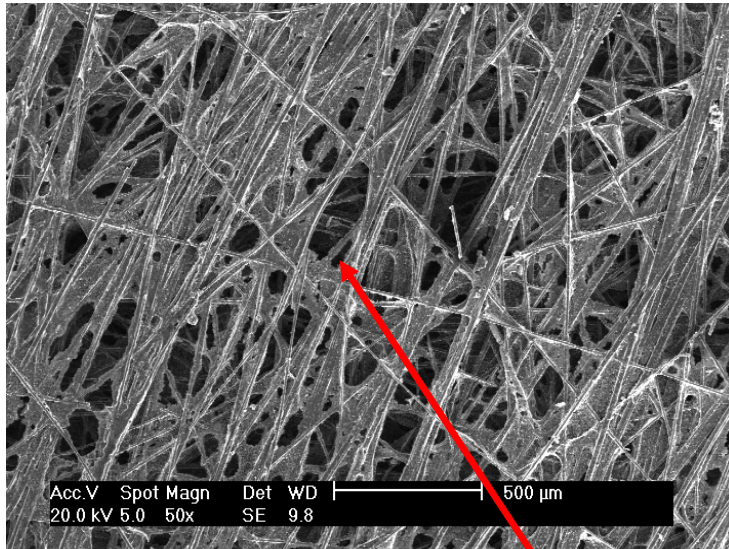
ECS Transactions, 3 (1) 717-733 (2006)  
10.1149/1.2356192, copyright The Electrochemical Society



- Catalyst Support
- Ionomer
- Catalyst

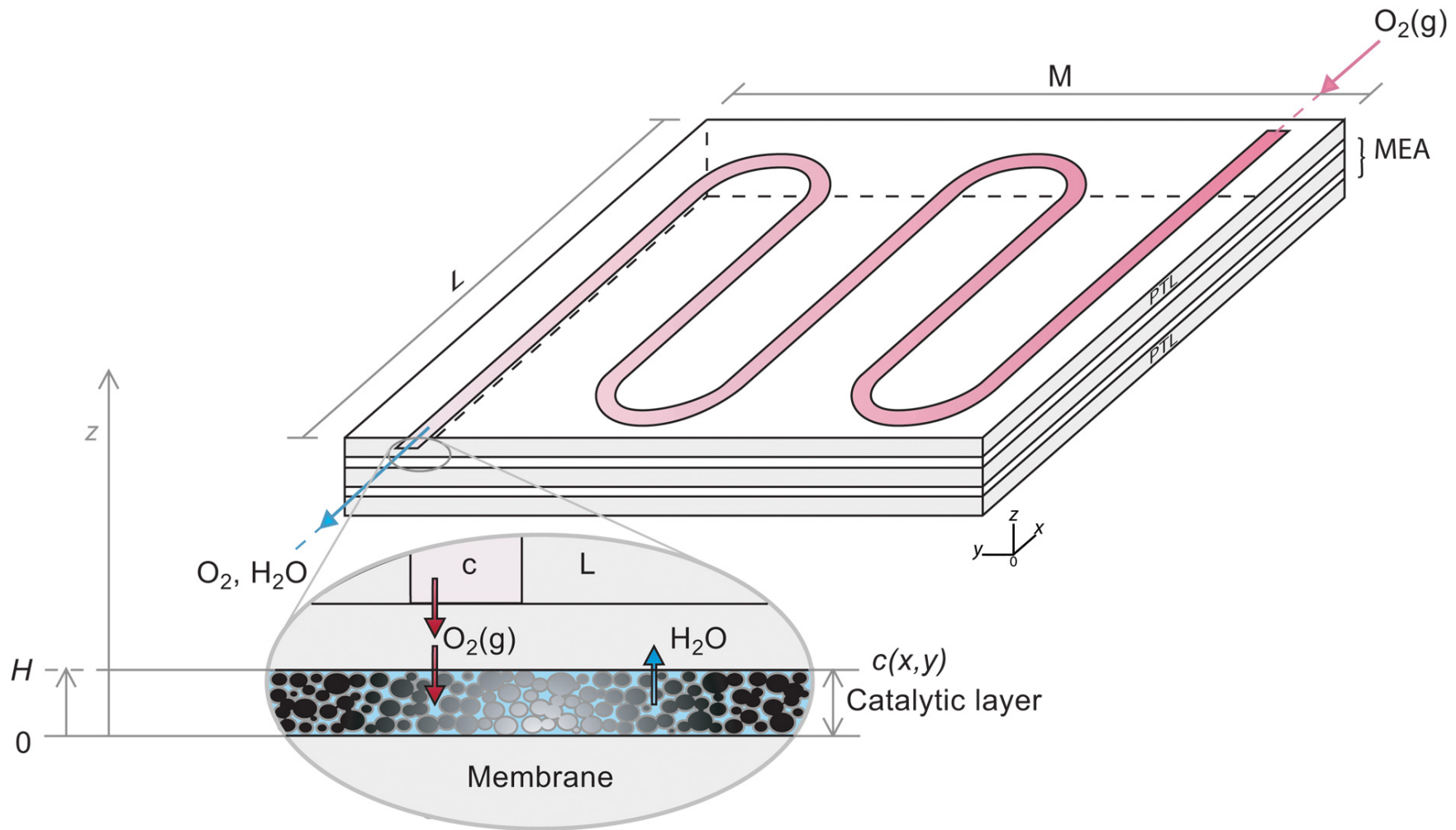
# PEMFC Description

## The microporous layers



Edge View

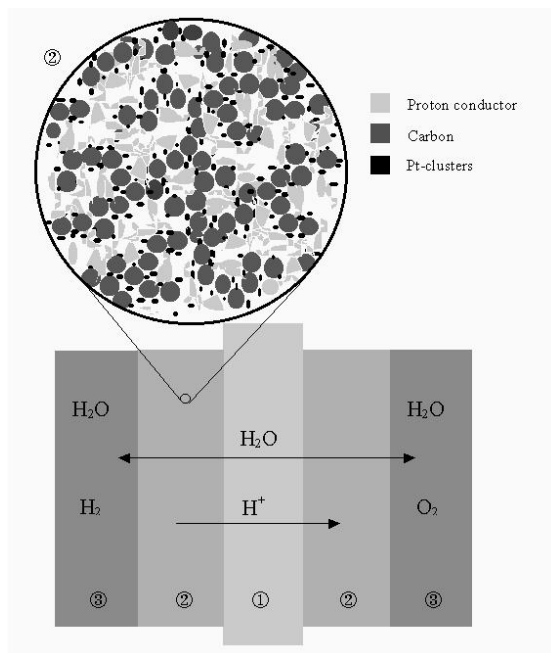
# Another common design





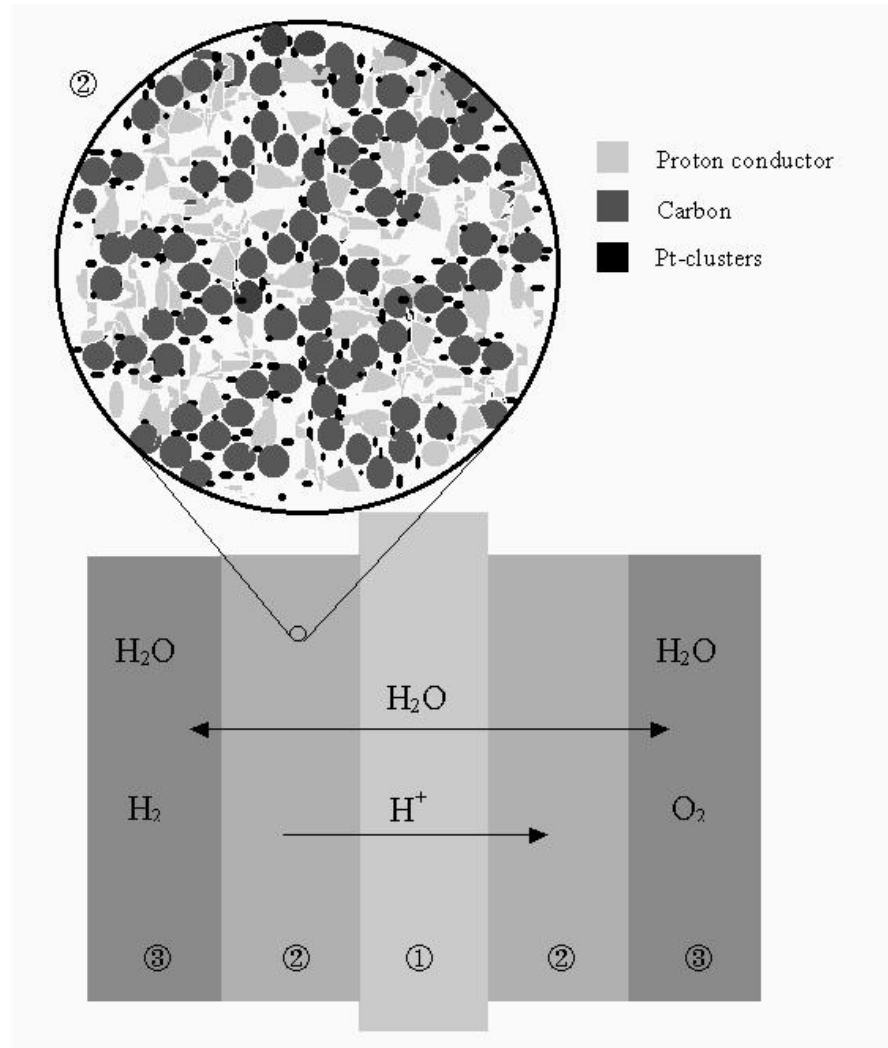
# Working procedure for one-dimensional model

1. The entropy production of five separate layers
2. The fluxes and conjugate forces
3. The coefficients from experiments
4. Electric work from chemical energy in the cell
5. The dissipation of energy; lost work



Limitations in this study:  
One-dimensional transports  
No pressure gradients

# Transport of heat, mass and charge across five parallel layers



*Possible questions:*

Nernst equation is:  $\Delta G = -nFE$   
What is the local potential profile?

Is there any temperature profile?

In which contexts are concentration profiles important?

What is the entropy production?

# A systematic way to describe transport processes

Example: The PEM fuel cell

- 2.law, local formulation

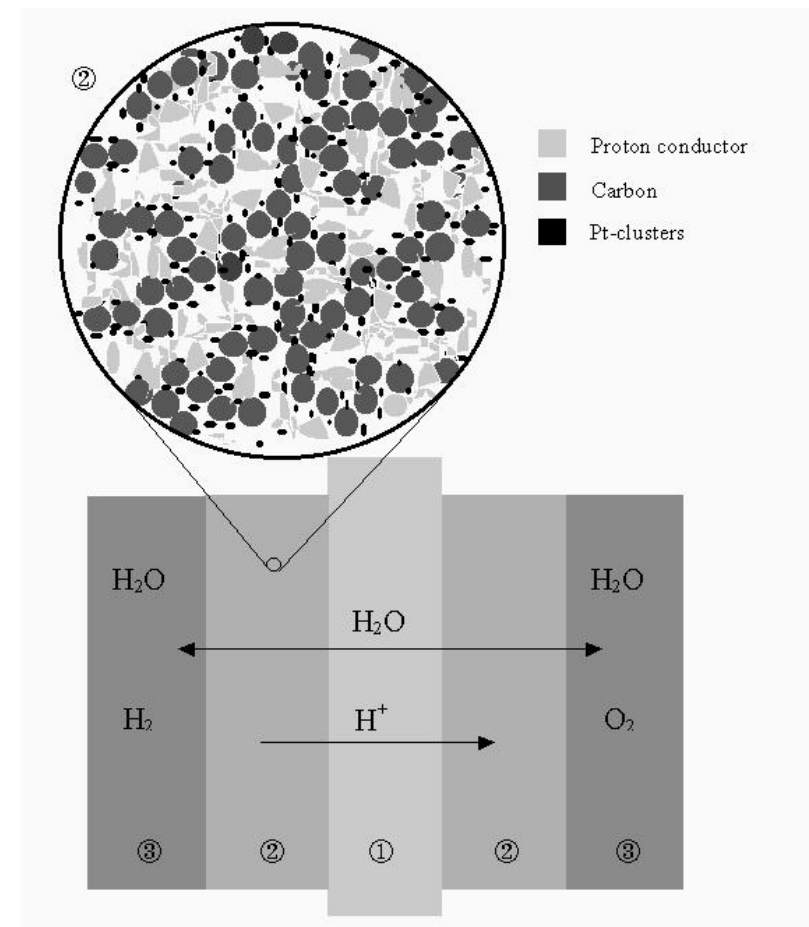
$$\sigma = \sum_i J_i X_i > 0$$

- Onsager's symmetry relations must be obeyed for any subsystem:

$$J_1 = L_{11} X_1 + L_{12} X_2 \dots\dots$$

$$J_2 = L_{21} X_1 + L_{22} X_2 \dots\dots\dots$$

.



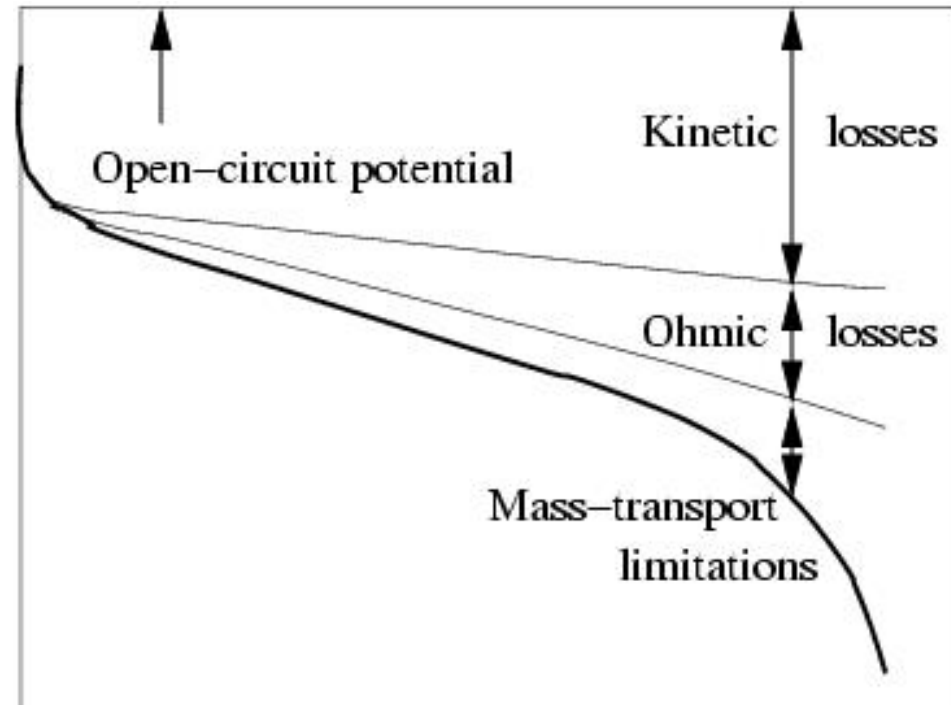
# Three ways to find the lost work:

1. By integrating over  $\sigma$
2. By calculating  $J_s^{in} J_s^{out}$
3. By measuring the heat production

$$\int \sigma dx = J_s^{out} - J_s^{in}$$

$$= \left[ \frac{1}{T^{out}} J_q^{out} + \sum J_i^{out} S_i \right]$$

$$- \left[ \frac{1}{T^{in}} J_q^{in} + \sum J_i^{in} S_i \right]$$



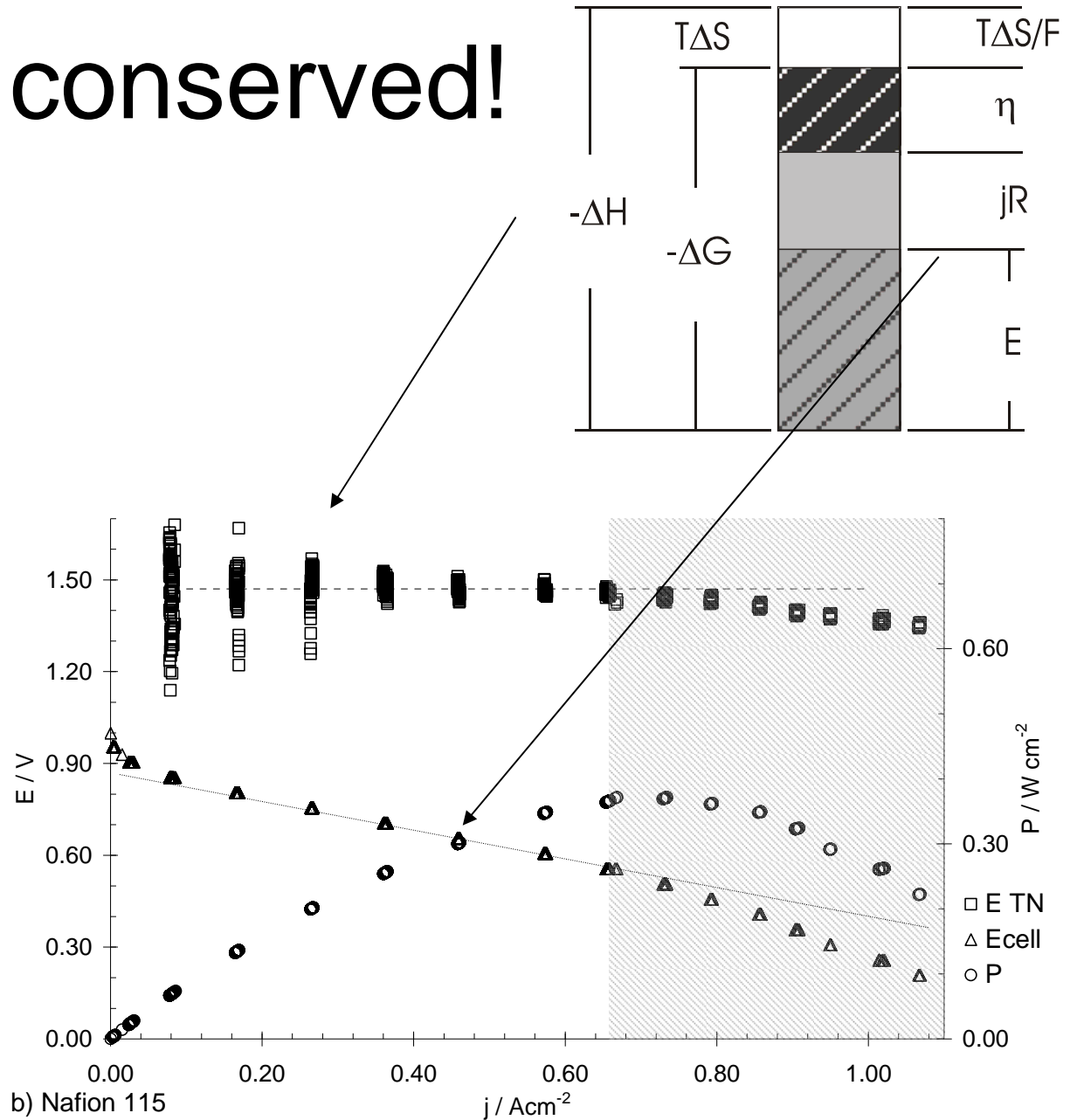
- The cell potential as function of the current density shows 3 distinct regimes (Eg. Weber and Newman, review, 2004)

# Energy is conserved!

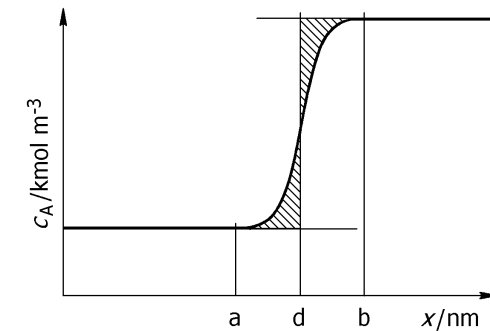
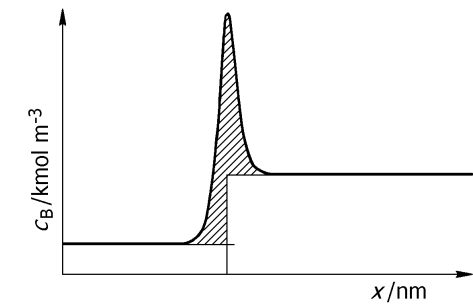
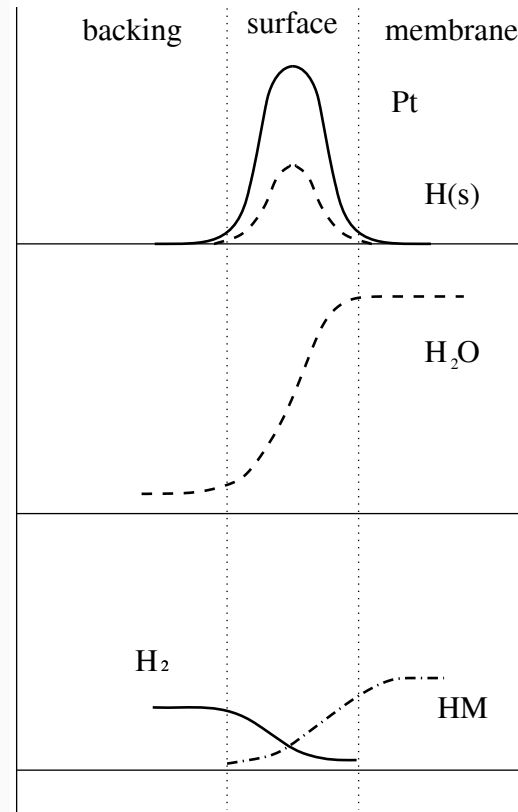
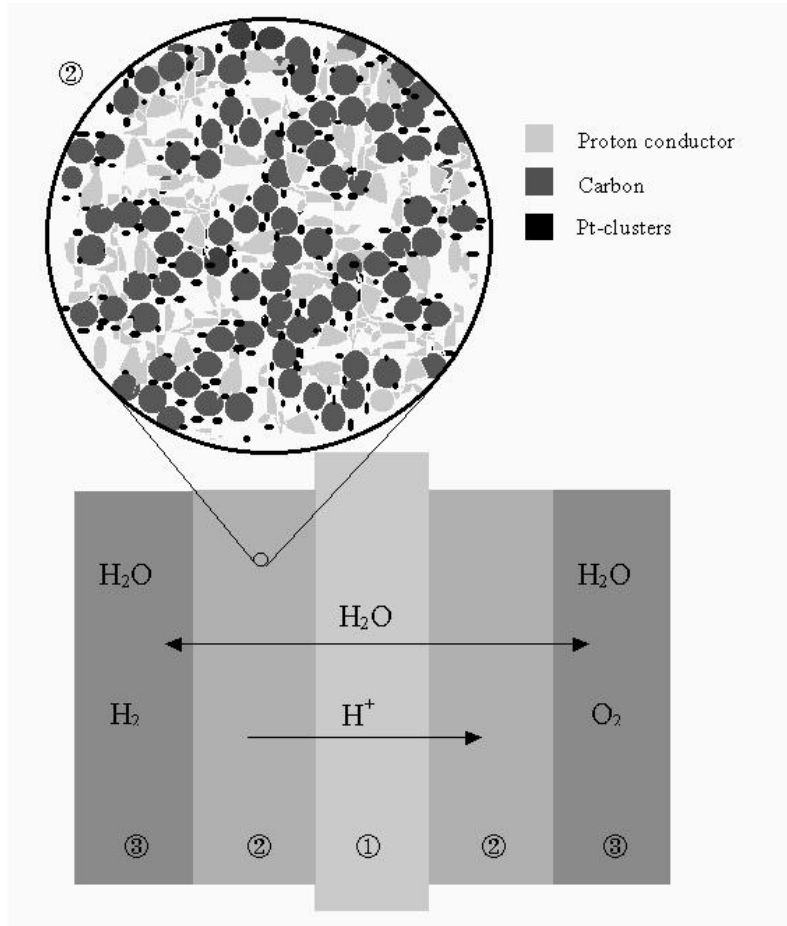
Thermoneutral  
potential (squares),  
polarisation curve  
(triangles)  
electric power (circles)

as functions of current  
density in a fuel cell  
operated at 323 K,  
1 atm, with oxygen  
and hydrogen

Burheim et al.  
*Electrochim. Acta.*  
55 (2010) 935-942



# Excess properties of the electrode surface according to Gibbs



Gibbs equation: 
$$U^s = TS^s + \gamma dA + \sum \mu_j dN_j^s$$

# The entropy production for the cathode surface

- We use:

Mass balances,  
first law,  
Gibbs equation

- One flux-force pair for each variable

- Reversible conditions give Nernst equation for the electrode!

$$\begin{aligned} \sigma = & J_q^{m,s} \Delta_{m,s} \left( \frac{1}{T} \right) + J_q^{s,c} \Delta_{s,c} \left( \frac{1}{T} \right) \\ & + J_w^m \left( -\frac{1}{T} \Delta_{m,s} \mu_{w,T} \right) + J_w^c \left( -\frac{1}{T} \Delta_{s,c} \mu_{w,T} \right) \\ & + j \left[ -\frac{1}{T} \left( \Delta_{m,c} \varphi + \frac{\Delta G^c}{F} \right) \right] \end{aligned}$$

# Part of the problem: Thermal osmosis

(cf. Lecture 6)

$$J'_q{}^{m,a} - J'_q{}^a = J \Delta H$$

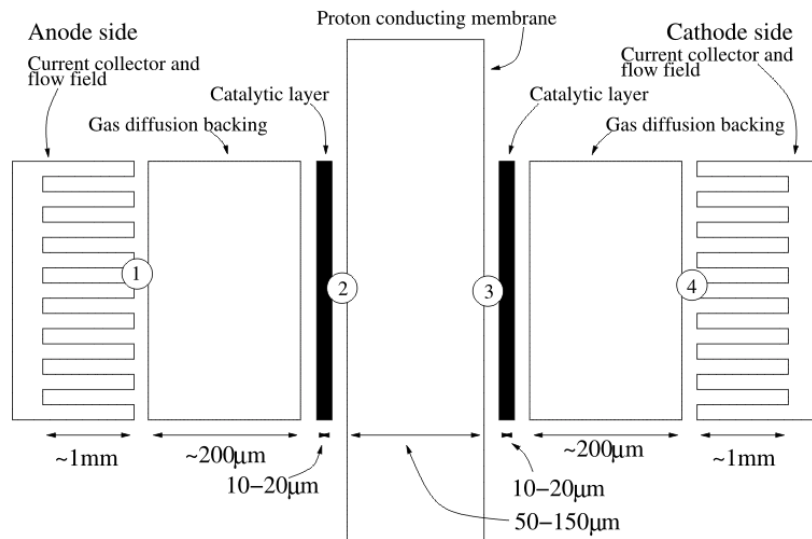
$$J'_q{}^c - J'_q{}^{m,c} = -J \Delta H$$

Energy balance  
T-profile  
Concentration  
profile

$$T^{m,a} - T^a = -\frac{1}{l^s} (J'_q{}^a - q^{*s} J)$$

$$\frac{dT}{dx} = -\frac{1}{l^m} (J'_q{}^m - q^{*m} J)$$

$$T^c - T^{m,c} = -\frac{1}{l^s} (J'_q{}^c - q^{*s} J)$$



$$\Delta_{a,m} \mu_T = -\frac{RT^{m,a}}{D^s c^{s,a}} J - \frac{q^{*s}}{T^{m,a}} \Delta_{a,m} T$$

$$\frac{d\mu_T}{dx} = -\frac{1}{D^m} J - \frac{q^{*m}}{T} \frac{c}{RT} \frac{dT}{dx}$$

$$\Delta_{m,c} \mu_T = -\frac{RT^{m,c}}{D^s c^{s,c}} J - \frac{q^{*s}}{T^{m,c}} \Delta_{m,c} T$$



# Flux-force relations - cathode surface

Temperature jumps:

$$\Delta_{m,s}T = -\frac{1}{\lambda_m^s} \left[ J_q^{m,c} - q^{*,m} \left( J_w^m - t_w^m \frac{j}{F} \right) - \pi^m \frac{j}{m} \right]$$

$$\Delta_{s,c}T = -\frac{1}{\lambda_c^s} \left[ J_q^{c,m} - q^{*,c} \left( J_w^c - t_w^c \frac{j}{F} \right) - \pi^c \frac{j}{m} \right]$$

Changes in chemical potential of water:

$$\Delta_{s,c}\mu_{w,T} = -\frac{q^{*,c}}{T^{c,m}} \Delta_{s,c}T - \frac{1}{l_{\mu}^s} \left( J_w^c - t_w^c \frac{j}{F} \right)$$

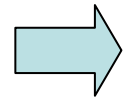
$$\Delta_{m,s}\mu_{w,T} = -\frac{q^{*,m}}{T^{m,c}} \Delta_{m,s}T - \frac{1}{l_{\mu}^s} \left( J_w^m - t_w^m \frac{j}{F} \right)$$

**Thermal osmosis and electro-osmosis!**

The jump in electric potential across the surface

$$\Delta_{m,c}\varphi + \Delta G^c = -\frac{\pi^m}{FT^m} \Delta_{m,s}T - \frac{\pi^c}{FT^c} \Delta_{s,c}T - \frac{t_w^m}{F} \Delta_{m,c}\mu_{w,T} - \frac{t_w^c}{F} \Delta_{s,c}\mu_{w,T} - r^s j$$

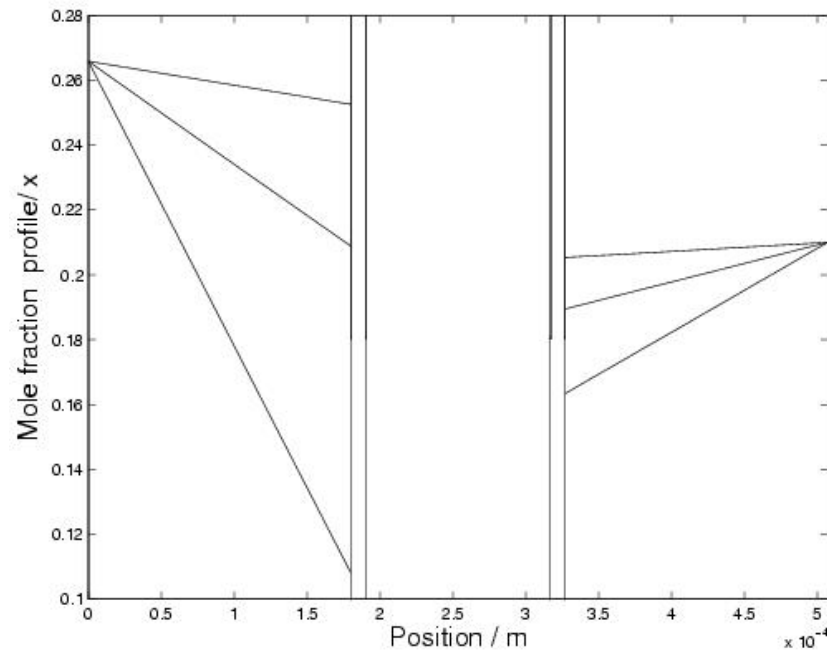
To do for each of the five subsystems:



Solve  $\mathbf{J} = \mathbf{L} \mathbf{X}$  for fluxes of heat, water and electric current

Boundary conditions used: Constant  $j$ ,  $J_w$ ,  $T^a = T^c = 370 \text{ K}$

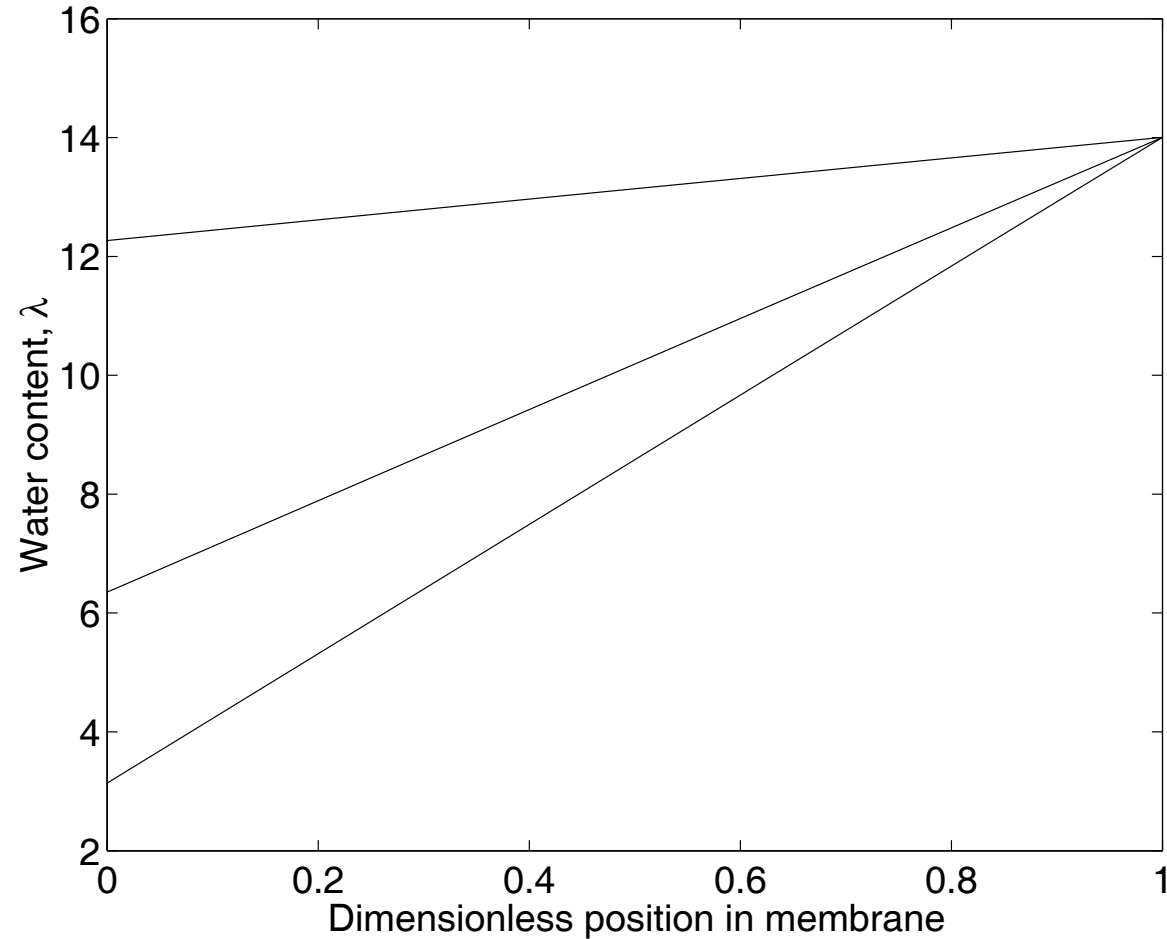
## Results<sup>1</sup>:



**Mole fractions of water (left) and oxygen (right)**

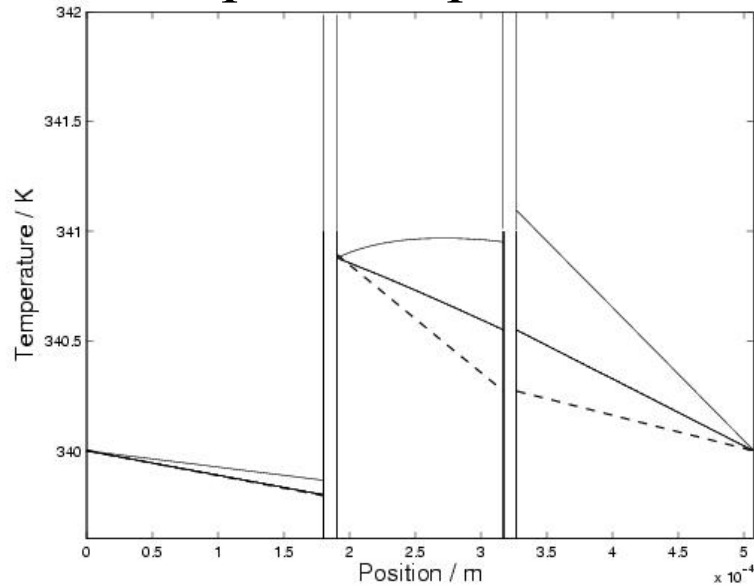
1. S.Kjelstrup and A. Røsørde, J. Phys. Chem. B, 109 (2005) 9020

# Results for water concentration profile in the membrane

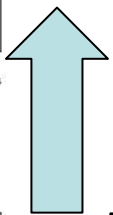
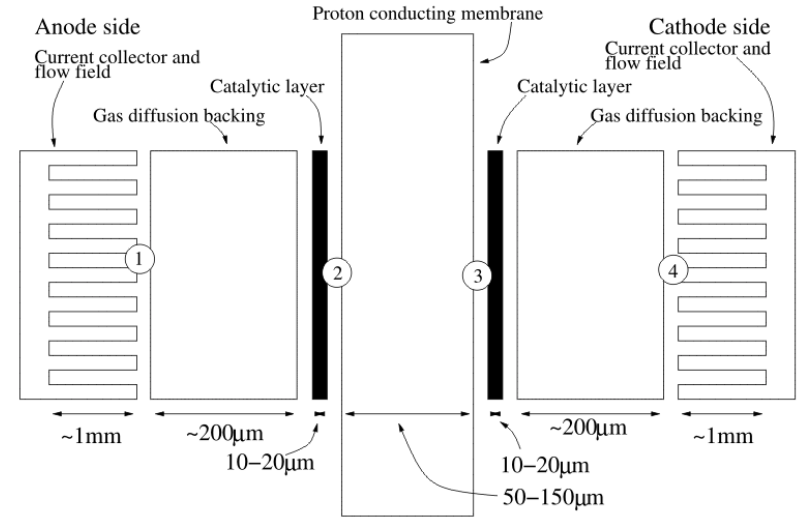


The surface jump: 
$$\Delta_{s,c} \mu_{w,T} = RT \Delta \lambda / \lambda^* = -\frac{q^{*,c}}{T^{c,m}} \Delta_{s,c} T - \frac{1}{l_{\mu}^s} \left( J_w^c - t_w^c \frac{j}{F} \right)$$

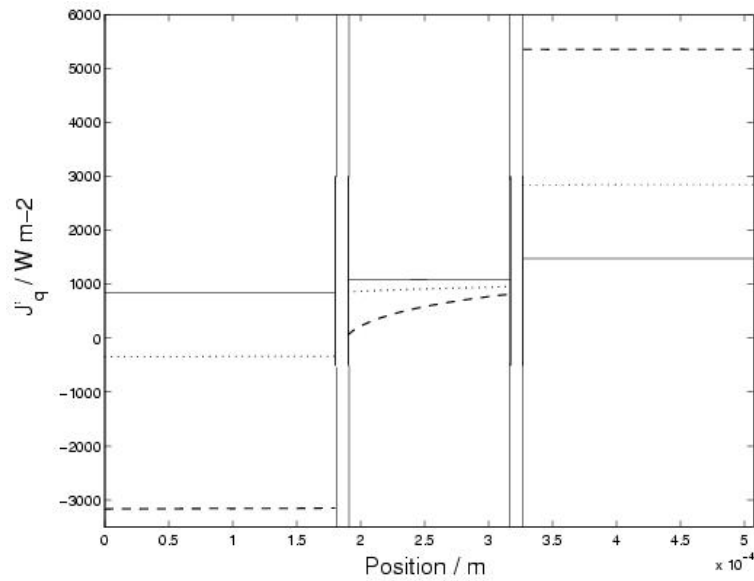
# Temperature profiles



P  
E  
M  
F  
C

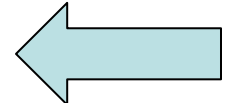


•  $T(x)$

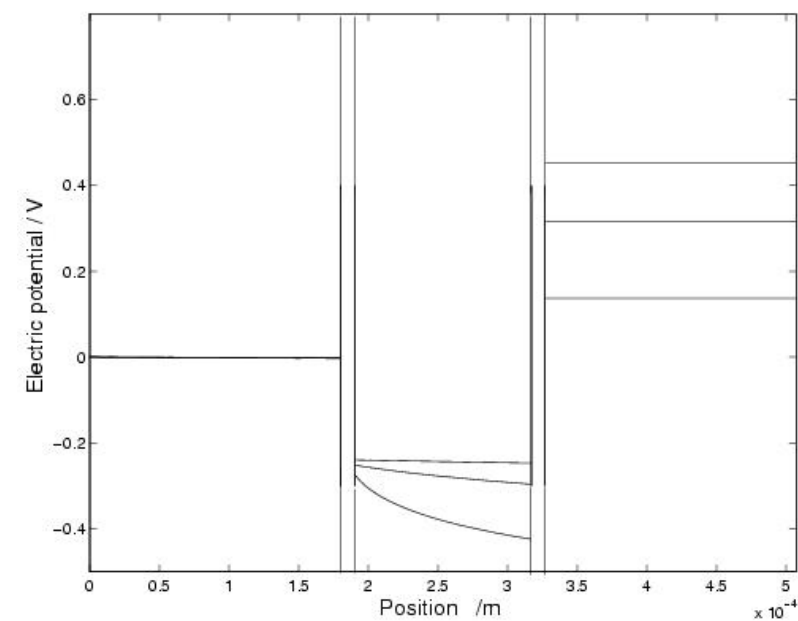


•  $J'_q(x)$

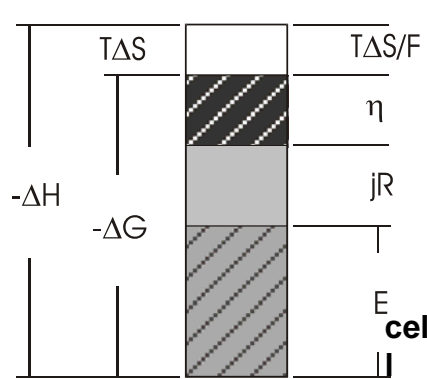
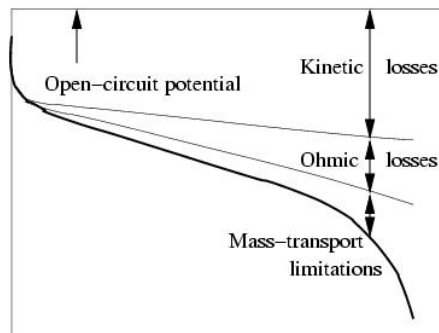
•  $E(x)$



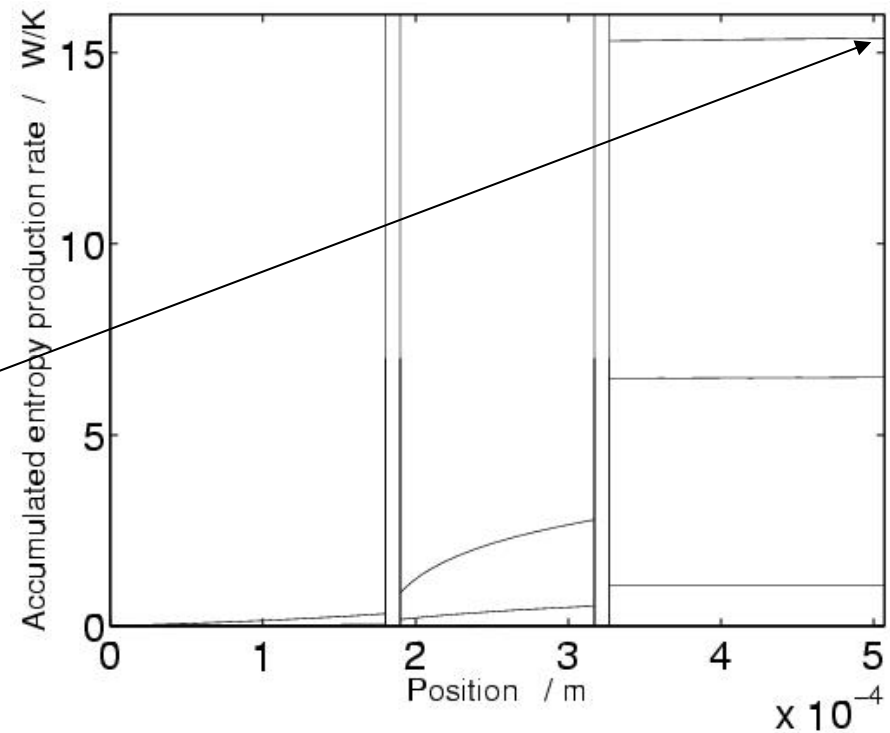
# Potential profiles



# Lost work and accumulated entropy production



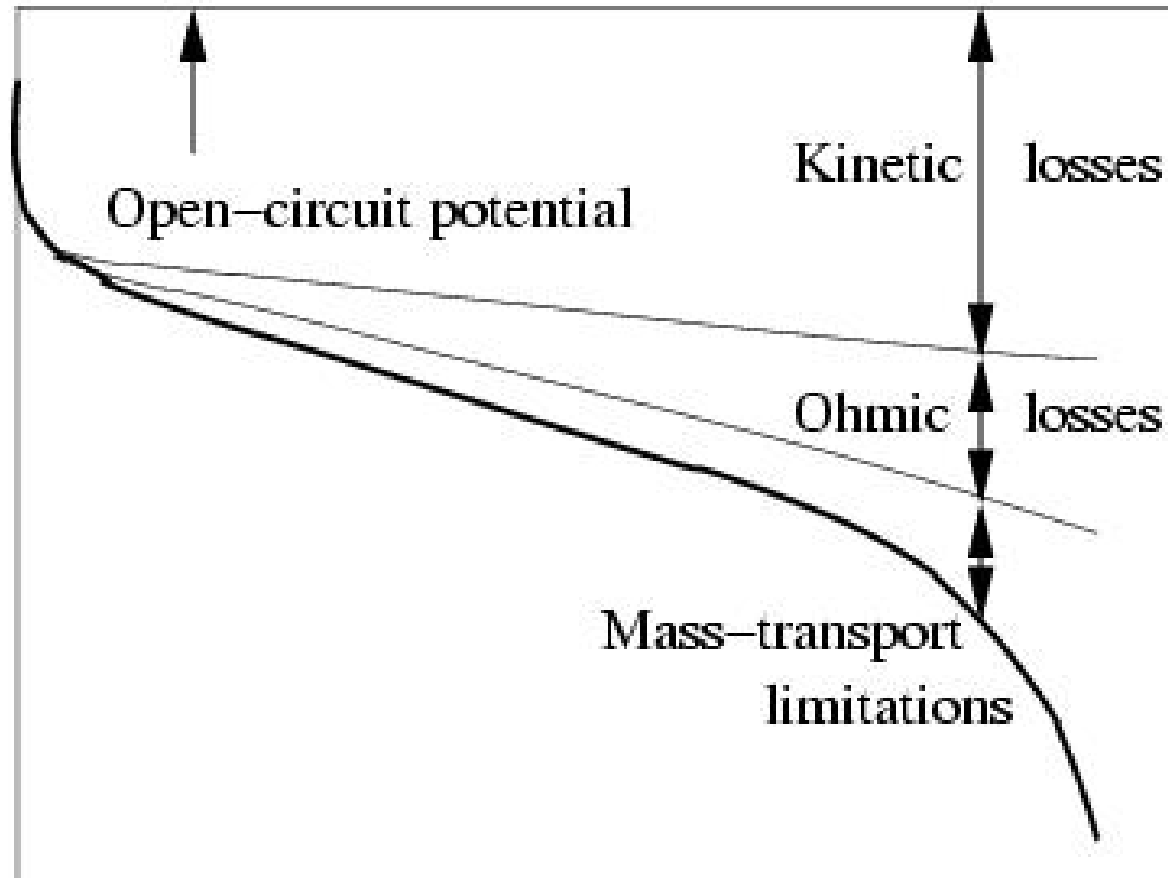
$$dS_{irr}/dt$$



The cell potential as a function of  $j$

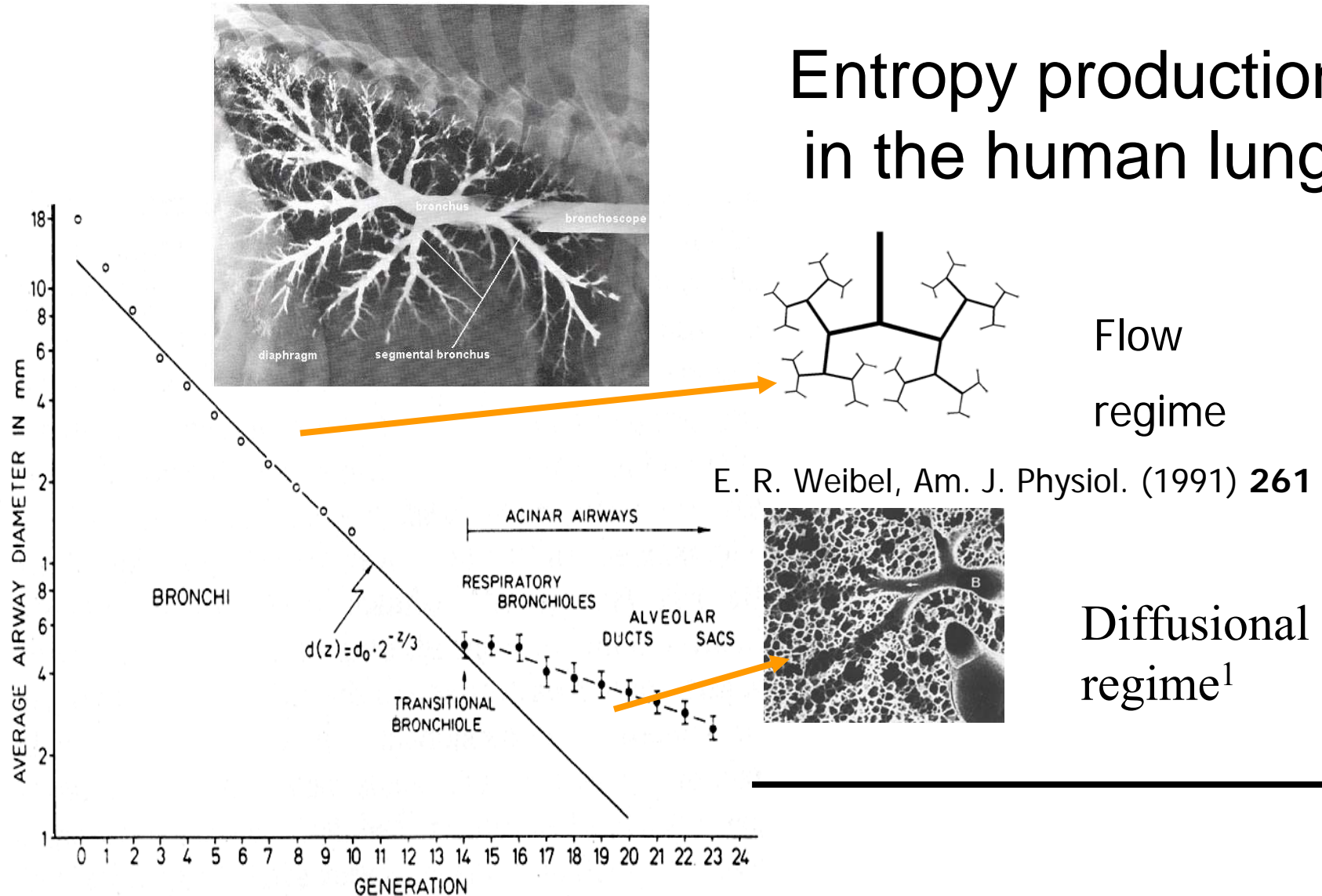
Accumulated entropy production

# The problem:



Losses are unevenly distributed across the membrane! Cf. Lecture 10

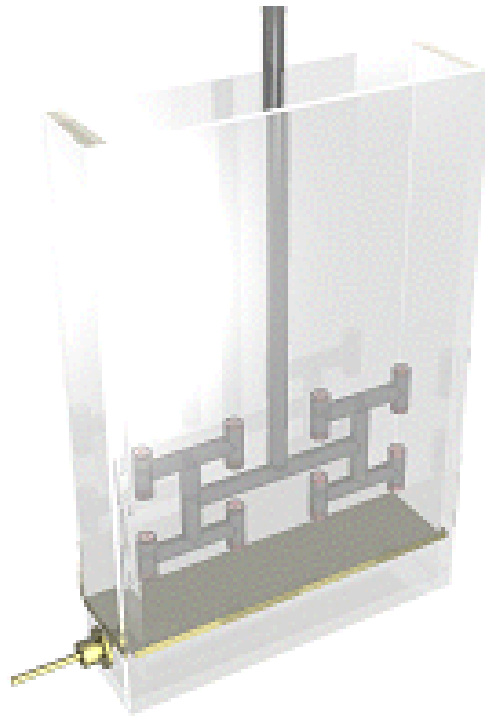
# Entropy production in the human lung



The entropy production (and the driving force) is constant in each of the flow regimes

S. Gheorghiu, S. Kjelstrup, P. Pfeifer and M.-O. Coppens (2005),  
 Fractals in Biology and Medicine, Vol. IV (Losa et al., ed. Birkhäuser Verlag, Basel), pp. 31-42.

# Can we make more energy efficient designs?



A fractal injector in fluidized beds gives higher yield per unit time (Coppens, US patent)

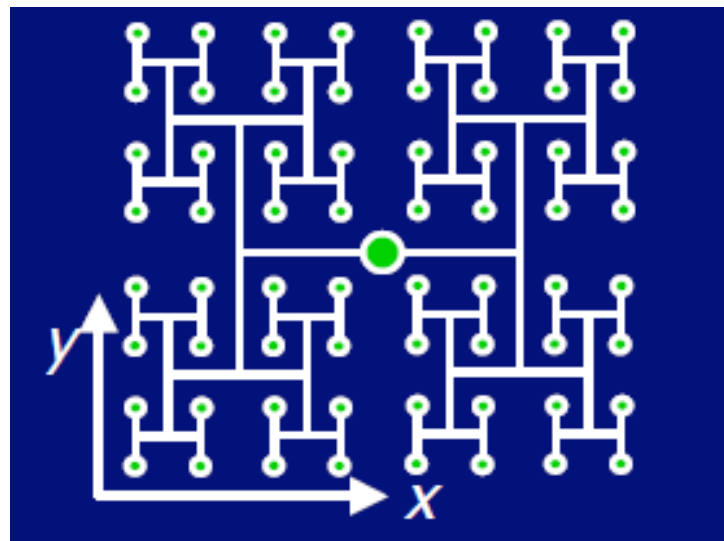


Highest thermodynamic efficiency with constant local entropy production and uniform feed over the area; or:

$$\nabla p(x, y) = C_1 \qquad j(c_x, c_y) = j = C_4$$
$$c(H) = c^0$$

Cf, Lectures 10,11

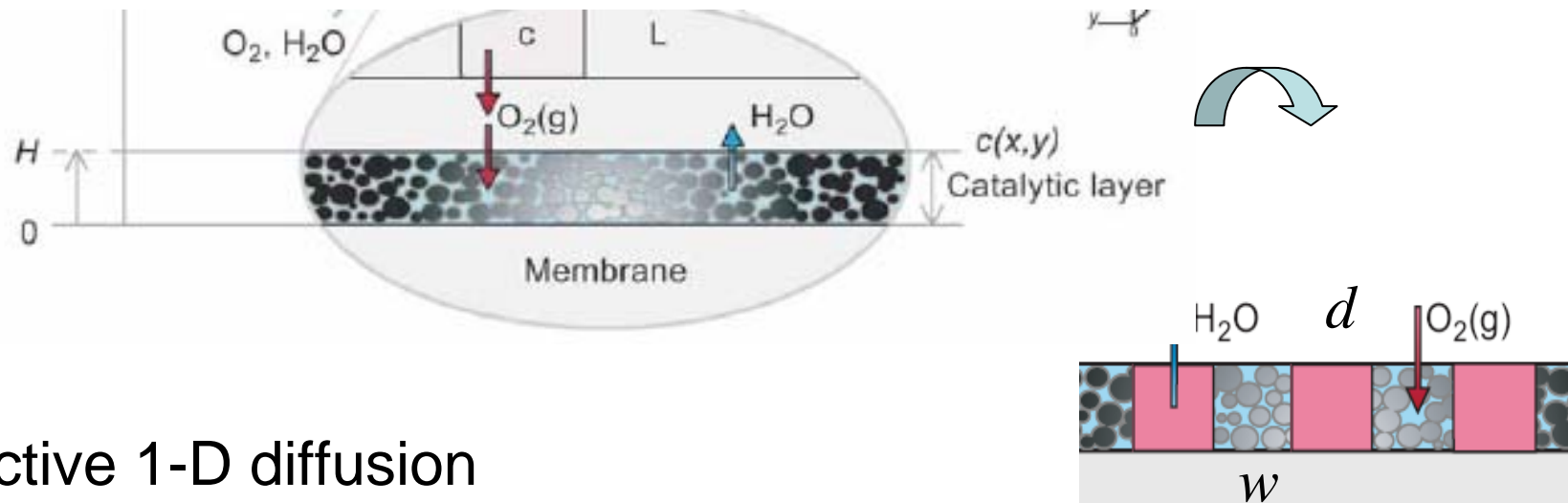
A fractal injector gives a uniform 2D distribution\*



Tondeur  
et al. 2004

Right angles: OK when pressure losses are small!

The reaction can be limited by diffusion in the nanoporous part



Effective 1-D diffusion

Reaction/diffusion  
Stationary state

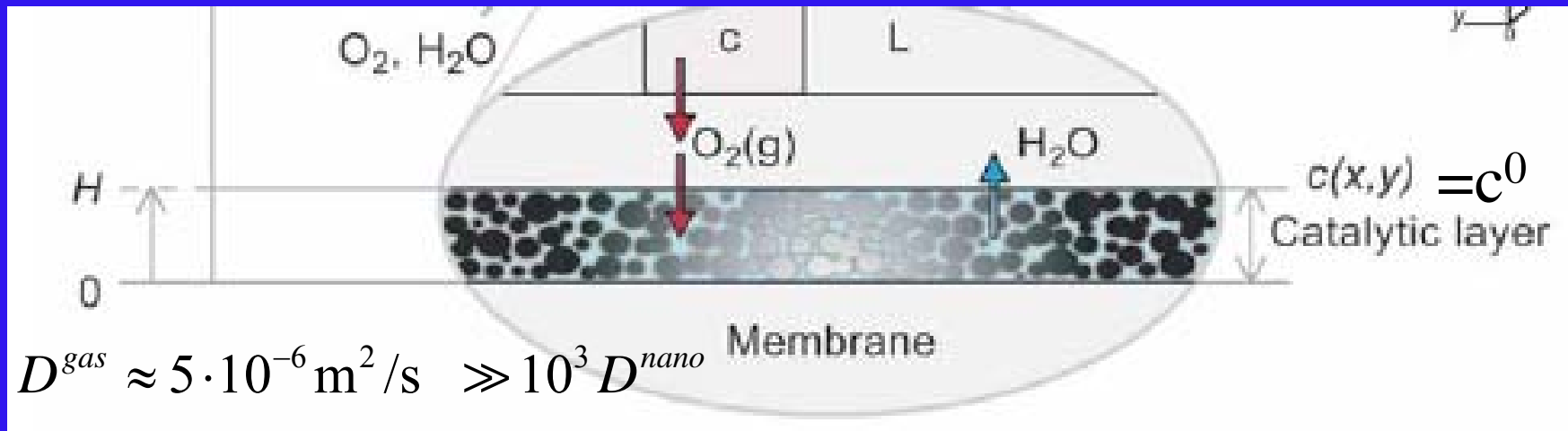
$$D(\varepsilon) \frac{\partial^2 c}{\partial y^2} - k(1 - \varepsilon)c(y) = 0$$

Porosity

$$\varepsilon = \frac{d}{d + w}$$

E. Johannessen, G. Wang, M.-O. Coppens. Ind. Eng. Chem. Res. (2007)

E. Johannessen, G. Wang, C.R. Kleijn, M.-O. Coppens. Ind. Eng. Chem. Res. (2007)



Given a constant production

$$J^0 = (1 - \epsilon)H\eta_E kc^0$$

with efficiency factor

$$\eta_E \equiv \frac{\int_V kcdV}{(1 - \epsilon)kc^0V} = \frac{\tanh \phi_0}{\phi_0}$$

Thiele modulus

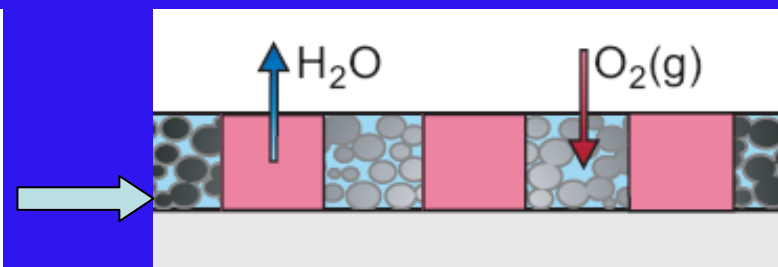
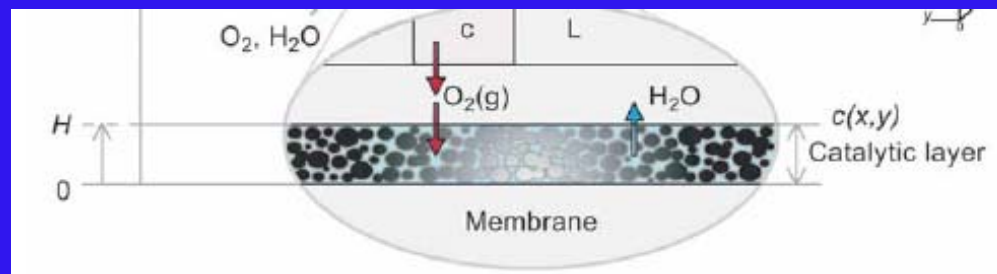
What is the optimal macroporosity  $\epsilon$  and height  $H$  of the layer?

Find the minimum catalyst volume for a given current

$$V_{cat} = (1 - \varepsilon)HLM + \lambda \left[ J - J^0 \right] LM$$

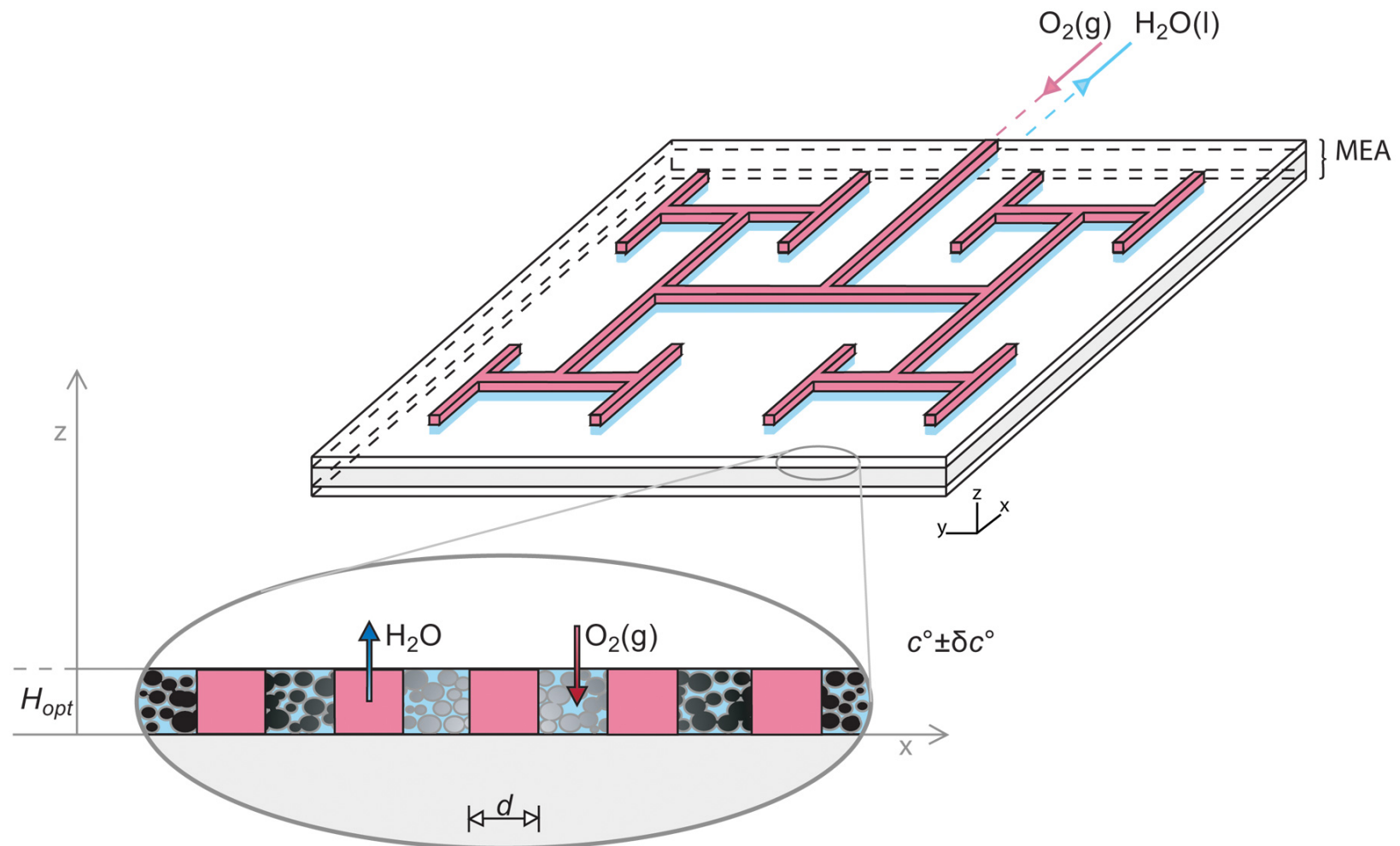
$$\varepsilon_{opt} = \frac{1}{2}$$

$$H_{opt} = \sqrt{\frac{D_0}{k}} \tanh^{-1} \left( \frac{DOI:10.1021/ef100610w}{c^0 \sqrt{D_0 k}} \right) = \sqrt{\frac{D_0}{k}} \tanh^{-1} \left( \frac{J^0}{J_{max}} \right)$$



Kjelstrup, Coppens, Pharoah, Pfeifer, Energy and Fuels (2010)

# Improving the material- and energy efficiency...

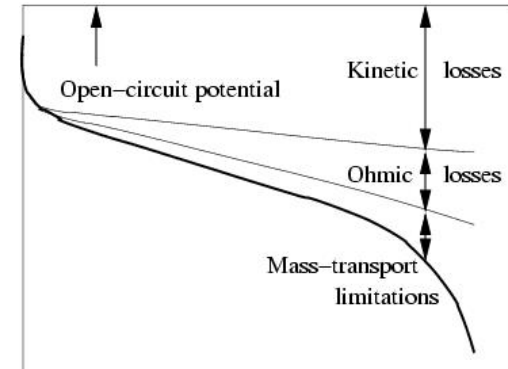


.... By uniform feed distribution  
and increasing access to the catalyst

# Numerical example: Pure oxygen

ETEK Elat: 0.5 mg Pt/cm<sup>2</sup> 353 K, 1 bar

Current density / Am <sup>-2</sup>	500	15000	15000
Transfer factor	1.0	1.0	0.8
Butler-Volmer Overpotential / V	0.192	0.296	0.371
Rate coefficient /s <sup>-1</sup>	3.8		
Rate coefficient /s <sup>-1</sup>		117	415
Optimal layer height/ μm	20.0	19.6	5.5



Energy  
dissipation  
reduced by  
≈  
100-200 mV  
10- 20 %  
Pt cost reduced  
by a factor 8

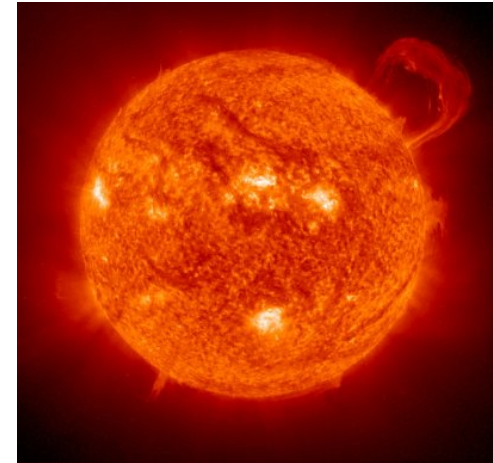
# Summary

- The coupling of transport phenomena in fuel cells is large
- The entropy production can be studied by calorimetry of fuel cells and by modeling
- The theory provides fundamental insight, and may help practical designs of experiments and equipments
- The entropy balance is not yet widely used in a systematic study of fuel cells. It can be used to find better designs (cf. Lectures 10,11).

# On a road towards the hydrogen society....

Where does H<sub>2</sub> come from?

- H<sub>2</sub> from natural gas
- Electrolysis of water
- Geothermal sources



wind



hydro



geo