



Introduction to Fuel Cell Modelling

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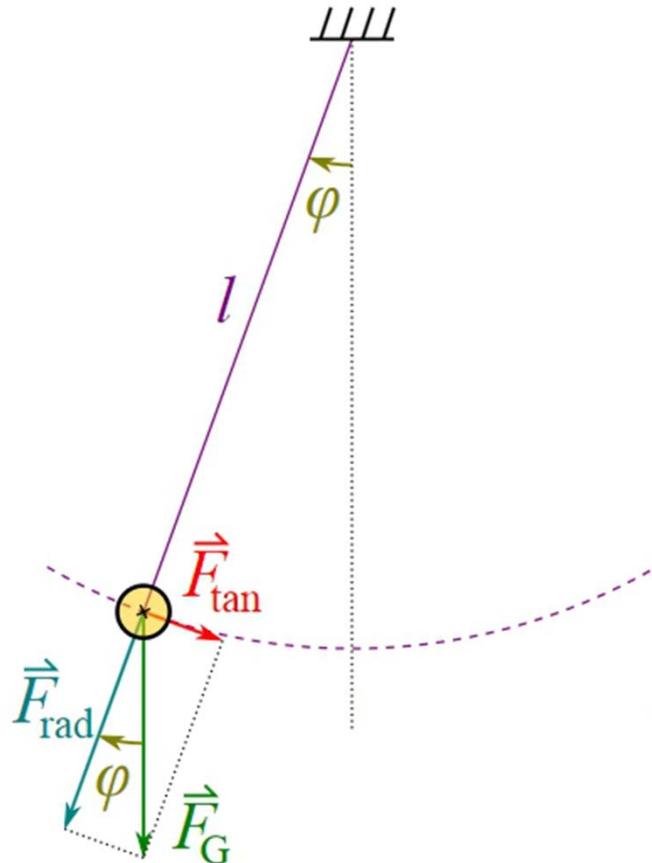
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Outline

- Introduction: The fuel cell effect
- Potentials and Butler—Volmer equation
- Cathode catalyst layer (CCL) transient model
- Going to the cell level: Oxygen transport in the GDL
- Oxygen consumption in the channel
- Heat flux from the catalyst layer
- CCL model and impedance spectroscopy
- How much is poor proton transport in the CCL?
- Other limiting cases / solutions
- What happens to the cathode channel flow
- Conclusions

What is modeling? Consider classic pendulum



A good picture is 90% of success

$$ma = -F_{\tan}$$

Newton's law

$$F_{\tan} = F_G \sin \varphi = mg \sin \varphi$$

$$v = l \frac{\partial \varphi}{\partial t}; \quad a = \frac{\partial v}{\partial t} = l \frac{\partial^2 \varphi}{\partial t^2}$$

Phi is small !

$$ml \frac{\partial^2 \varphi}{\partial t^2} = -mg \sin \varphi \simeq -mg\varphi$$

$$\frac{\partial^2 \varphi}{\partial t^2} + \frac{g}{l} \varphi = 0$$

The mass disappeared

Classic pendulum: Omega

Phi is periodic, the equation is linear, make Fourier transform!

$$\frac{\partial^2 \varphi}{\partial t^2} + \frac{g}{l} \varphi = 0; \quad \varphi(t) = \hat{\varphi}(\omega) \exp(i\omega t)$$

$$(i\omega)(i\omega)\hat{\varphi} \exp(i\omega t) + \frac{g}{l}\hat{\varphi} \exp(i\omega t) = 0$$

$$\omega = \sqrt{\frac{g}{l}}$$

$$f = \frac{1}{2\pi} \sqrt{\frac{g}{l}}$$

$$T = 2\pi \sqrt{\frac{l}{g}}$$

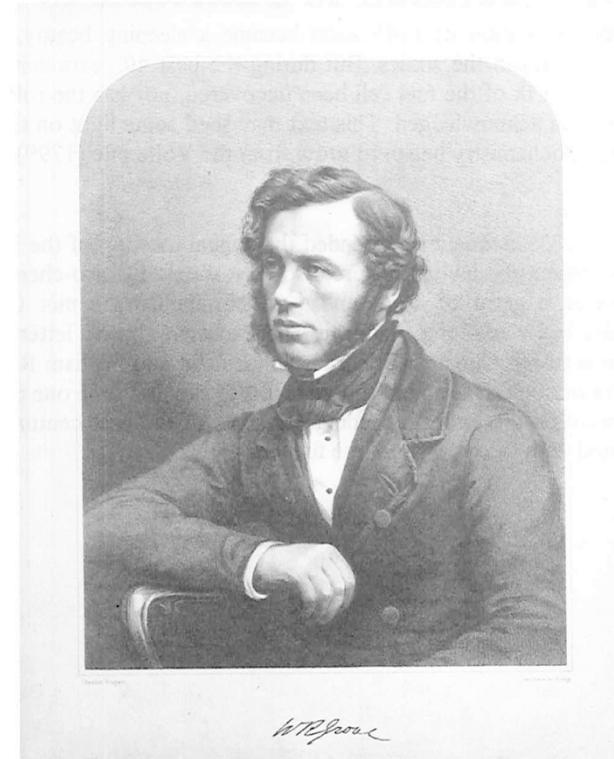
That is what we are going to do this evening

1838: The birth of the fuel cell



Christian Friedrich Schönbein
(October 18, 1799 - August 29, 1868)

Photo: Foto-Atelier Braun, Metzingen (Naturhistorisches Museum Basel)

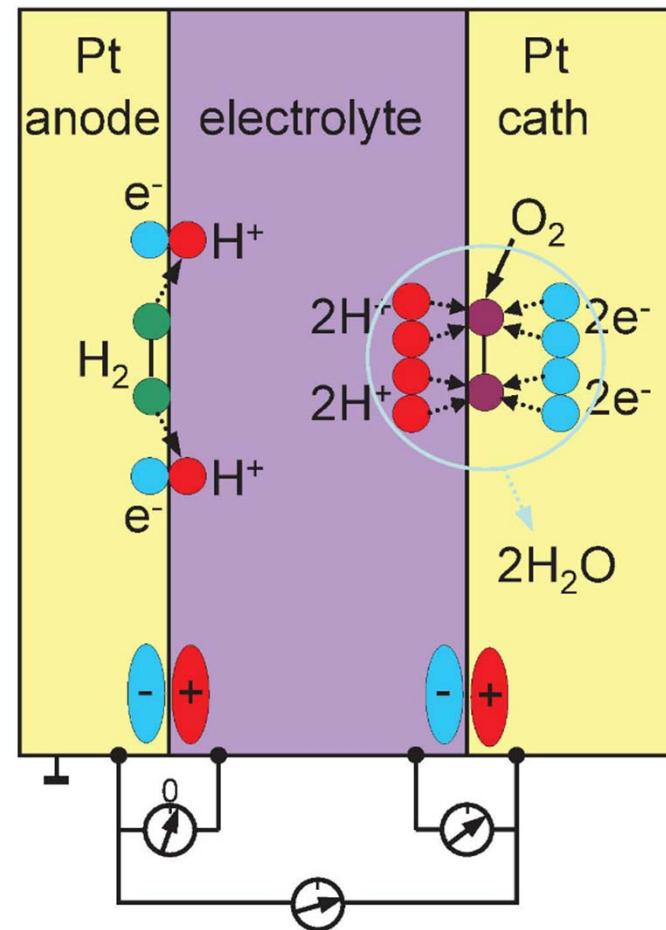


Sir William Robert Grove
(July 11, 1811 - August 1, 1896)

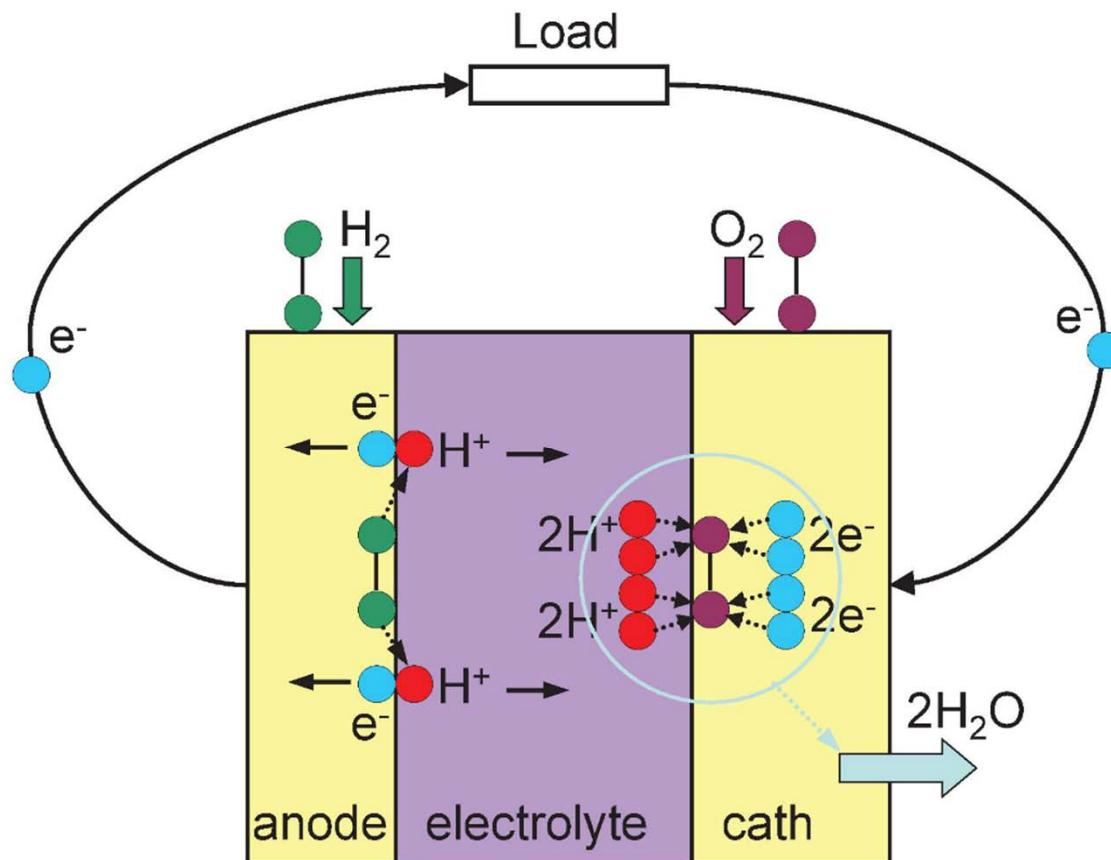
Photo: The Bridgeman Art Library, London (The Royal Institution, London)

In spite of 174 years of research, we don't see fuel cells in a supermarket. The reason is tremendous complexity of the problem.

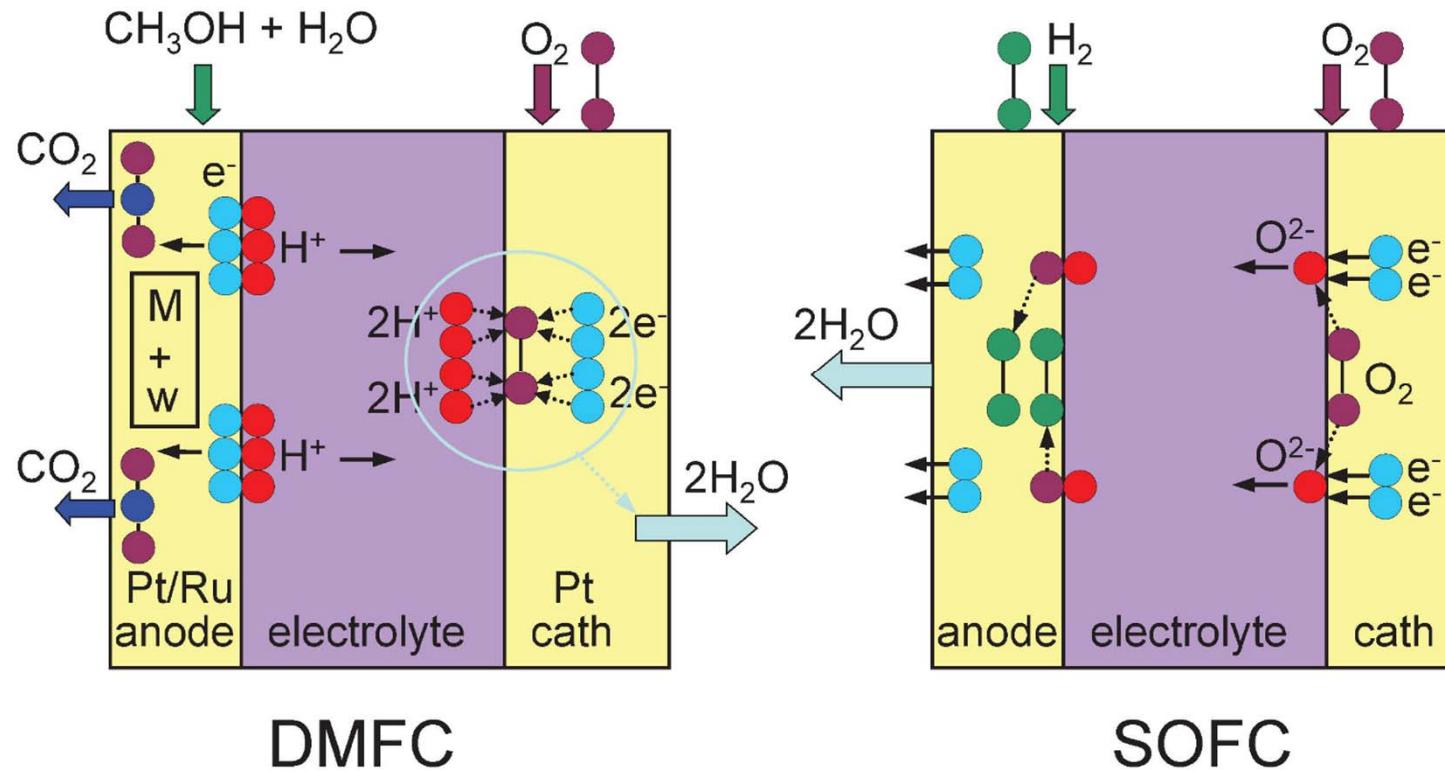
The fuel cell effect



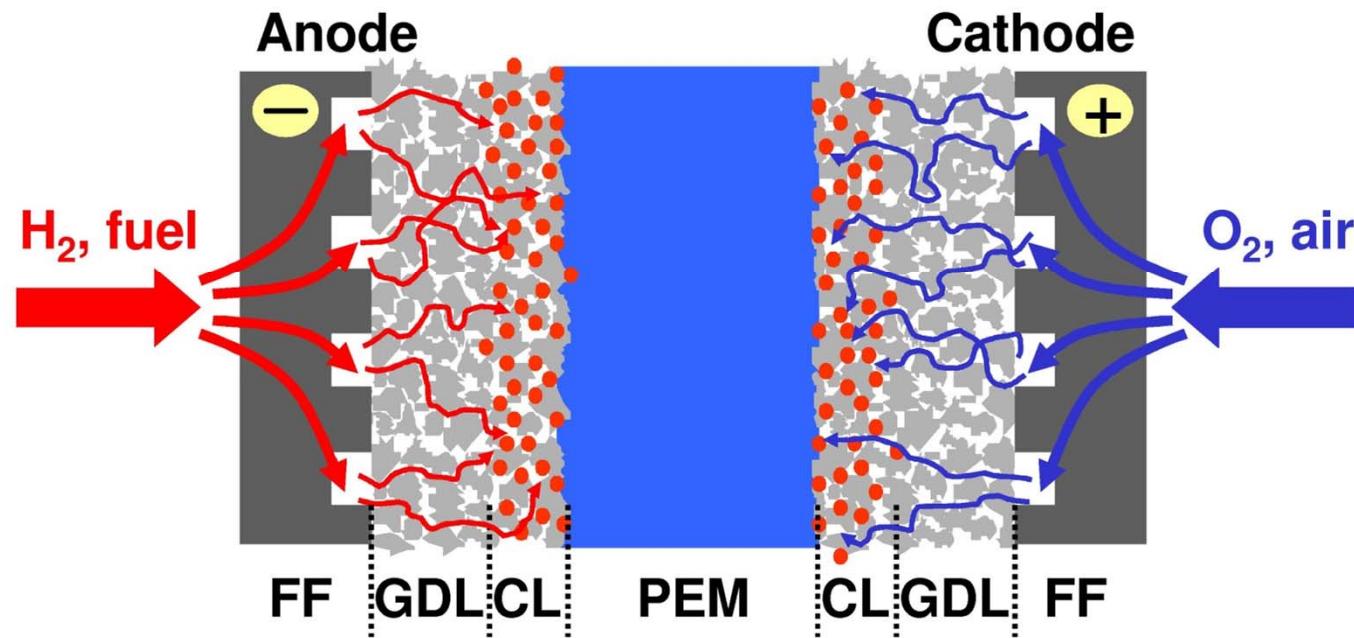
PEMFC: How it works



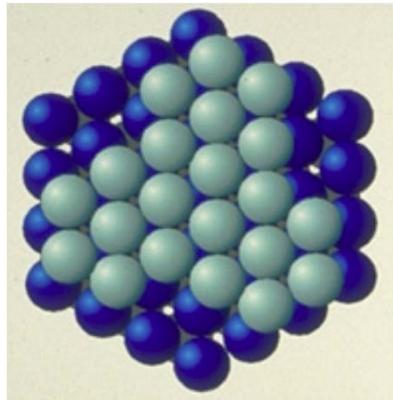
Direct methanol and solid oxide FCs



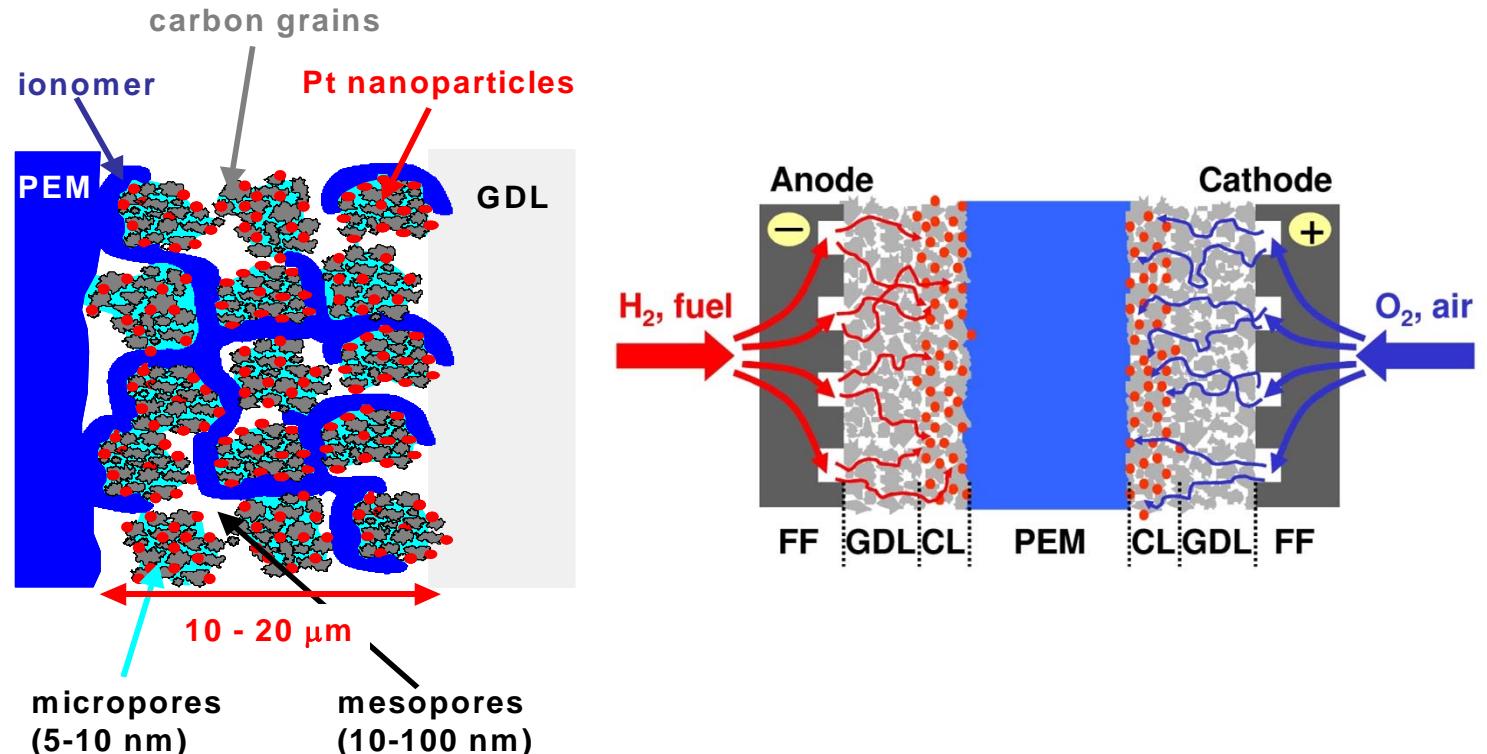
Real PEM fuel cell schematic



The problem



(a) Structural Picture of CCL



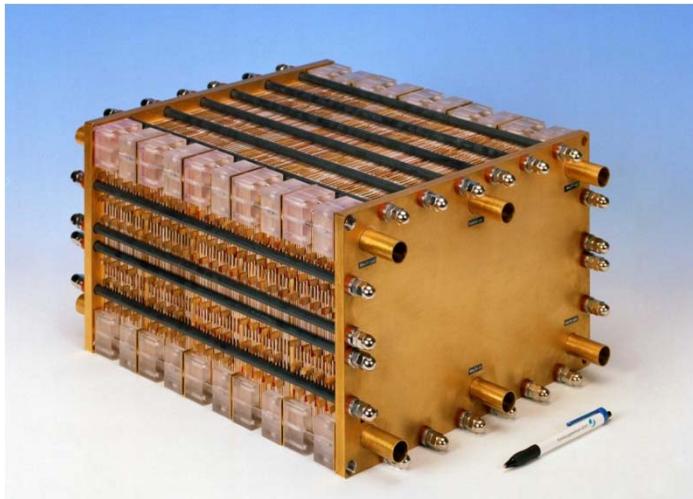
Pt particle

Catalyst layer

Fuel cell

Space scale

The problem



Stack

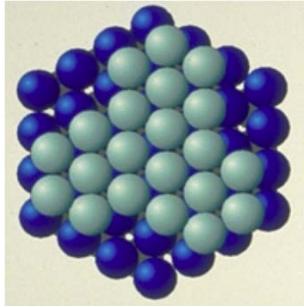
System



Space scale: 9 orders of magnitude (nm to m)

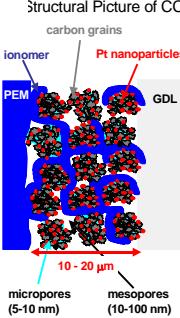
Time scale: 20 orders of magnitude (ps to years)

The models we will discuss

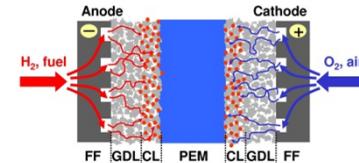


Basic solvable models

Structural Picture of CCL



micropores (5-10 nm)
mesopores (10-100 nm)



Anode Cathode

H_2 , fuel O_2 , air



Understanding CL, cell and stack function



What is overpotential?

$$\eta = \varphi_m - \varphi_c - E^{eq}$$

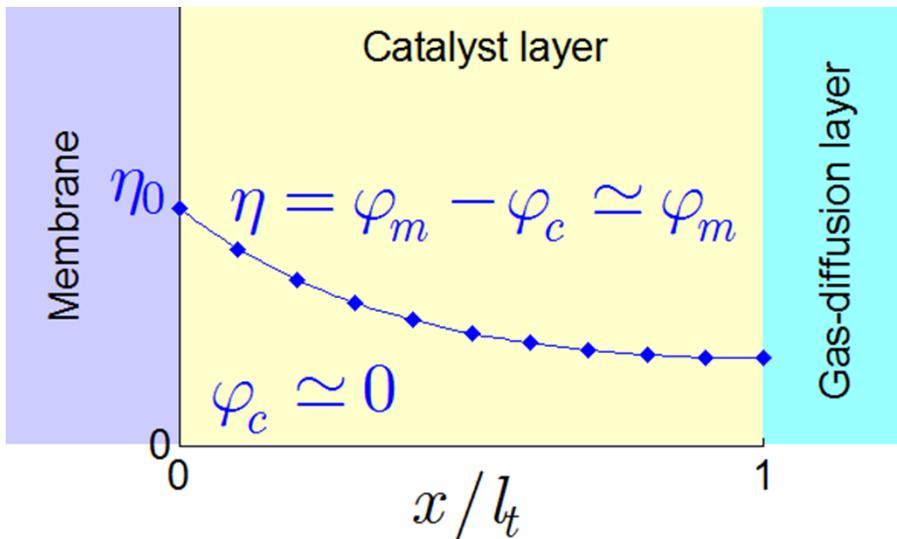
Electrolyte potential minus
electrode potential minus
equilibrium potential

At equilibrium the capacitor is charged and

$$\varphi_c = -E^{eq}, \varphi_m = 0, \eta = 0$$

In FC modeling, it is convenient to forget about E^{eq} for a moment, and to calculate the voltage loss first.

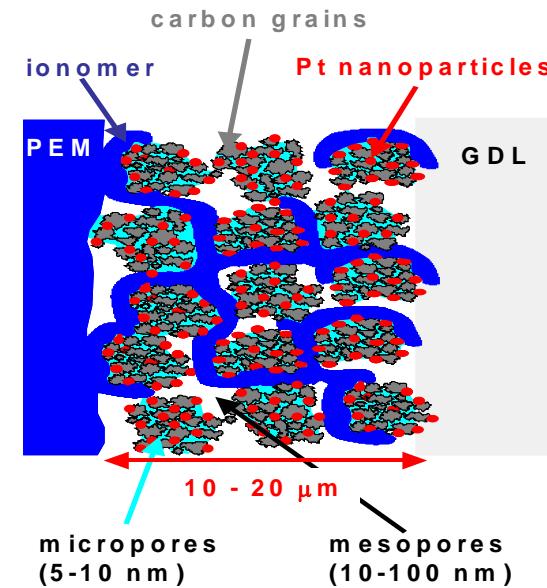
Two potentials in the catalyst layer



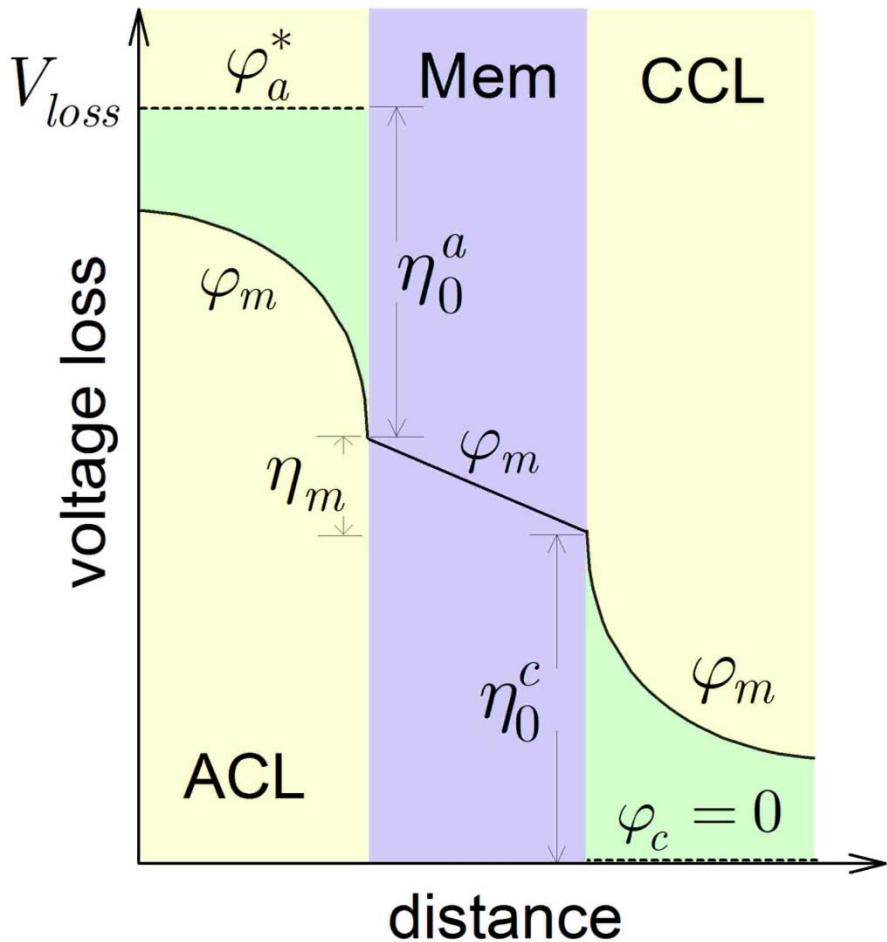
φ_c drives electrons, while φ_m drives protons, overpotential is $\varphi_m - \varphi_c$ (here we forget about OCV). **The total voltage loss is η_0 at the membrane interface.**

CL is a mixture of electrolyte and “electrode” (carbon phase). Each potential forms a porous cluster. This is modeled as a continuous media with two potentials, φ_m and φ_c .

(a) Structural Picture of CCL



Total voltage loss in a fuel cell



$$V_{loss} = \eta_0^a + \eta_0^c + \eta_m + R_c j$$

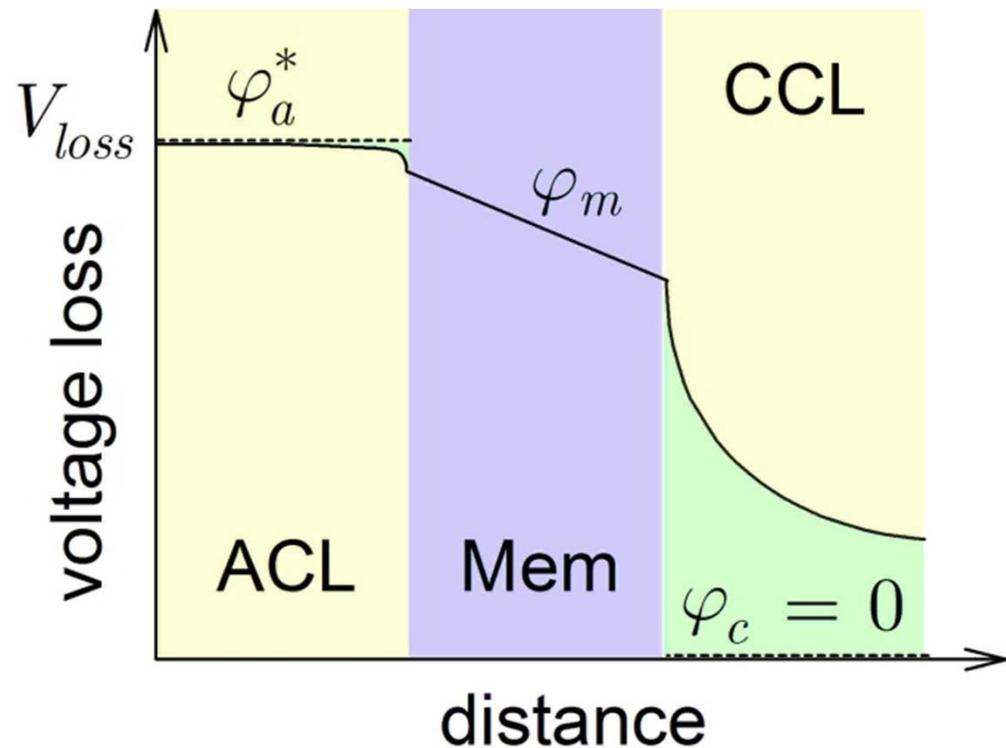
Once V_{loss} is calculated, the cell voltage is

$$V_{cell} = V_{oc} - V_{loss}$$

What happens to this figure when the cell current decreases? The point V_{loss} goes down. When $j=0$, all overpotentials are zero and

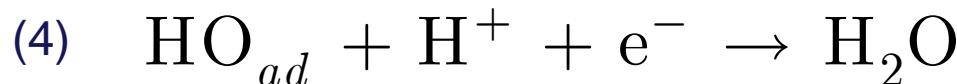
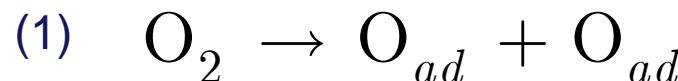
$$V_{cell} = V_{oc}$$

PEMFC



Anodic voltage loss is very small, as HOR kinetics are excellent. In PEMFCs, all the problems are on the cathode side.

ORR chain



Analysis of rate constants shows that

$$k_4 \ll \max\{k_1, k_2, k_3\}$$

Eq.(4) is ***the rate-determining step***; this is a single-electron transfer. Now we say that we will ignore all the reaction steps but the RDS, and consider an equivalent single-step 4-electron transfer, in which 3 electrons are transferred “for free”.

Butler-Volmer equation I

The rate of equivalent single-step reaction is

$$Q_f = \left(\frac{c_{ox}}{c_{ref}} \right) k_f(\eta)$$

The rate constant depends on overpotential.
This is what electrochemistry is about.

$$k_f(\eta) = i_{ref} \exp\left(-\frac{E_{act}}{RT}\right) = i_{ref} \exp\left(-\frac{E_{act} - \alpha F \eta}{RT}\right)$$

Eta lowers the barrier

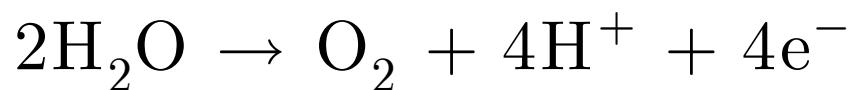
$$k_f(\eta) = i_* \exp\left(\frac{\alpha F \eta}{RT}\right), \text{ where } i_* = i_{ref} \exp\left(-\frac{E_{act}^{eq}}{RT}\right)$$

Exchange current density

Butler-Volmer equation II

$$Q_f = i_* \left(\frac{c_{ox}}{c_{ref}} \right) \exp \left(\frac{\alpha F \eta}{RT} \right)$$

Rate of forward reaction (ORR)



Reverse reaction of water electrolysis.
RDS also is a single-electron transfer.

$$Q_r = i_* \left(\frac{c_w}{c_{ref}^w} \right)^2 \exp \left(-\frac{(1-\alpha)F\eta}{RT} \right)$$

Rate of reverse reaction (WE)

$$Q = Q_f - Q_r$$

Total rate

Butler-Volmer equation III

$$Q = i_* \left[\left(\frac{c_{ox}}{c_{ref}} \right) \exp \left(\frac{\alpha F \eta}{RT} \right) - \left(\frac{c_w}{c_{ref}^w} \right)^2 \exp \left(-\frac{(1-\alpha)F\eta}{RT} \right) \right]$$

$$Q \simeq i_* \left(\frac{c_{ox}}{c_{ref}} \right) \left[\exp \left(\frac{\alpha F \eta}{RT} \right) - \exp \left(-\frac{(1-\alpha)F\eta}{RT} \right) \right]$$

If alpha=1/2,
we get

$$Q \simeq 2i_* \left(\frac{c_{ox}}{c_{ref}} \right) \sinh \left(\frac{\eta}{b} \right),$$

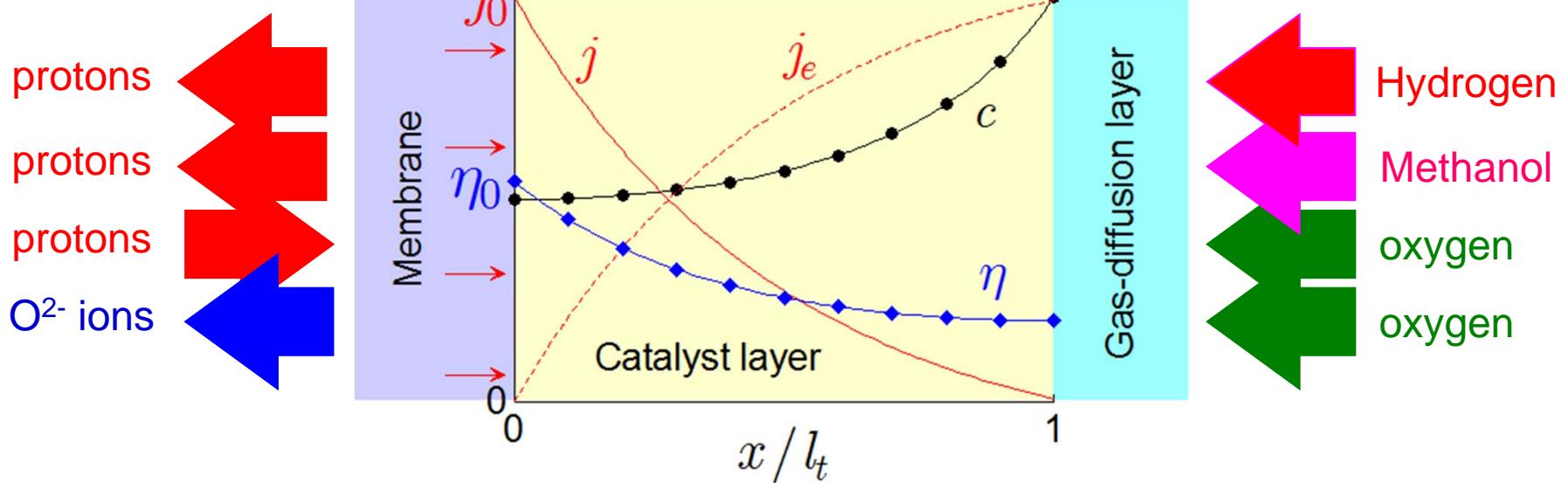
where

$$b = \frac{RT}{\alpha F}$$

Tafel slope

alpha=1/2 is a real constrain close to equilibrium only. Far from equilibrium, the rate of reverse reaction is negligible and alpha may have any value.

Generic catalyst layer



Polarization curve $\eta_0(j_0)$?
 The shapes?

A model for the CL performance

DL charging

$$C_{dl} \frac{\partial \eta}{\partial t} + \frac{\partial j}{\partial x} = -2i_* \left(\frac{c}{c_{ref}} \right) \sinh \left(\frac{\eta}{b} \right)$$

$$j = -\sigma_t \frac{\partial \eta}{\partial x}$$

$$\frac{\partial c}{\partial t} - D \frac{\partial^2 c}{\partial x^2} = -\frac{2i_*}{4F} \left(\frac{c}{c_{ref}} \right) \sinh \left(\frac{\eta}{b} \right)$$

Butler-Volmer ORR rate

Charge conservation

Ohm's law

Oxygen mass transport

The steady-state system

$$\frac{\partial j}{\partial x} = -2i_* \left(\frac{c}{c_{ref}} \right) \sinh \left(\frac{\eta}{b} \right)$$

$$j = -\sigma_t \frac{\partial \eta}{\partial x}$$

Charge conservation

Ohm's law

Oxygen mass transport

$$-D \frac{\partial^2 c}{\partial x^2} = -\frac{2i_*}{4F} \left(\frac{c}{c_{ref}} \right) \sinh \left(\frac{\eta}{b} \right)$$

We can integrate it once

$$-D \frac{\partial^2 c}{\partial x^2} = \frac{1}{4F} \frac{\partial j}{\partial x}$$

$$D \frac{\partial c}{\partial x} + \frac{1}{4F} j = D \frac{\partial c}{\partial x} \Big|_0 + \frac{1}{4F} j_0 = \frac{1}{4F} j_0$$

$$D \frac{\partial c}{\partial x} = \frac{1}{4F} (j_0 - j)$$

How to nondimensionalize equations

$$\frac{\partial j}{\partial x} = -2i_* \left(\frac{c}{c_h^0} \right) \sinh \left(\frac{\eta}{b} \right)$$

$$\left(\frac{j_*}{2i_* l_t} \right) \frac{\partial(j / j_*)}{\partial(x / l_t)} = -c \sinh(\eta)$$

$$\left(\frac{j_*}{2i_* l_t} \right) \frac{\partial j}{\partial x} = -c \sinh(\eta)$$

**Dimensionless terms
have this color**

$$j_* = \frac{\sigma b}{l_t}, \quad c = \frac{c}{c_h^0}, \quad \eta = \frac{\eta}{b}$$

$$\varepsilon^2 \frac{\partial j}{\partial x} = -c \sinh(\eta)$$

**With these variables, our equation
is controlled by a single parameter
epsilon.**

Dimensionless steady-state model

Equations

$$\varepsilon^2 \frac{\partial j}{\partial x} = -c \sinh \eta$$

$$j = -\frac{\partial \eta}{\partial x}$$

$$D \frac{\partial c}{\partial x} = j_0 - j$$

Cell current density

Parameters

$$\varepsilon = \sqrt{\frac{\sigma_t b}{2i_* l_t^2}}$$

Newman's reaction penetration depth

$$D = \frac{4FDc_{ref}}{\sigma_t b}$$

$$j = \frac{j l_t}{\sigma_t b}$$

In spite of apparent model simplicity, a full analytical solution still is unknown

Large ionic conductivity, fast oxygen transport

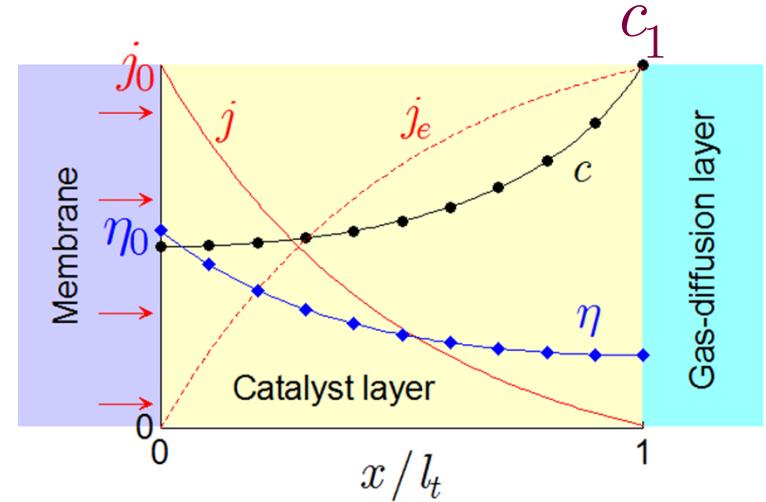
$$\varepsilon^2 \frac{\partial j}{\partial x} = +c_1 \sinh \eta_0$$

constants

$$\varepsilon^2 \int_0^1 \frac{\partial j}{\partial x} dx = - \int_0^1 c_1 \sinh \eta_0 dx$$

$$\varepsilon^2 j_0 = c_1 \sinh \eta_0$$

$$\eta_0 = \operatorname{arcsinh} \left(\frac{\varepsilon^2 j_0}{c_1} \right) \quad \rightarrow \quad \eta_0 = b \operatorname{arcsinh} \left(\frac{j_0}{2i_* l_t c_1 / c_h^0} \right)$$

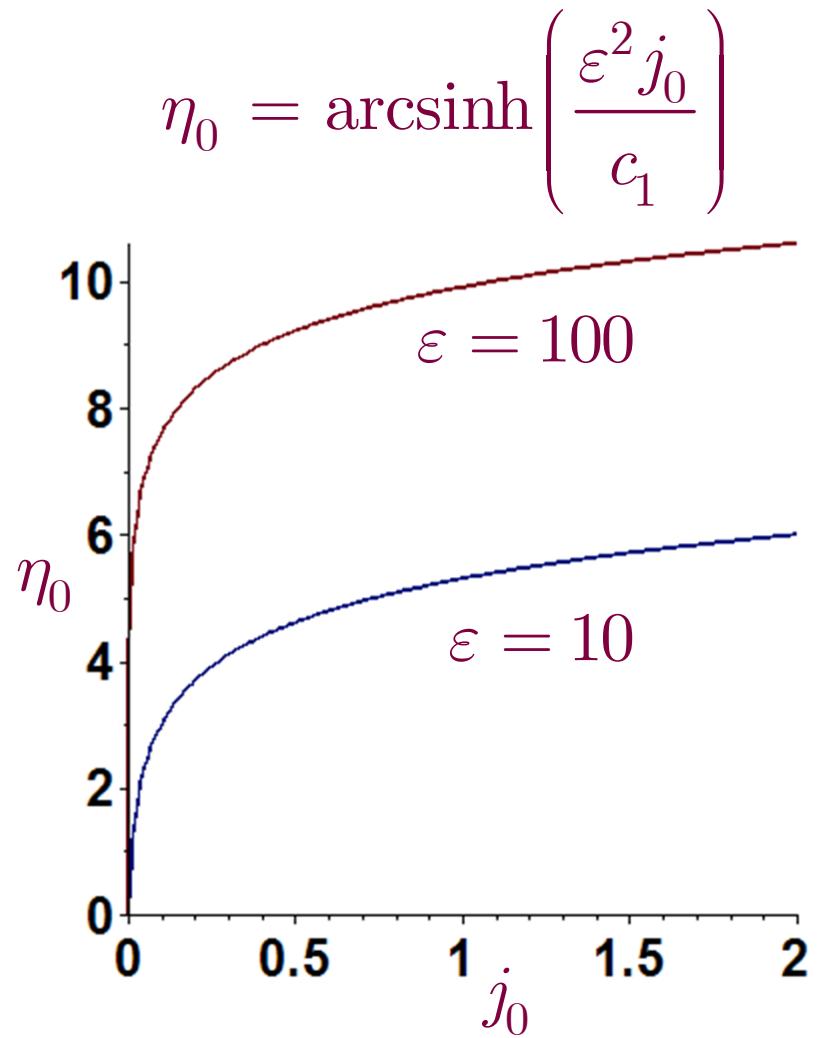


Tafel equation

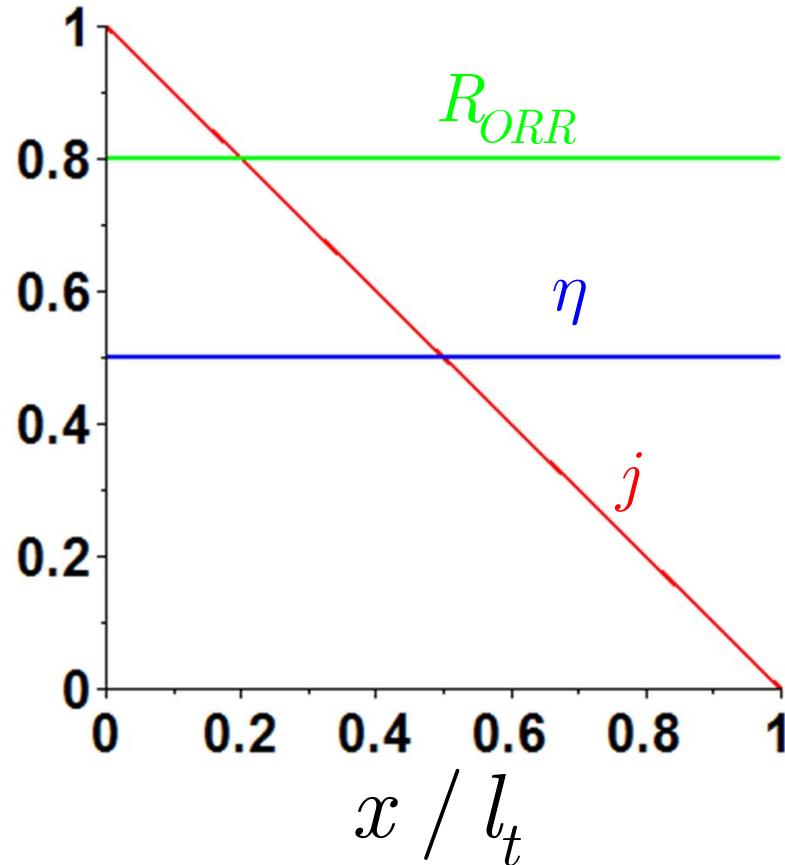
for $x \geq 2$, $\text{arcsinh}(x) \simeq \ln(2x)$

$$\eta_0 = b \text{arcsinh} \left(\frac{j_0}{2i_* l_t c_1 / c_h^0} \right)$$

$$\simeq b \ln \left(\frac{j_0}{i_* l_t c_1 / c_h^0} \right)$$

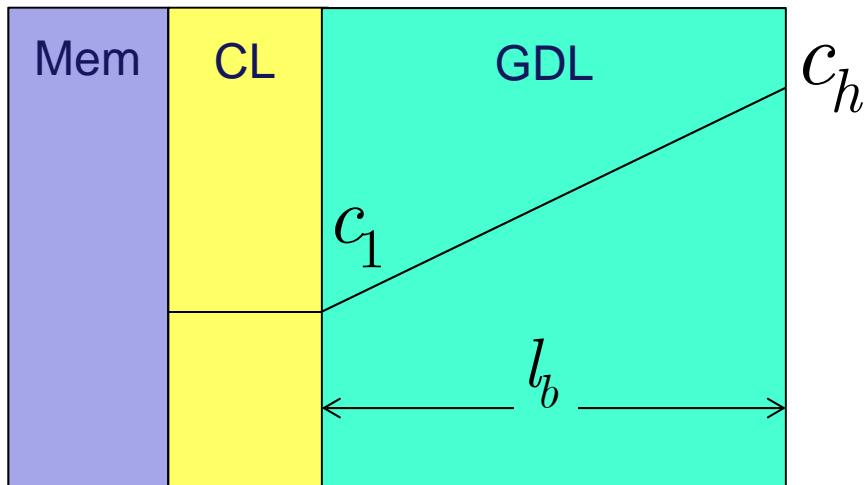


Ideal ORR electrode (Tafel mode)



Overpotential and reaction rate are constant through the CL thickness.
Optimal catalyst utilization.

How to account for the oxygen transport in the GDL?



$$D_b \frac{c_h - c_1}{l_b} = \frac{j_0}{4F} \quad \text{Balance of fluxes}$$

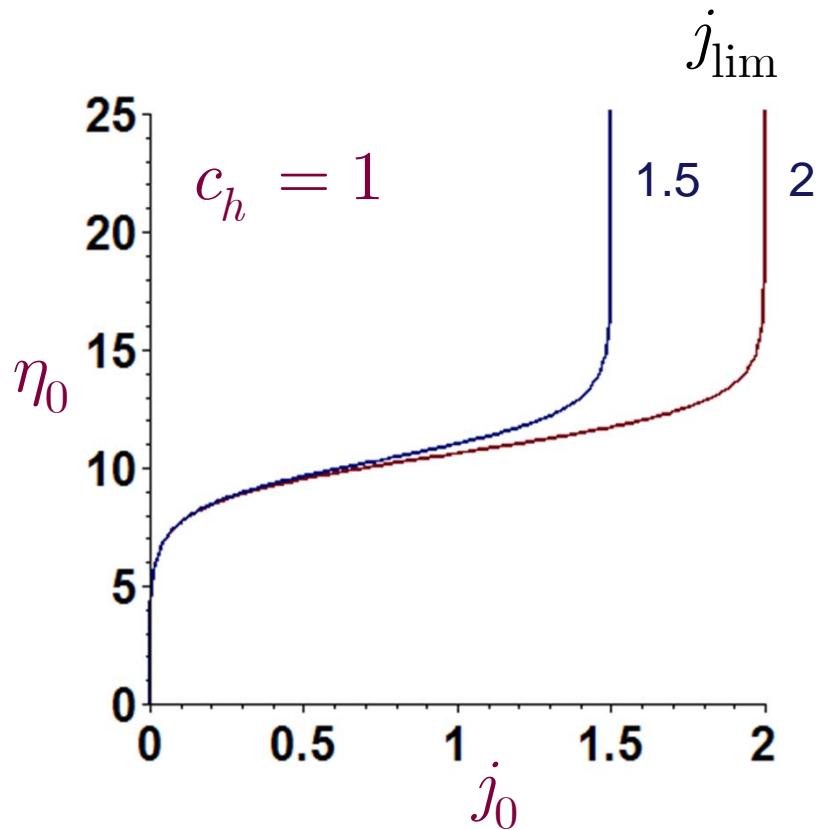
$$c_1 = c_h - \frac{j_0}{j_{\text{lim}}}, \quad j_{\text{lim}} = \frac{4FD_b c_h^0}{l_b}$$

$$\eta_0 = \operatorname{arcsinh} \left(\frac{\varepsilon^2 j_0}{c_1} \right)$$

$$\eta_0 = \operatorname{arcsinh} \left(\frac{\varepsilon^2 j_0}{c_h - (j_0 / j_{\text{lim}})} \right) \simeq \ln \left(2\varepsilon^2 j_0 \right) - \ln \left(c_h - \frac{j_0}{j_{\text{lim}}} \right)$$

ORR activation O₂ transport in GDL

Limiting current density



$$\eta_0 = \ln\left(2\varepsilon^2 j_0\right) - \ln\left(c_h - \frac{j_0}{j_{\text{lim}}}\right)$$

When the cell current reaches j_{lim} , no oxygen left in the catalyst layer.

The effect of oxygen stoichiometry

$$v^0 \frac{\partial c}{\partial z} = -\frac{j_0}{4Fh} \rightarrow \boxed{\lambda J \frac{\partial c}{\partial z} = -j_0}$$

where $\lambda = \frac{4Fhv^0 c_h^0}{LJ}$

Oxygen stoichiometry

$$\eta_0 = \ln\left(2\varepsilon^2 j_0\right) - \ln\left(c_h - \frac{j_0}{j_{\lim}}\right) + \ln c_h - \ln c_h$$

$$\eta_0 = \ln\left(2\varepsilon^2 \frac{j_0}{c_h}\right) - \ln\left(1 - \frac{j_0}{j_{\lim} c_h}\right)$$

j_0 and c_h depend on coordinate z . However, their ratio j_0/c_h must be constant:

$$\boxed{j_0 = \alpha c_h}$$

The effect of oxygen stoichiometry

$$\lambda J \frac{\partial c}{\partial z} = -\alpha c_h, \quad c(0) = 1$$

We don't know alpha. Let's integrate the mass balance equation.

$$\lambda J \int_0^1 \frac{\partial c}{\partial z} dz = - \int_0^1 j_0 dz = J \quad \Rightarrow$$

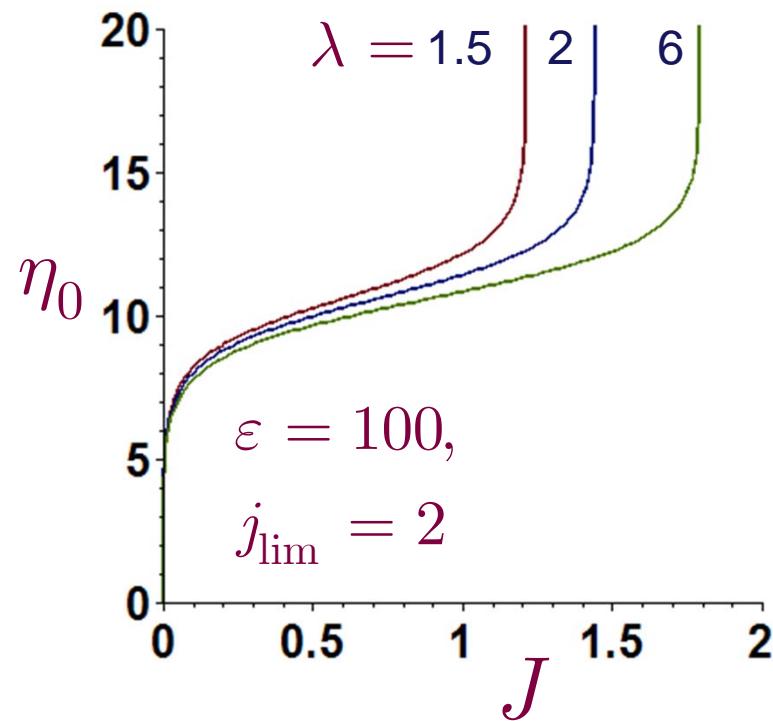
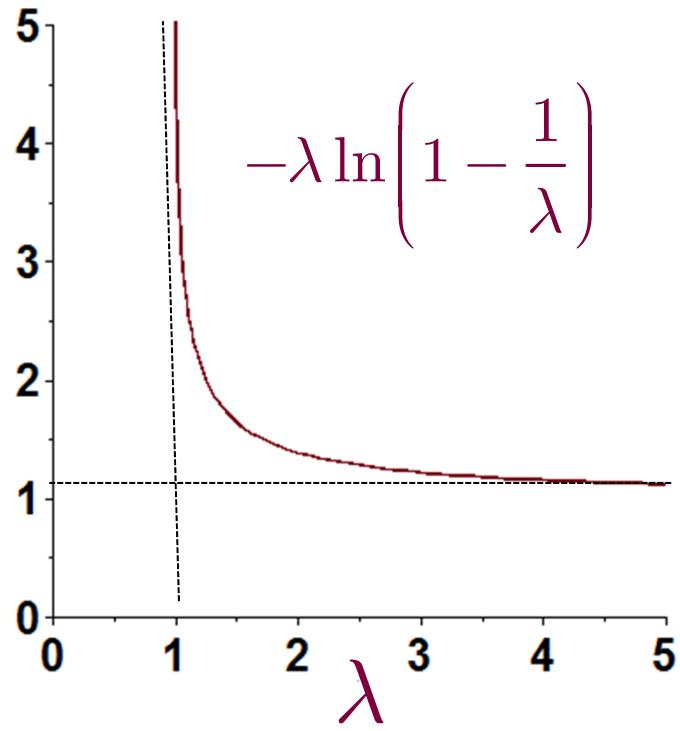
$$c(1) = 1 - \frac{1}{\lambda}$$

We have a first-order equation and two boundary conditions. This gives us alpha:

$$\frac{j_0}{c_h} = -\lambda \ln \left(1 - \frac{1}{\lambda} \right) J \quad \Rightarrow \quad \eta_0 = \ln \left(2\varepsilon^2 \frac{j_0}{c_h} \right) - \ln \left(1 - \frac{j_0}{j_{\lim} c_h} \right)$$

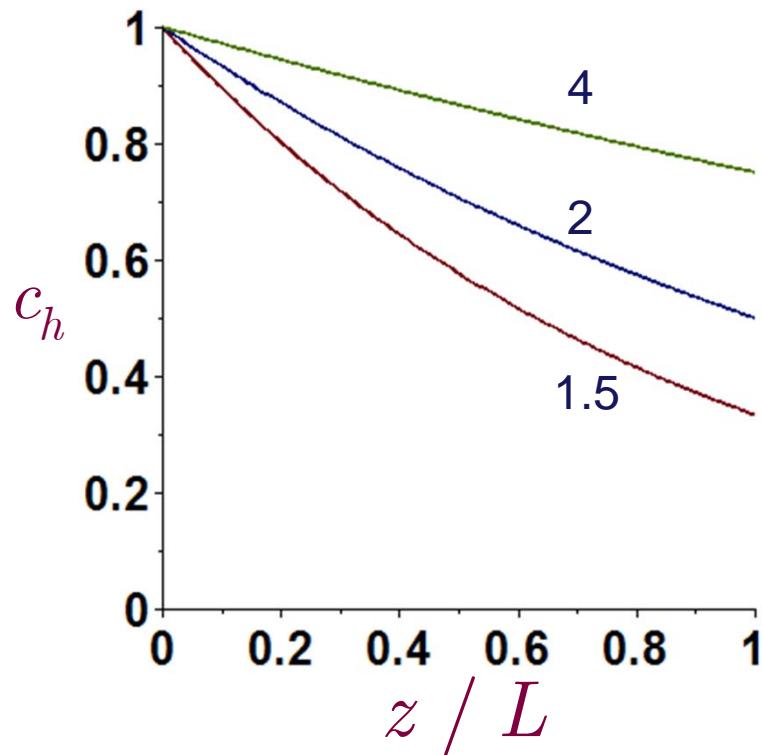
Polarization curve with the stoichiometry effect

$$\eta_0 = \ln\left(2\varepsilon^2 f_\lambda J\right) - \ln\left(1 - \frac{f_\lambda J}{j_{\lim}}\right), \quad f_\lambda = -\lambda \ln\left(1 - \frac{1}{\lambda}\right)$$

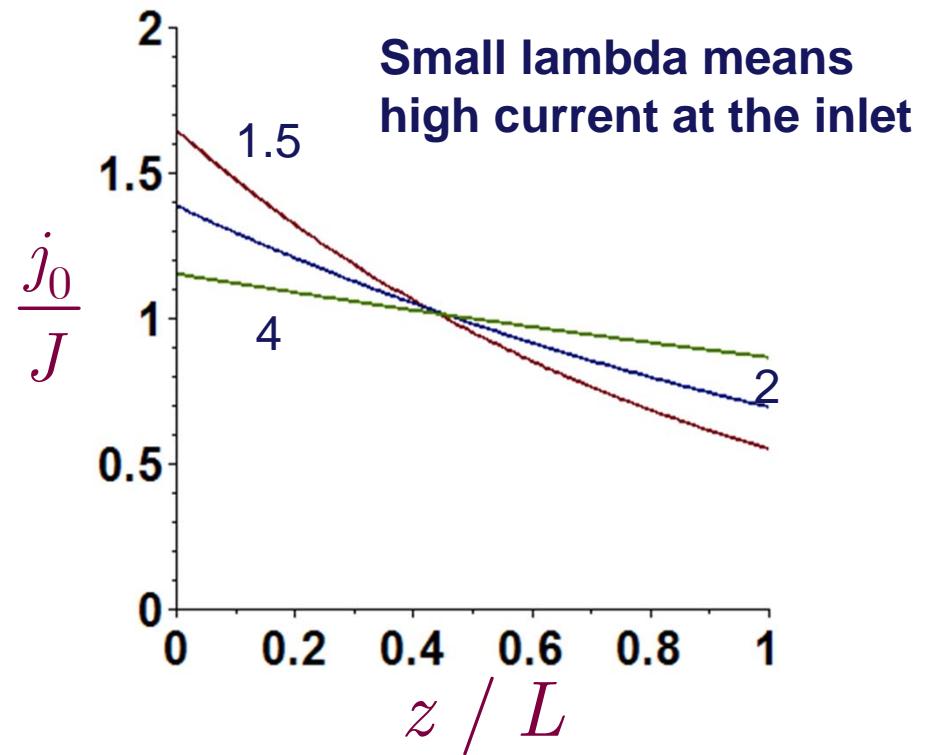


The shapes along the channel

$$c_h = \left(1 - \frac{1}{\lambda}\right)^{z/L}$$



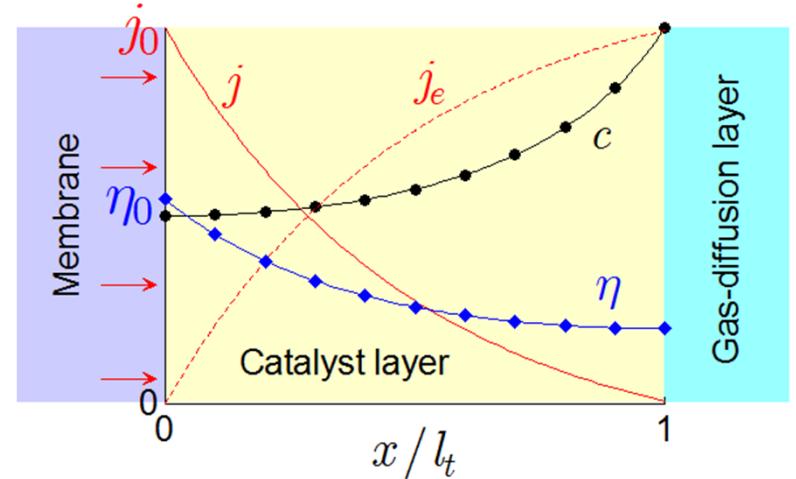
$$j_0 = J f_\lambda \left(1 - \frac{1}{\lambda}\right)^{z/L}$$



Heat flux from the catalyst layer I

$$-\lambda \frac{\partial^2 T}{\partial x^2} = \left(\frac{T \Delta S}{nF} + \eta \right) R_{ORR} + \frac{j^2}{\sigma_t}$$

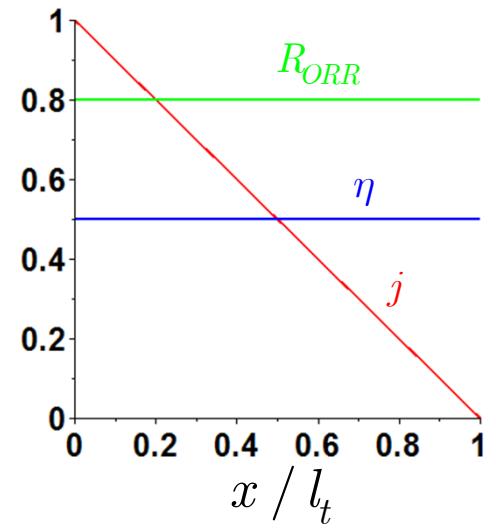
Reversible
Irreversible
Joule



In the general case the problem is tricky, as it includes eta and R_{ORR} . However if we “think a little” (Einstein) , it became clear that in the ideal—transport case

$$T \simeq T_1, \quad \eta \simeq \eta_0, \quad j = j_0 \left(1 - \frac{x}{l_t} \right)$$

$$R_{ORR} = -\frac{\partial j}{\partial x} = \frac{j_0}{l_t}$$



Heat flux from the catalyst layer II

$$-\lambda \frac{\partial^2 T}{\partial x^2} = \left(\frac{T_1 \Delta S}{nF} + \eta_0 \right) \frac{j_0}{l_t} + \frac{j_0^2}{\sigma_t} \left(1 - \frac{x}{l_t} \right)^2$$

$$\left. \frac{\partial T}{\partial x} \right|_0 = 0, \quad T(l_t) = T_1$$

By definition $q = -\lambda \left. \frac{\partial T}{\partial x} \right|_{l_t}$

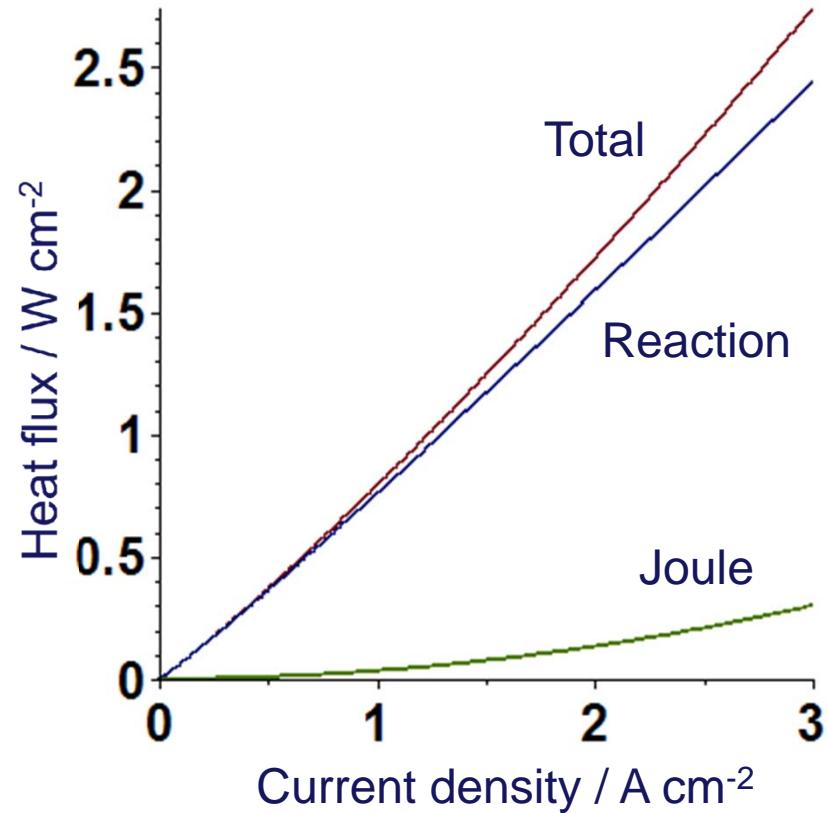
$$q = \left(\frac{T_1 \Delta S}{nF} + \eta_0 \right) j_0 + \frac{j_0^2 l_t}{3\sigma_t}$$

Where

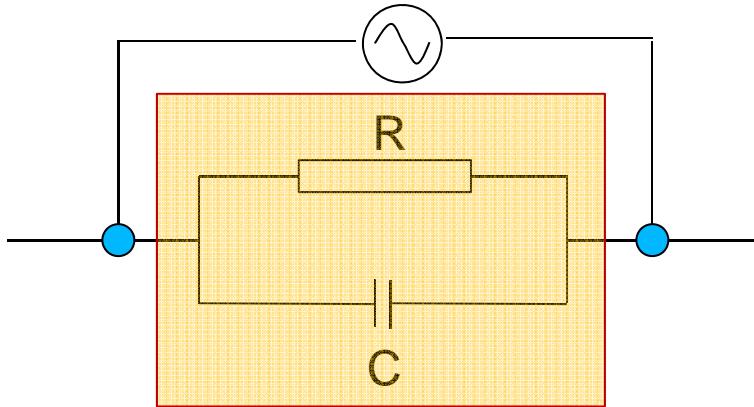
$$\eta_0 = b \ln \left(\frac{j_0}{i_* l_t} \right)$$

Tafel equation

Heat “pie” for the ORR in PEMFC



Parallel RC-circuit in a “black box”



Can we understand what is inside?

$$i_R = \frac{\varphi}{R}$$

$$i_C = \frac{\partial q}{\partial t} = C \frac{\partial \varphi}{\partial t}$$

$$i = \frac{\varphi}{R} + C \frac{\partial \varphi}{\partial t}$$

$$\varphi = \varphi(\omega) \exp(i\omega t)$$

$$i = i(\omega) \exp(i\omega t)$$

$$i = \frac{\varphi}{R} + i\omega C \varphi = \left(\frac{1}{R} + i\omega C \right) \varphi$$

$$Z = \frac{\varphi}{i} \quad \text{Impedance definition}$$

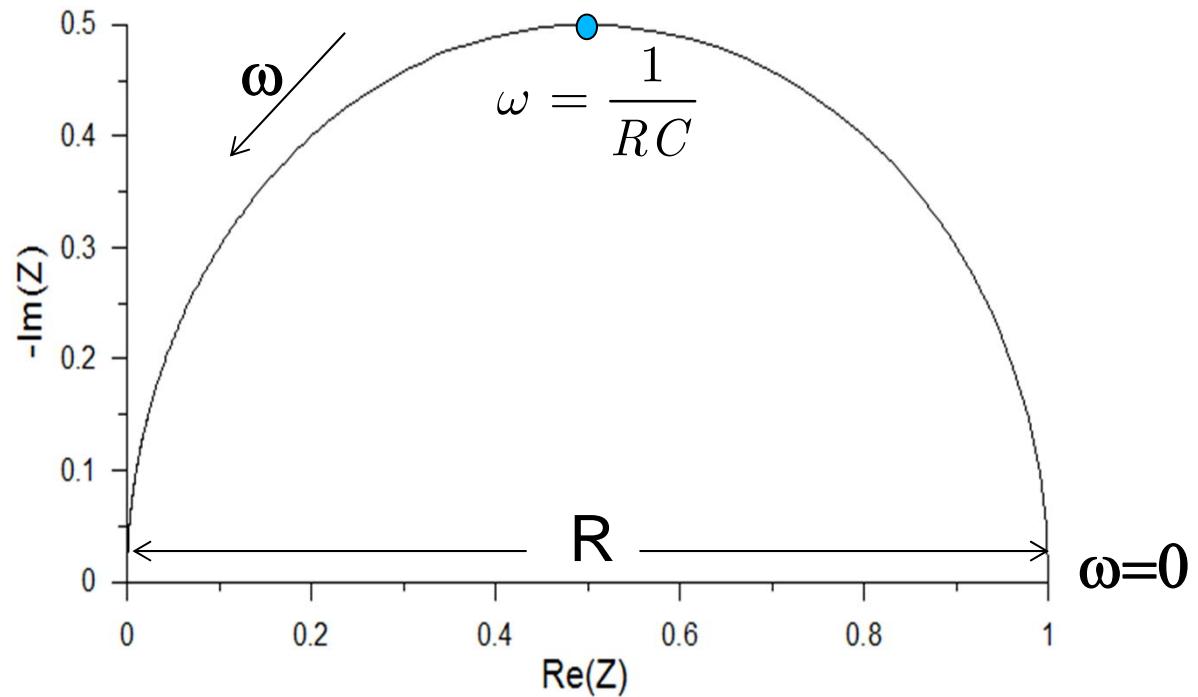
$$\frac{1}{Z} = \frac{1}{R} + i\omega C$$

$$Z = \frac{R}{1 + (\omega R C)^2} - i \frac{\omega R^2 C}{1 + (\omega R C)^2}$$

Nyquist plot



Harry Nyquist
 (1889-1976)

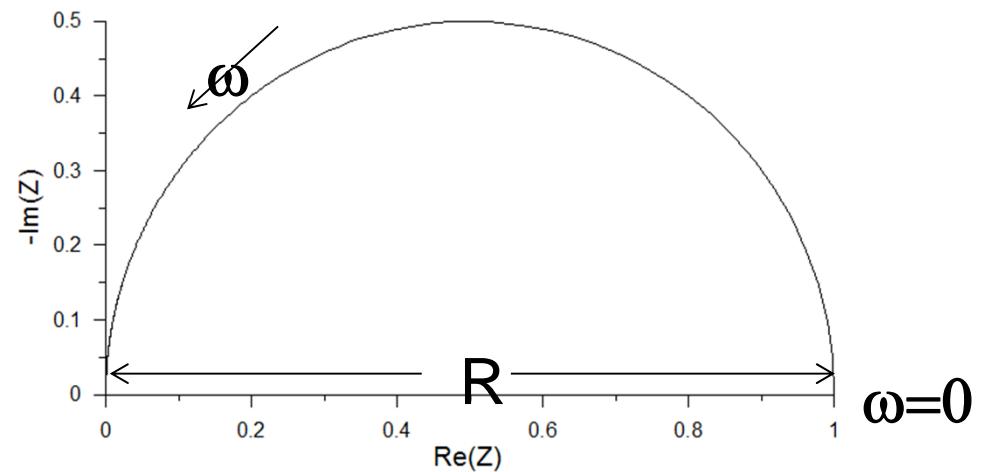


$$\text{Re}(Z) = \frac{R}{1 + (\omega RC)^2}; \quad \text{Im}(Z) = -\frac{\omega R^2 C}{1 + (\omega RC)^2}$$

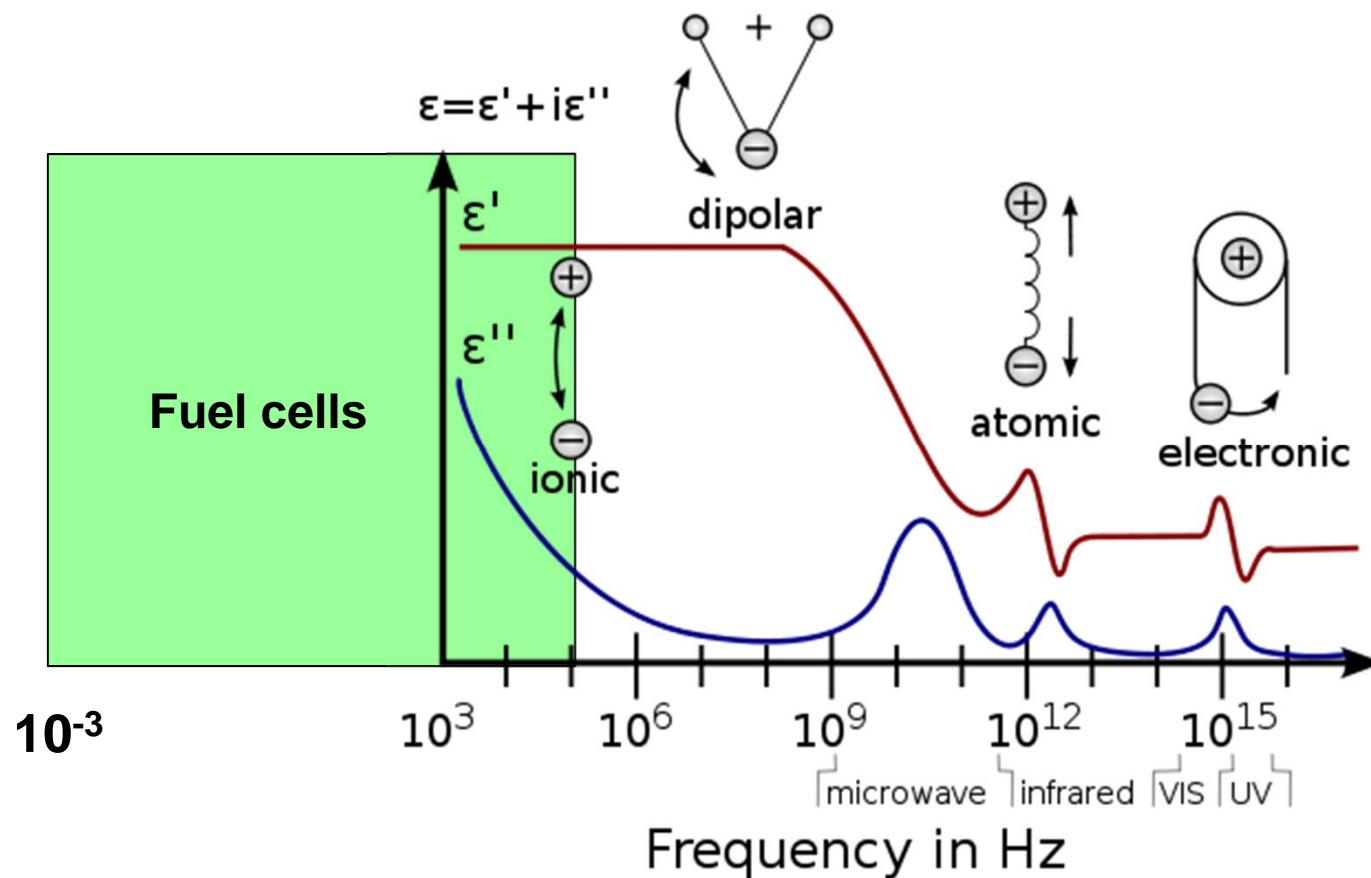
Some comments

Our simple RC-system is linear, while real systems are not, and we must apply a **small—amplitude** disturbance to get a linear response.

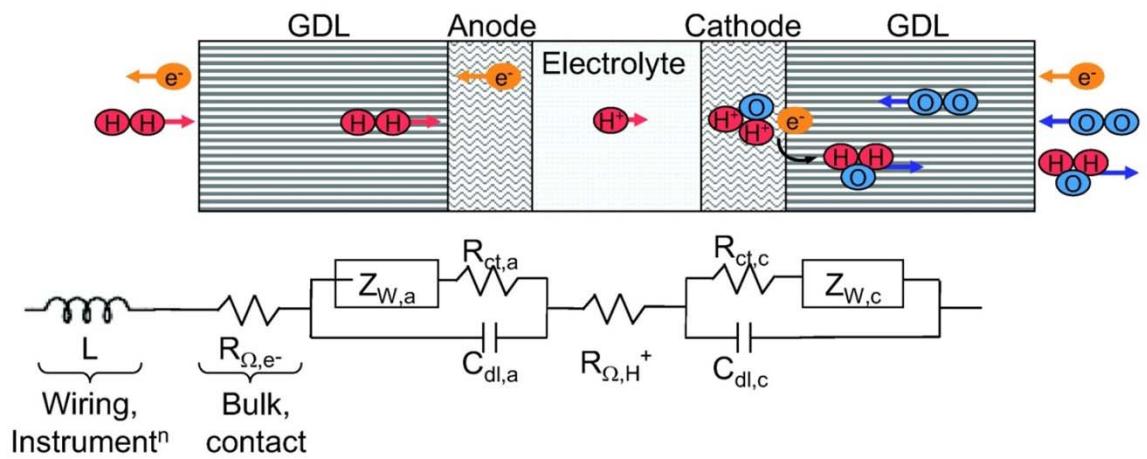
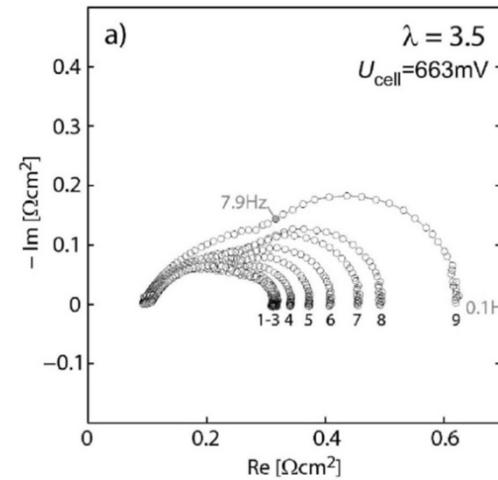
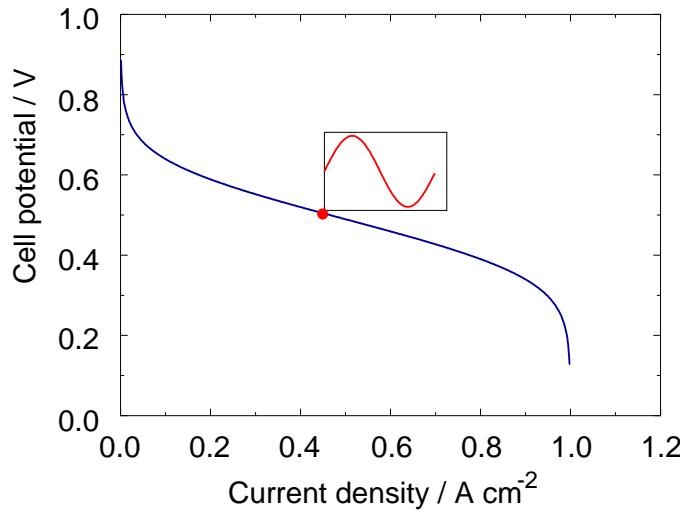
In the case of nonlinear system, the right intercept is a **differential static resistivity**.



Impedance spectroscopy



Impedance spectroscopy of fuel cells



Impedance of the CCL with ideal O₂ transport

$$C_{dl} \frac{\partial \eta}{\partial t} + \frac{\partial j}{\partial x} = -2i_* \left(\frac{c}{c_{ref}} \right) \sinh \left(\frac{\eta}{b} \right)$$

$$j = -\sigma_t \frac{\partial \eta}{\partial x}$$

$$j_0 \ll \frac{4FDc_1}{l_l}$$

Charge conservation

Ohm's law

$$\frac{\partial \eta}{\partial t} - \varepsilon^2 \frac{\partial^2 \eta}{\partial x^2} = -c_1 \sinh \eta$$

Nonlinear equation

$$\eta = \eta^0 + \eta^1, \quad \eta^1 \ll 1$$

The disturbance is small and harmonic; we will linearize equation and go to the complex plane.

Linearization

$$\frac{\partial \eta}{\partial t} - \varepsilon^2 \frac{\partial^2 \eta}{\partial x^2} = -c_1 \sinh \eta \quad \Longleftrightarrow \quad \eta = \eta^0(x) + \eta^1(x,t), \quad \eta^1 \ll 1$$

$$\frac{\partial \eta^1}{\partial t} - \varepsilon^2 \frac{\partial^2 \eta^0}{\partial x^2} - \varepsilon^2 \frac{\partial^2 \eta^1}{\partial x^2} = -c_1 \sinh(\eta^0 + \eta^1)$$

$$\frac{\partial \eta^1}{\partial t} \left(-\varepsilon^2 \frac{\partial^2 \eta^0}{\partial x^2} \right) - \varepsilon^2 \frac{\partial^2 \eta^1}{\partial x^2} = \left(-c_1 \sinh(\eta^0) - c_1 \cosh(\eta^0) \eta^1 \right)$$

$$\frac{\partial \eta^1}{\partial t} - \varepsilon^2 \frac{\partial^2 \eta^1}{\partial x^2} = -c_1 \cosh(\eta^0) \eta^1$$

Linear equation for the disturbance.
 Eta_0 – solution to the steady-state problem.

Fourier transform

$$\frac{\partial \eta^1}{\partial t} - \varepsilon^2 \frac{\partial^2 \eta^1}{\partial x^2} = -c_1 \cosh(\eta^0) \eta^1 \quad \Longleftrightarrow \quad \eta^1(x, t) = \eta^1(x, \omega) \exp(i\omega t)$$

Fourier transform

$$\varepsilon^2 \frac{\partial^2 \eta^1}{\partial x^2} = c_1 \cosh(\eta^0) \eta^1 + i\omega \eta^1$$

We are in the (x, omega) space

From the steady-state analysis we know that $c_1 \cosh(\eta^0) \simeq \varepsilon^2 j_0$ (Tafel at small current)

$$\varepsilon^2 \frac{\partial^2 \eta^1}{\partial x^2} = (\varepsilon^2 j_0 + i\omega) \eta^1, \quad \eta^1(0) = \eta_0^1, \quad \left. \frac{\partial \eta^1}{\partial x} \right|_1 = 0$$

Applied disturbance

Zero proton current

Solution: Impedance of the CCL at small current

Impedance is

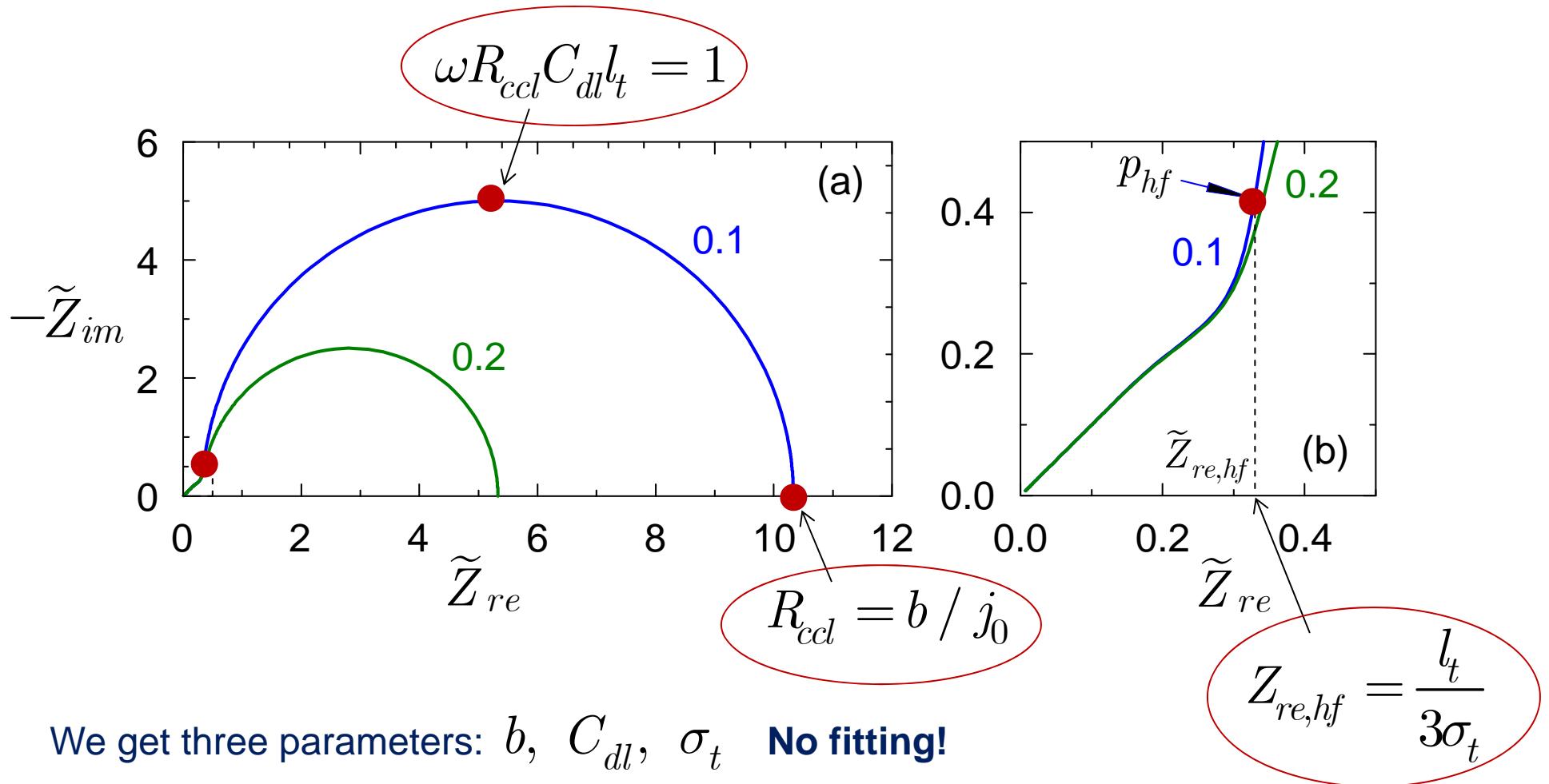
$$Z = \frac{\eta^1}{j^1} \Big|_0 = -\frac{\eta^1}{\partial \eta^1 / \partial x} \Big|_0 \quad \text{At } x=0 \text{ (membrane interface)}$$

Solving for η^1 and calculating Z we get

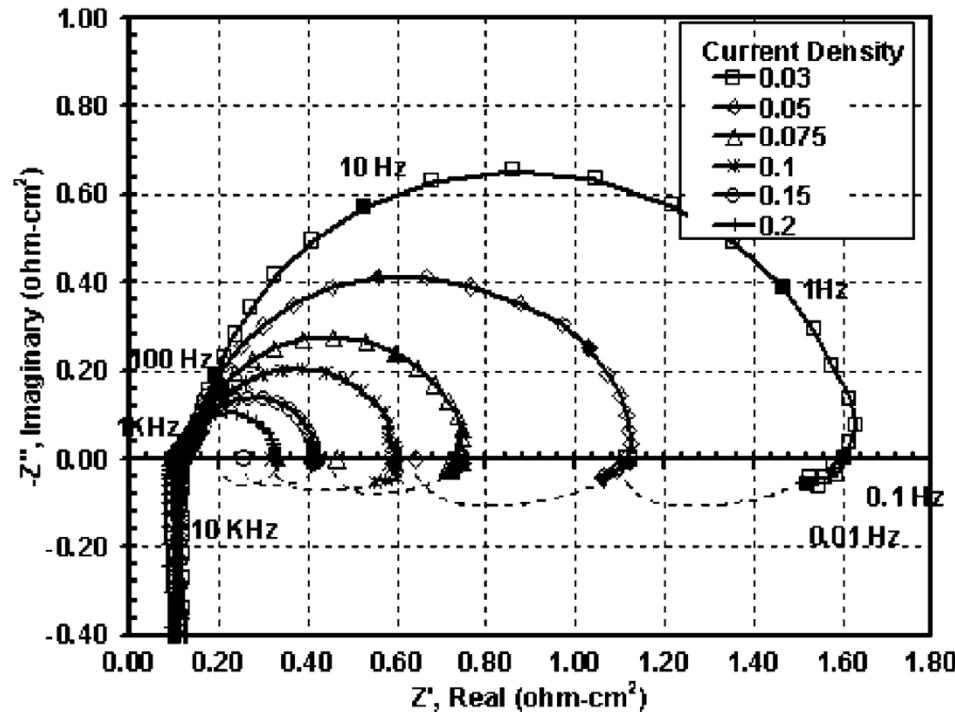
$$Z = -\frac{1}{\varphi \tan \varphi}, \text{ where } \varphi = \sqrt{-j_0 - i \frac{\omega}{\varepsilon^2}}$$

Separating real and imaginary parts, we obtain a Nyquist plot:

Nyquist plot and the points of interest



Experiment: Pure oxygen at high flow rate



R. Makharia, M. F. Mathias, D. R. Baker,
 J. Electrochem. Soc. **152** (2005) A970

$$b = 0.045 \text{ V} \quad (\text{None})$$

$$C_{dl} = 12.4 \text{ F cm}^{-3} \quad (15.3)$$

$$\sigma_t = 0.011 \text{ S cm}^{-1} \quad (\text{same})$$

The model works if

$$\sqrt{2i_*\sigma_t b} \ll j_0 \ll \frac{\sigma_t b}{l_t}$$

$$10 \leq j_0 \leq 100 \text{ mA cm}^{-2}$$

A.A.Kulikovsky, M.Eikerling. J. Electroanal. Chem., (2012, under review)

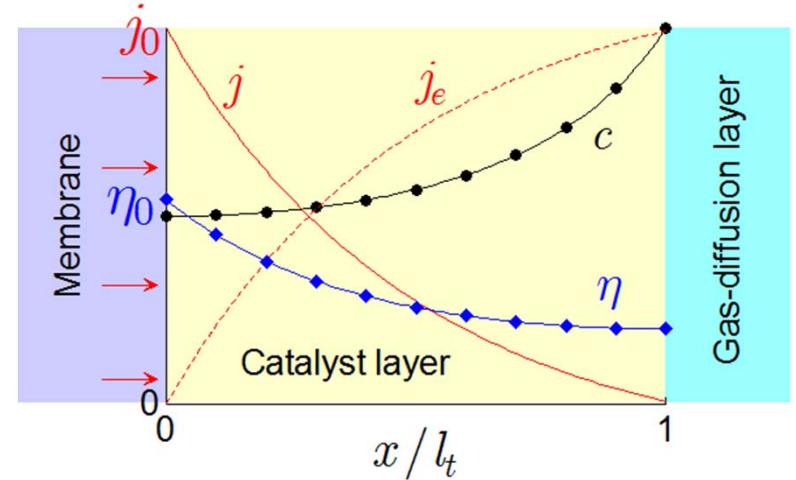
Catalyst layer with poor ionic (proton) transport I

$$\varepsilon^2 \frac{\partial j}{\partial x} = -c \sinh \eta$$

charge

$$j = -\frac{\partial \eta}{\partial x}$$

Ohm's law



Direct substitution of Ohm's law into charge conservation leads to

$$\varepsilon^2 \frac{\partial^2 \eta}{\partial x^2} = c \sinh \eta$$

Cannot be solved, unless eta is small

CL with poor proton transport II

$$\varepsilon^2 \frac{\partial j}{\partial x} = -c_1 \sinh \eta$$

$$j = -\frac{\partial \eta}{\partial x}$$

$$\varepsilon^2 \frac{\partial^2 j}{\partial x^2} = -c_1 \cosh \eta \frac{\partial \eta}{\partial x} = c_1 j \sqrt{1 + \sinh^2 \eta}$$

$$\varepsilon^2 \frac{\partial^2 j}{\partial x^2} = -c_1 j \sqrt{1 + \frac{\varepsilon^4}{c_1^2} \left(\frac{\partial j}{\partial x} \right)^2}$$

In PEMFCs $\varepsilon \gg 1$. Further, $c_1 < 1$ and we may expect that the unity under the square root can be neglected. This gives

$$\frac{\partial^2 j}{\partial x^2} + j \frac{\partial j}{\partial x} = 0$$

BC: $j(0) = j_0, j(1) = 0$

Epsilon disappears.

Solution

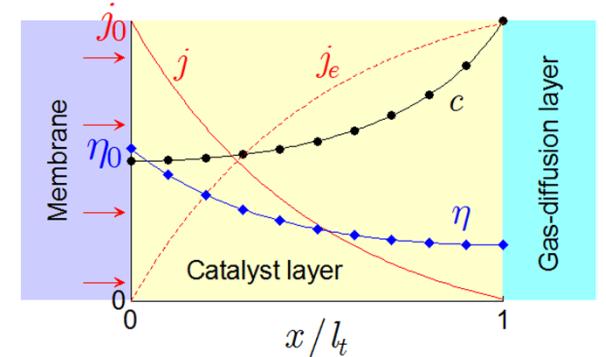
$$\frac{\partial^2 j}{\partial x^2} + j \frac{\partial j}{\partial x} = 0 \quad \Rightarrow \quad \frac{\partial^2 j}{\partial x^2} + \frac{1}{2} \frac{\partial j^2}{\partial x} = 0$$

$$\frac{\partial j}{\partial x} + \frac{j^2}{2} = \left. \frac{\partial j}{\partial x} \right|_0 + \frac{j_0^2}{2} = \left. \frac{\partial j}{\partial x} \right|_1 = -\frac{\beta^2}{2}$$

$$\frac{\partial j}{\partial x} + \frac{j^2}{2} = -\frac{\beta^2}{2}, \quad j(1) = 0$$

$$j = \beta \tan \left(\frac{\beta}{2} (1 - x) \right)$$

Great, we have the shape of current.
OK, but what is beta? We set $x=0$



Beta

$$j_0 = \beta \tan\left(\frac{\beta}{2}\right)$$

Can we solve it? Yes, we can!

For small current, beta must be small, $\tan(a) \simeq a$ and $j_0 \simeq \frac{\beta^2}{2}$

$$\beta = \sqrt{2j_0}, \quad j_0 \ll 1$$

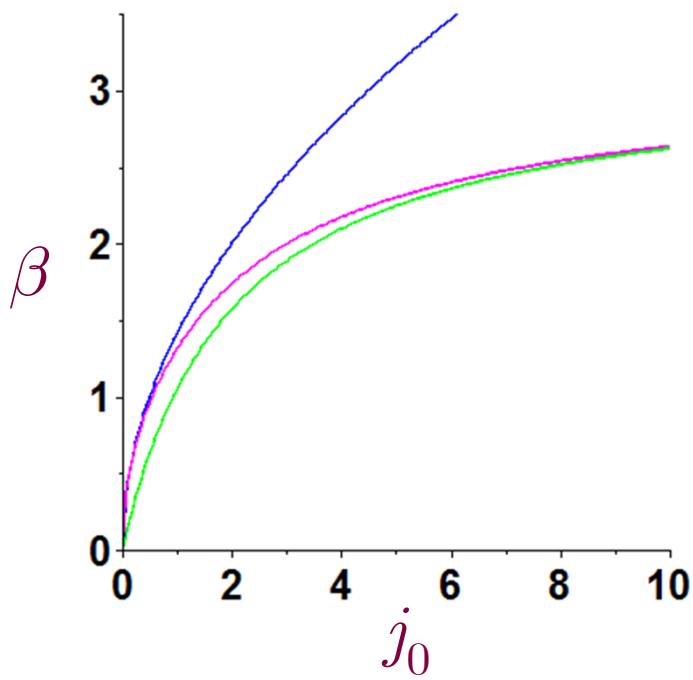
For large current, beta tends to pi and $\tan(a) \simeq \frac{1}{(\pi / 2) - a}$ (use Maple to find this asymptotic)

$$\beta = \frac{\pi j_0}{2 + j_0}, \quad j_0 \gg 1$$

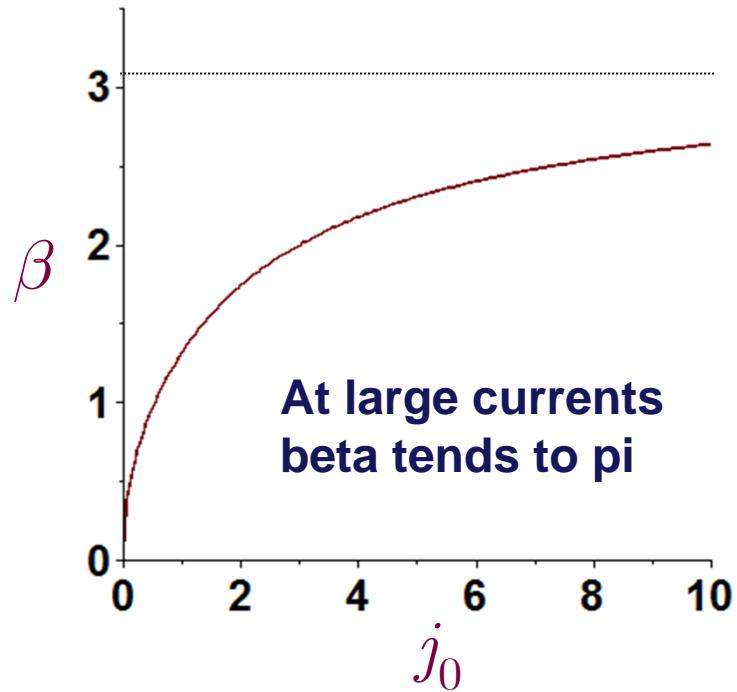
Beta II

$$\beta = \sqrt{2j_0}, \quad j_0 \ll 1$$

$$\beta = \frac{\pi j_0}{2 + j_0}, \quad j_0 \gg 1$$



$$\boxed{\beta = \frac{\sqrt{2j_0}}{1 + \sqrt{1.12j_0} \exp(\sqrt{2j_0})} + \frac{\pi j_0}{2 + j_0}}$$



Return to our solutions

$$j = \beta \tan\left(\frac{\beta}{2}(1 - x)\right)$$

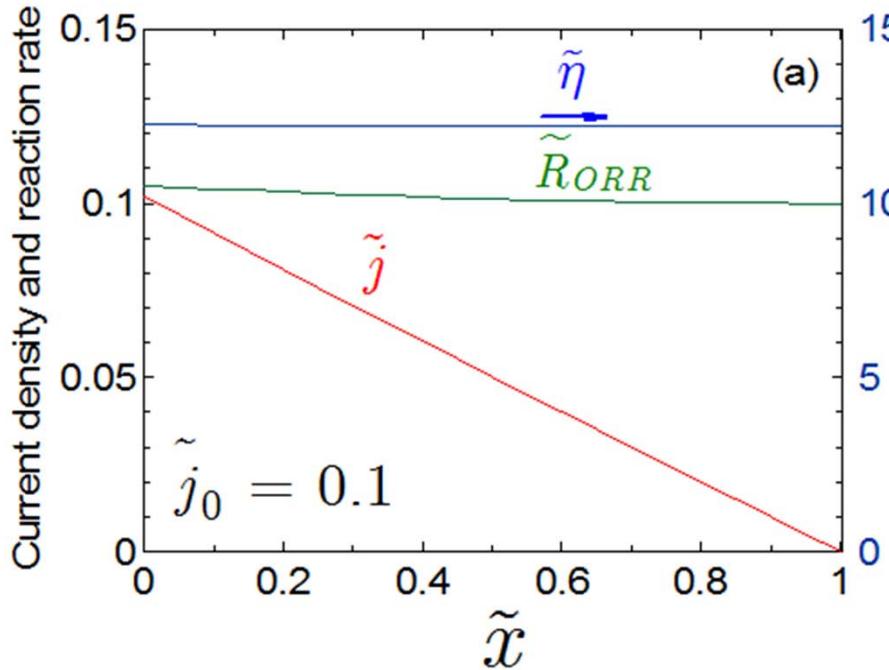
$$\eta = \operatorname{arcsinh}\left(\frac{\varepsilon^2 (\beta^2 + j^2)}{2c_1}\right)$$

Solve for eta $\varepsilon^2 \frac{\partial j}{\partial x} = -c_1 \sinh \eta$

Beta is a function of j_0 only. Thus, if we fix the cell current j_0 , the shape $j(x)$ does not depend on any other parameters. However, $\eta(x)$ “feels” ε and oxygen concentration c_1 .

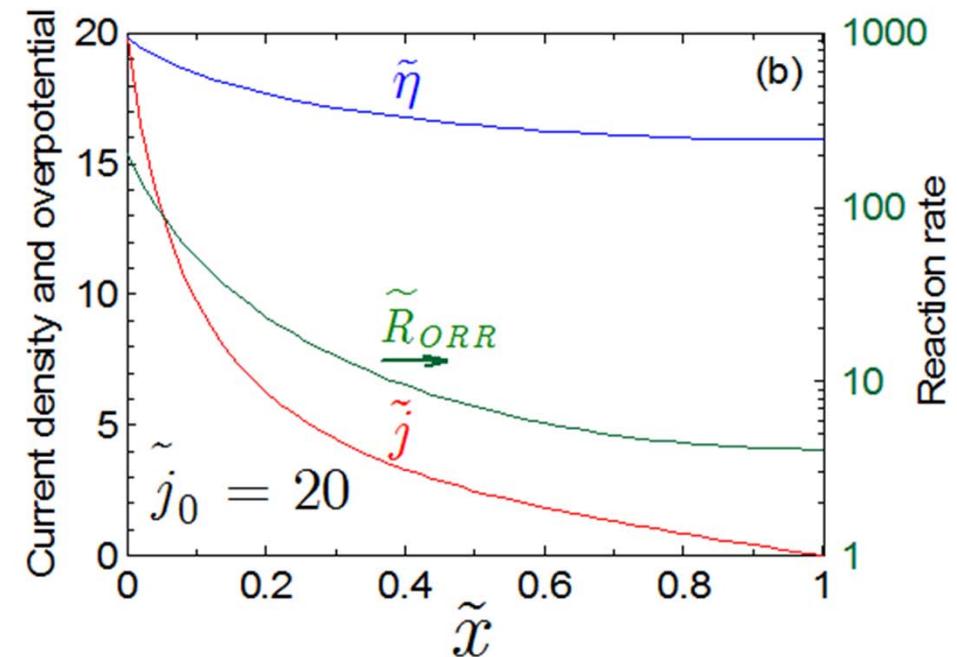
The shapes

Small current



Ideal ORR electrode

Large current



Reaction runs close to the membrane, where protons are “cheaper”. Non-uniform reaction is costly in terms of potential. How much is this regime?

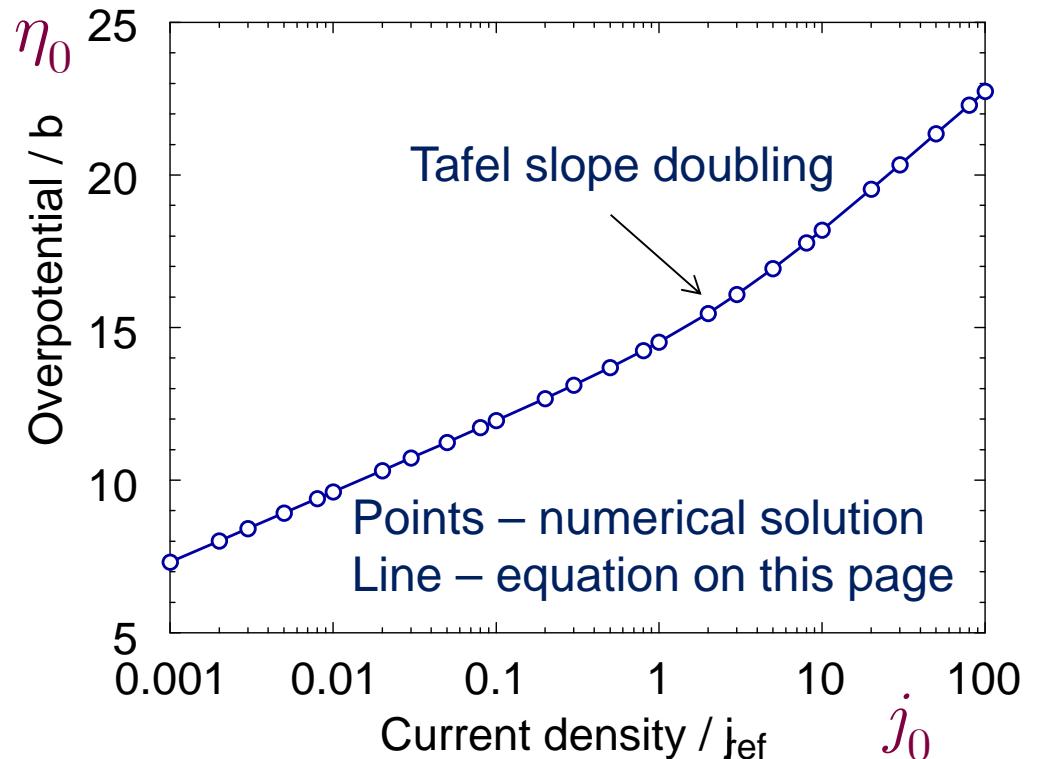
Polarization curve

$$\eta = \operatorname{arcsinh} \left(\frac{\varepsilon^2 (\beta^2 + j^2)}{2c_1} \right)$$

$$\eta_0 = \operatorname{arcsinh} \left(\frac{\varepsilon^2 (\beta^2 + j_0^2)}{2c_1} \right)$$

Activation polarization + proton transport in the CCL.

Setting here $x=0$, we get the polarization curve



Tafel slope doubling

$$\eta_0 = \operatorname{arcsinh} \left(\frac{\varepsilon^2 (\beta^2 + j_0^2)}{2c_1} \right)$$

$$\eta_0 = \operatorname{arcsinh} \left(\frac{\varepsilon^2 j_0^2}{2c_1} \right), \quad j_0 \gg 1$$

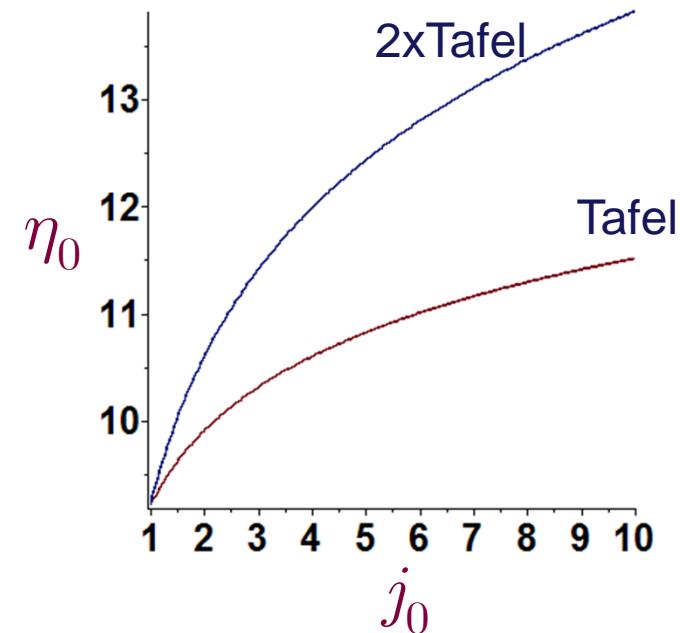
$$\eta_0 = \ln \left(\frac{\varepsilon^2 j_0^2}{c_1} \right) = \textcircled{2} \ln \left(\frac{\varepsilon j_0}{\sqrt{c_1}} \right)$$

$$\eta_0 = \textcircled{2b} \ln \left(\frac{j_0}{\sqrt{2i_* \sigma_t b c_1 / c_{ref}}} \right)$$

No CL thickness here; internal scale arises (the 3-rd lecture)

For large j_0 , beta tends to pi and it can be neglected.

For large x $\operatorname{arcsinh}(x) \simeq \ln(2x)$



How to account for the oxygen transport in the GDL?

$$\eta_0 = \operatorname{arcsinh} \left(\frac{\varepsilon^2(\beta^2 + j_0^2)}{2c_1} \right) \approx \ln \left(\frac{\varepsilon^2(\beta^2 + j_0^2)}{2c_1} \right)$$

Linear diffusion in the GDL gives

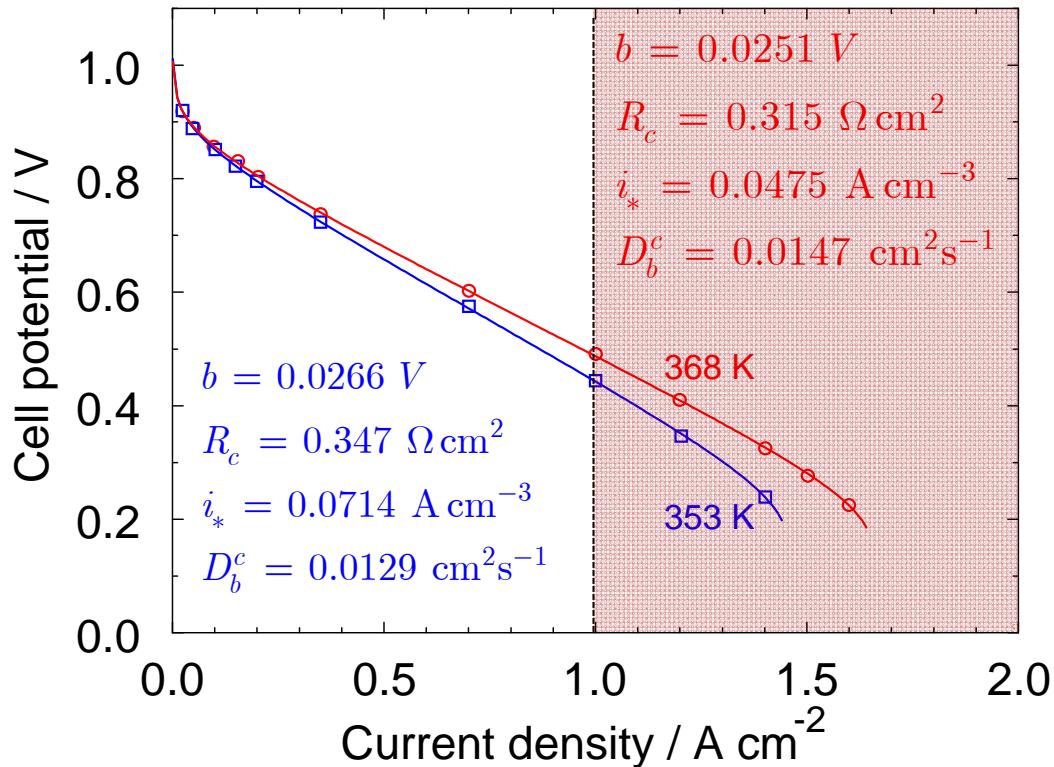
$$c_1 = 1 - \frac{j_0}{j_{\text{lim}}}$$

$$\eta_0 = \ln \left(\varepsilon^2(\beta^2 + j_0^2) \right) - \ln \left(1 - \frac{j_0}{j_{\text{lim}}} \right)$$

ORR activation
+ proton transport

O₂ transport in the GDL

Fitting the experiment



The points are from: P.Dobson, C.Lei, T.Navessin and M.Secanell. JES, 159 (2012), B514

$$V_{cell} = V_{oc} - \ln \left(\varepsilon^2 (\beta^2 + j_0^2) \right) + \ln \left(1 - \frac{j_0}{j_{\lim}} \right) - R j_0$$

Ideal oxygen transport in the CCL, large oxygen stoichiometry

Parameters are reasonable, but unreliable. The curves cross the “black line”, beyond which the oxygen transport cannot be ignored.

Impedance is much better alternative.

CCL + GDL + channel flow

$$\eta_0 = \text{activation} - \text{transport}$$

$$\eta_0 = 2b \ln \left(\frac{2\lambda \varphi_\lambda J}{j_{\sigma*}} \right) - b \ln \left(1 - \frac{f_\lambda J}{j_{\lim}^0} \right)$$

Poor proton, ideal oxygen transport in the CCL

$$\eta_0 = 2b \ln \left(\frac{f_\lambda J}{j_{D*}} \right) - 2b \ln \left(1 - \frac{f_\lambda J}{j_{\lim}^0} \right)$$

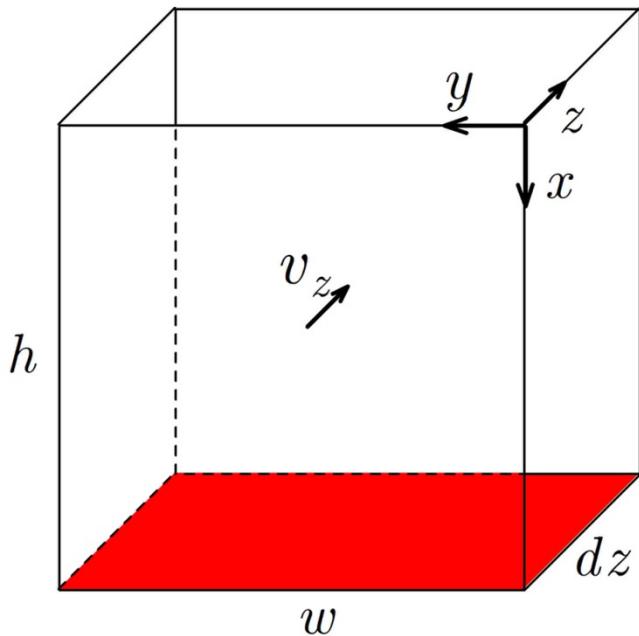
Poor oxygen, ideal proton transport in the CCL

Here

$$f_\lambda = -\lambda \ln \left(1 - \frac{1}{\lambda} \right), \quad \varphi_\lambda = 1 - \sqrt{1 - \frac{1}{\lambda}}$$

Poor O₂ transport in the CCL doubles the cost of O₂ transport in the GDL!

Flow in the cathode channel I



$$\nabla \cdot (\rho \mathbf{v}) = 0$$

$$\int_V \nabla \cdot (\rho \mathbf{v}) = \int_S \rho v_n dS \quad \text{Gauss theorem}$$

$$[(\rho v_z)_{z+dz} - (\rho v_z)_z] hw - (\rho v_x) w dz = 0$$

$$\frac{\partial(\rho v_z)}{\partial z} = \frac{\rho v_x}{h}$$

Variation (divergence) of flux along the z-axis is due to the flux along the x-axis.
 Note that the x-flux is divided by the channel height h .

Now we have to collect all the x-fluxes

$$\rho_{ox} v_{ox} = -\frac{j_0 M_{ox}}{4F}$$

oxygen

$$\rho_w v_w = \frac{j_0 M_w}{2F} + \alpha_w \frac{j_0 M_w}{F}$$

water

Water transfer coefficient

$$\rho v_x = \rho_w v_w + \rho_{ox} v_{ox} = \frac{j_0}{4F} (2(1 + 2\alpha_w)M_w - M_{ox})$$

$$\frac{\partial(\rho v_z)}{\partial z} = \frac{j_0}{4Fh} (2(1 + 2\alpha_w)M_w - M_{ox})$$

Mass conservation
equation

Mass conservation: Solution

Subsonic flow is incompressible

$$\rho^0 \frac{\partial v_z}{\partial z} = \frac{j_0(z)}{4Fh} \left(2(1 + 2\alpha_w)M_w - M_{ox} \right) \quad (*)$$

OK, but the local current changes along the channel. We know solution for $v_z = \text{const}$; let's take it as a zero-order approximation:

$$j_0(z) = -J\lambda \ln \left(1 - \frac{1}{\lambda} \right) \left(1 - \frac{1}{\lambda} \right)^{z/L}$$

We insert it into Eq.(*) and solve the resulting equation with the boundary condition $v(0) = v^0$:

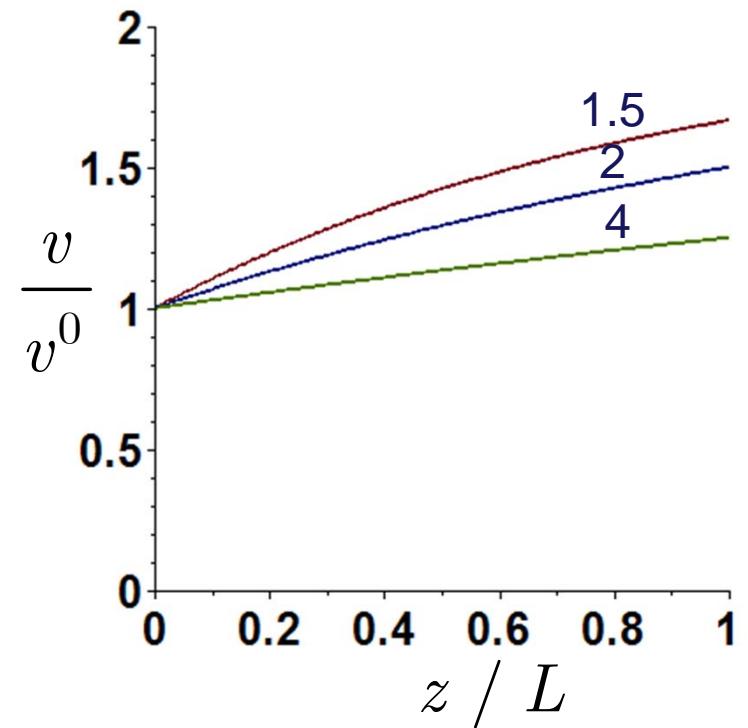
Solution for the flow velocity

$$v = v^0 \left(1 + \frac{2(1 + 2\alpha_w)M_w - M_{ox}}{M_{air}} \xi_{ox} \right) \left(1 - \left(1 - \frac{1}{\lambda} \right)^{z/L} \right)$$

≈ 1

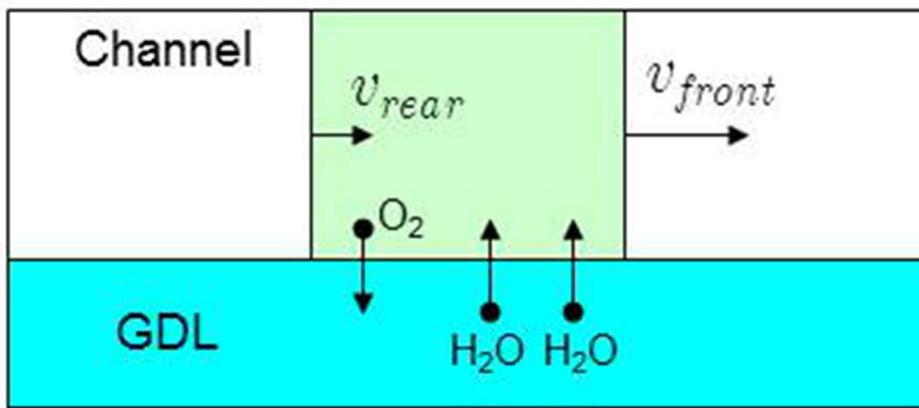
$$\xi_{ox} = \frac{c_{ox}}{c_{air}}$$

$$v \approx v^0 \left(2 - \left(1 - \frac{1}{\lambda} \right)^{z/L} \right)$$



The cathode flow accelerates. Why?

What happens with the flow?



The guys on the front must run faster to keep pressure behind them constant. The flow accelerates to preserve incompressibility.

Conclusions

- Modeling is the only way to understand what is going on in complex systems
- Modeling is a very general principle of thinking. To predict, you always need a model (of a phenomenon, person, situation etc.)
- Always start with the simplest model
- Go ahead step-by-step
- Never change more than one parameter at a time
- Light bulb was invented without modeling. Why?