Fuel Cells

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Agenda:

12:30 – 14:00(?)

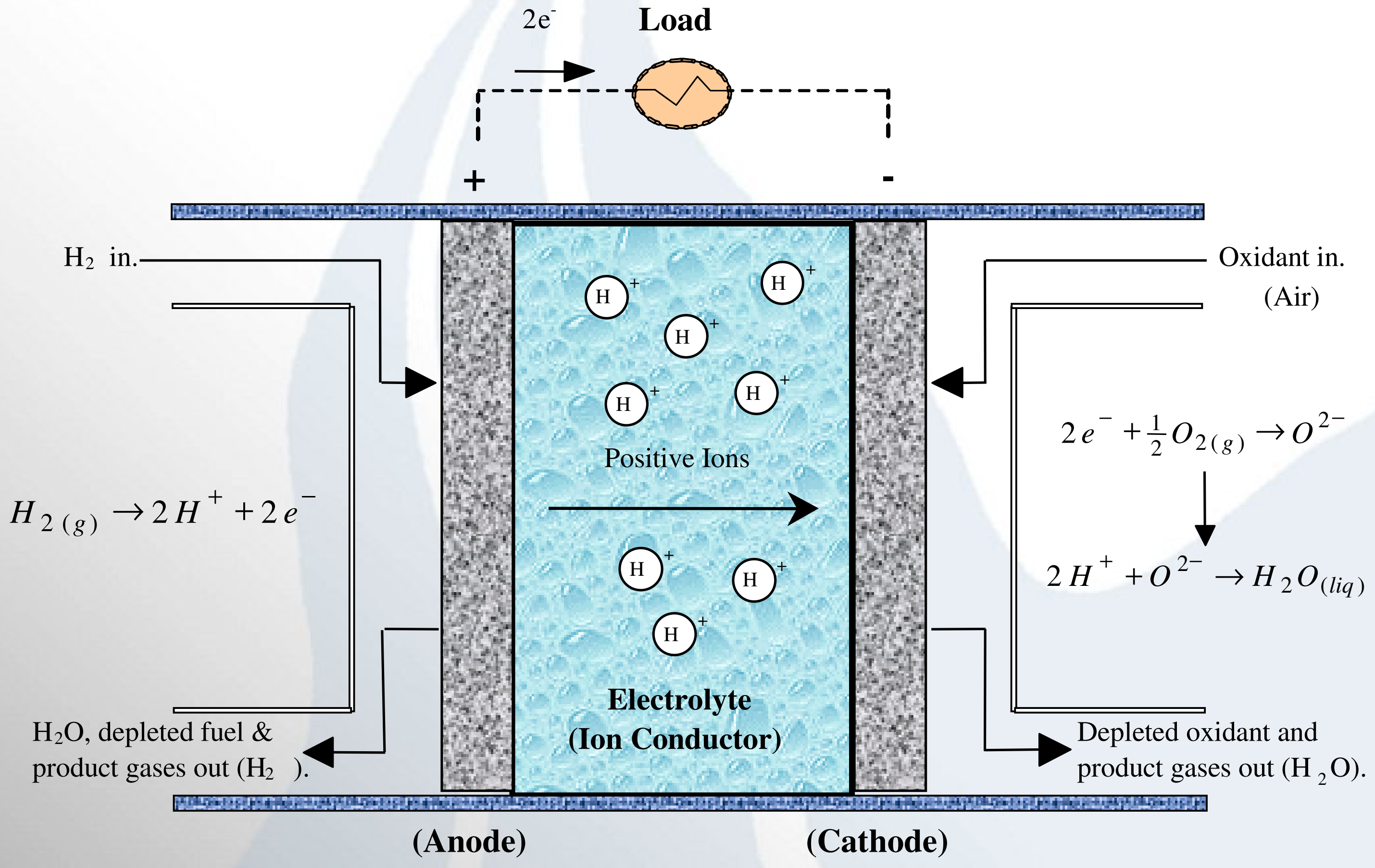
- Fuel Cell Systems (Mads Pagh Nielsen)
- Fuel Cell Stack Development (Mads Bang)
- Controlling Fuel Cell Systems (Anders Korsgaard)

14:00(?)-16:00(?)

- Experimental work (ARK, MBA & MPN)

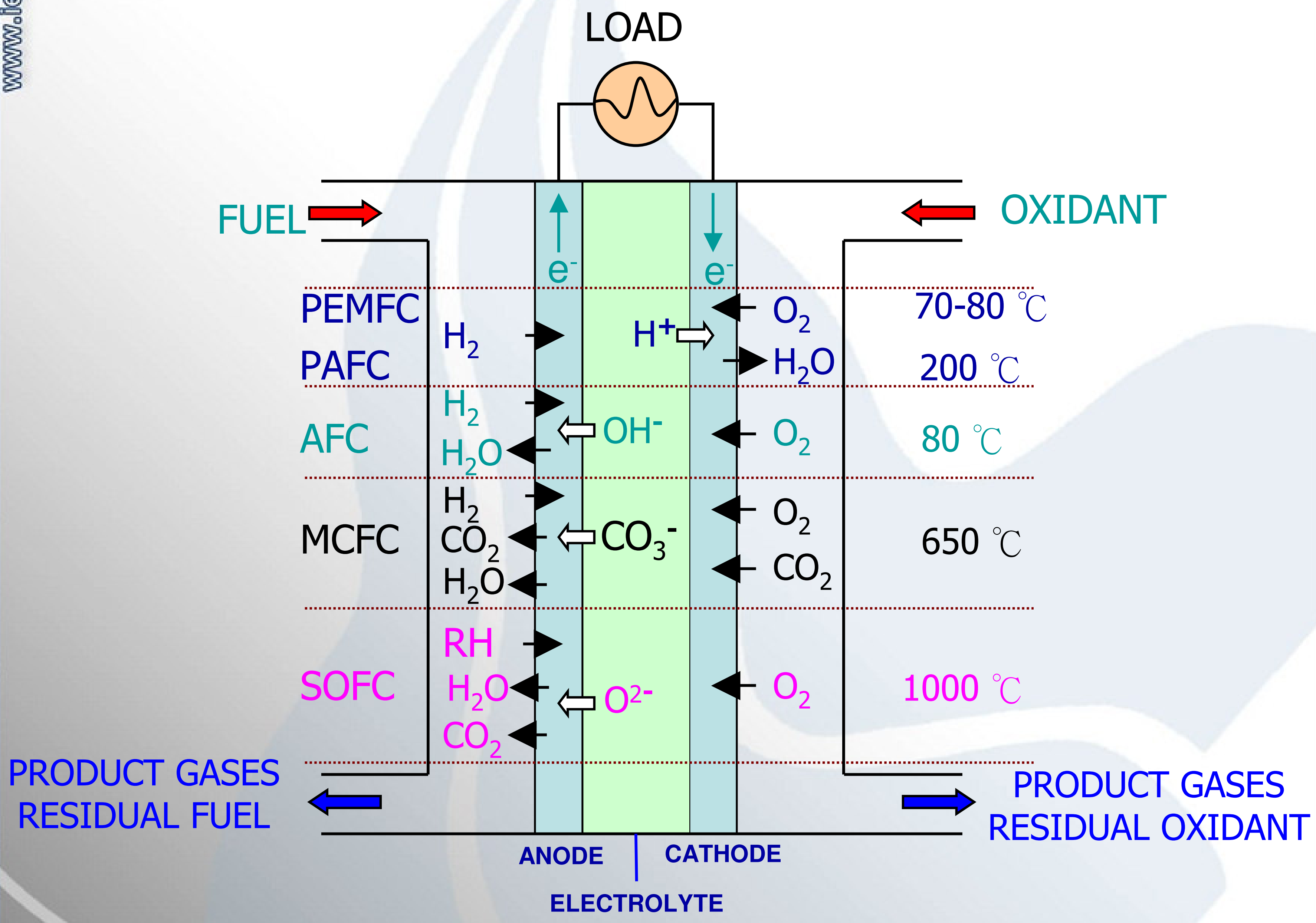
We go in the lab. (Pontoppidanstraede 107) and start up and work with the fuel cell test facility.

What is a fuel cell?



- Fuel cells are electrochemical devices, which highly efficiently convert energy in a fuel directly into electricity **without prior combustion** and with no moving parts.
- The process is the opposite of electrolysis.
- Fundamentally, all fuel cells operate on hydrogen and oxygen.

Chemical Reactions For Various FC-Types



LOAD

FUEL

OXIDANT

e^-

e^-

PEMFC
PAFC
H_2
H^+
O_2
H_2O
70-80 ℃
200 ℃

AFC
H_2
H_2O
OH^-
O_2
80 ℃

MCFC
H_2
CO_2
H_2O
CO_3^-
O_2
CO_2
650 ℃

SOFC
RH
H_2O
CO_2
O^{2-}
O_2
1000 ℃

PRODUCT GASES
RESIDUAL FUEL

PRODUCT GASES
RESIDUAL OXIDANT

ANODE
CATHODE
ELECTROLYTE

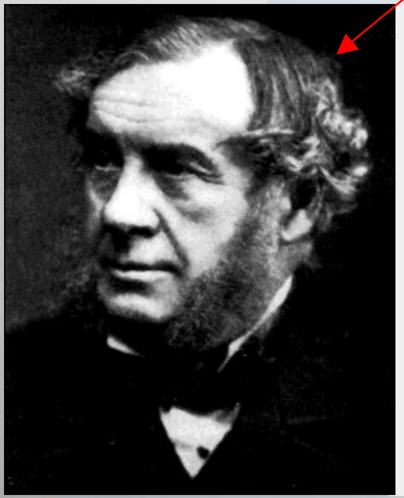
(Various types have different electrodes)

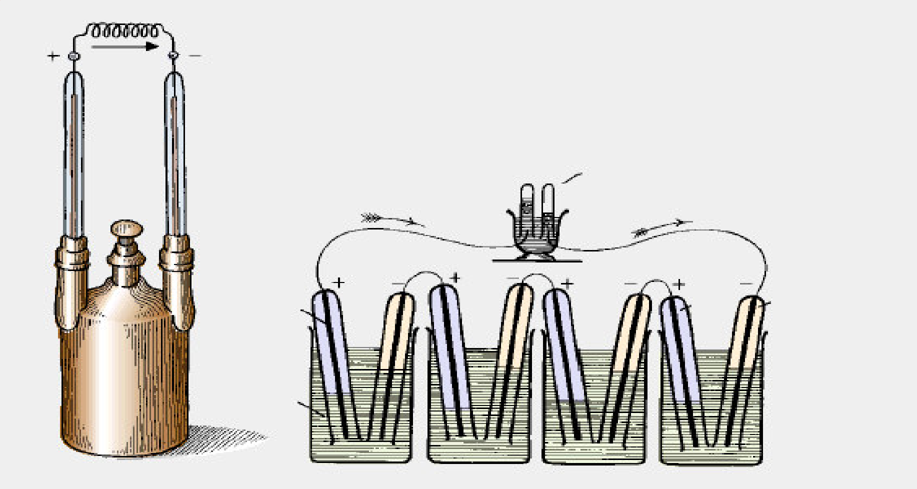
Inventors of the Fuel Cell

Christian Frederic Schönbein & William Robert Grove

CFS: Discoverer of the fuel cell effect (1838)

WRG: Inventor of the first fuel cell (1845)

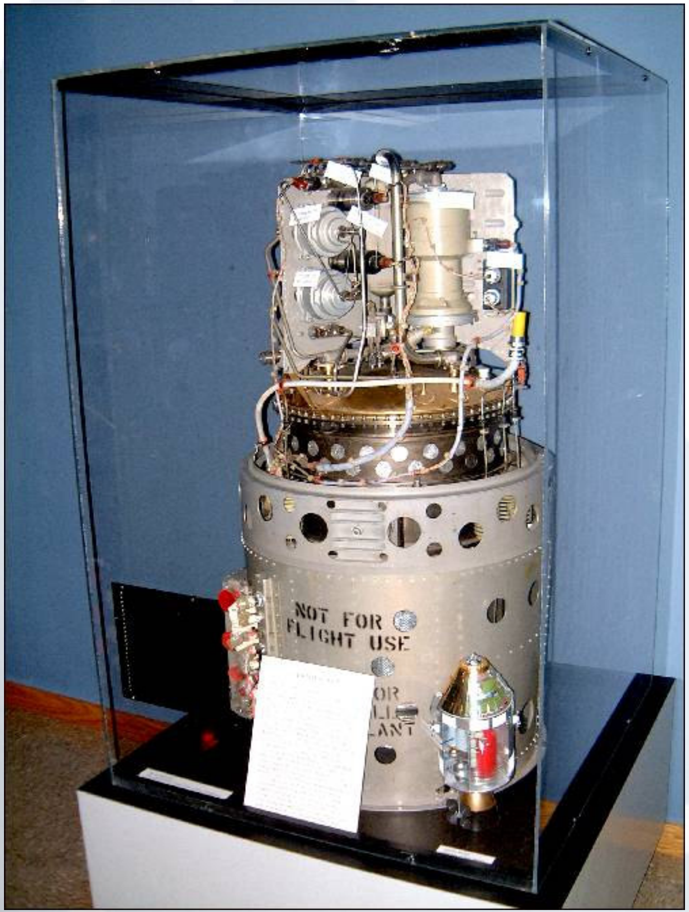




Francis Bacon

(1930-1950'ies invention of the Alkaline Fuel Cell)

Apollo Fuel Cell Stack



Why are fuel cells interesting?

- High efficiencies – best known way to convert the chemical energy of a fuel into electricity.
- Low acoustic- and other environmental emissions.
- Fuel Cells have excellent part-load characteristics *even at low power applications*!
- Scalability advantages compared to batteries.
- No moving mechanical parts ⇒ less wear & long lifetimes (note: There are still moving parts in the electrical traction system in a fuel cell vehicle!).
- More than 40,000 hours operation demonstrated with only minor degradation of efficiencies of PEM fuel cells – compares to typically 2000-5000 hours nominal operational time of internal combustion engines for cars).

Fuel Cell Types

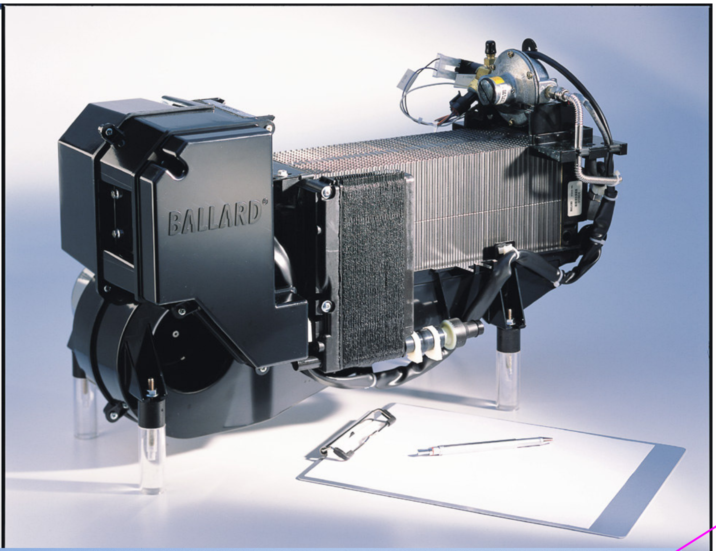
Low Temperature
(Consumer electronic, residential CHP & Automotive (PEM))

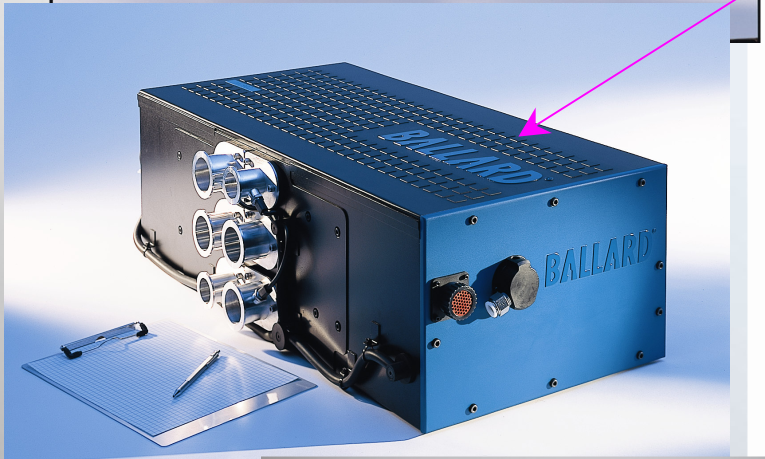
- **PEM/DMFC** *(Polymer Electrolyte Membrane Fuel Cells/Direct Methanol Fuel Cells 50-120℃)*
  - Lightweight, rugged, fast start-up (PEM temp ~ 70-80℃, HTPEM's~200℃ under dev.)
  - No liquid electrolyte
  - Poisoned by CO (content must be less than 10-50ppm in reformate)
  - Suited for transportation (buses and cars)
  - Used (PEM) on Gemini and Skylab
- **AFC** *(Alkaline Fuel Cells ~ 80℃)*
  - High power density (as high or even higher than PEM)
  - Is poisoned by CO_2 (impossible to use air as oxidant!)
  - Used in the Apollo space shuttles
- **PAFC** *(Phosphoric Acid Fuel Cells ~ 200℃)*
  - Most developed fuel cell type – commercially available
  - Not quite as efficient as PEM
  - Used in stationary power applications – particularly in Japan

High Temperature
(Only stationary applications, Large CHP (combined cycle), & residential CHP)

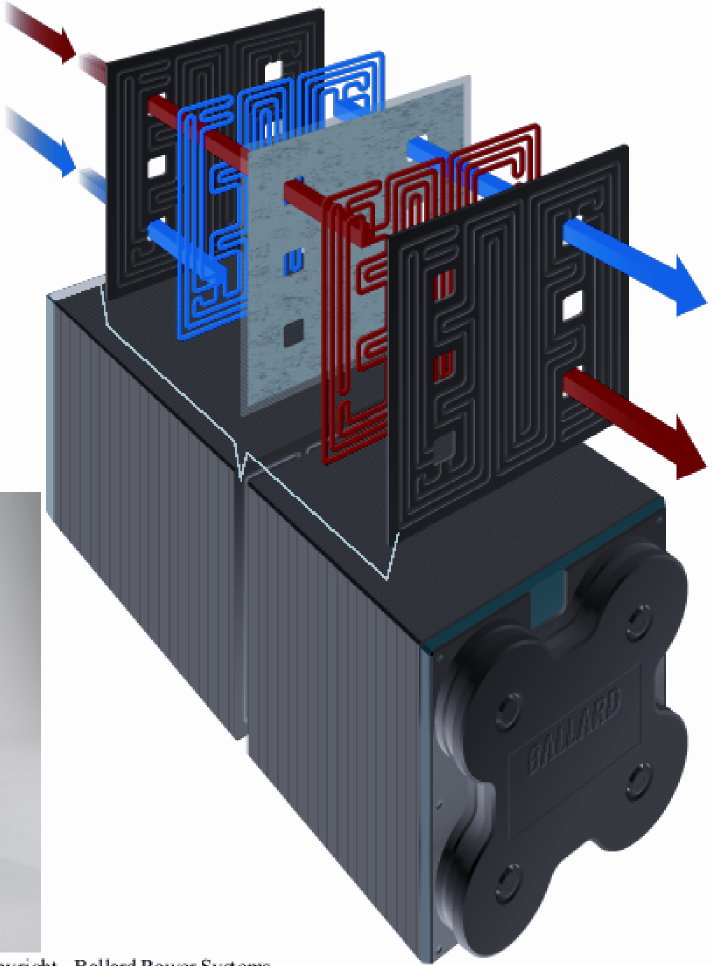
- **MCFC** *(Molten Carbonate Fuel Cells ~ 650℃)*
  - High temperature (corrosion and catalyst deactivation)
  - Complex system requirements
  - Can use methane directly by internal reforming with Ni-catalyst.

SOFC *(Solid Oxide Fuel Cells ~ 1000℃)*
  - Monolithic design possible (simpler than fixed beds – low pressure drops)
  - High temperature – internal reforming might be possible
  - Still developmental – electrolyte conductivity the main problem along with designing ceramic materials and catalysts that can withstand the high operational temperatures

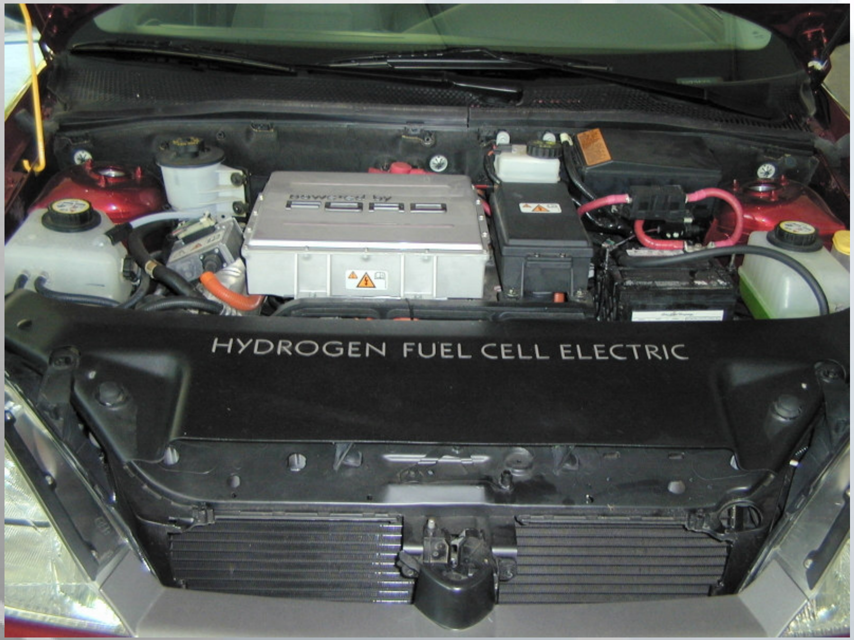


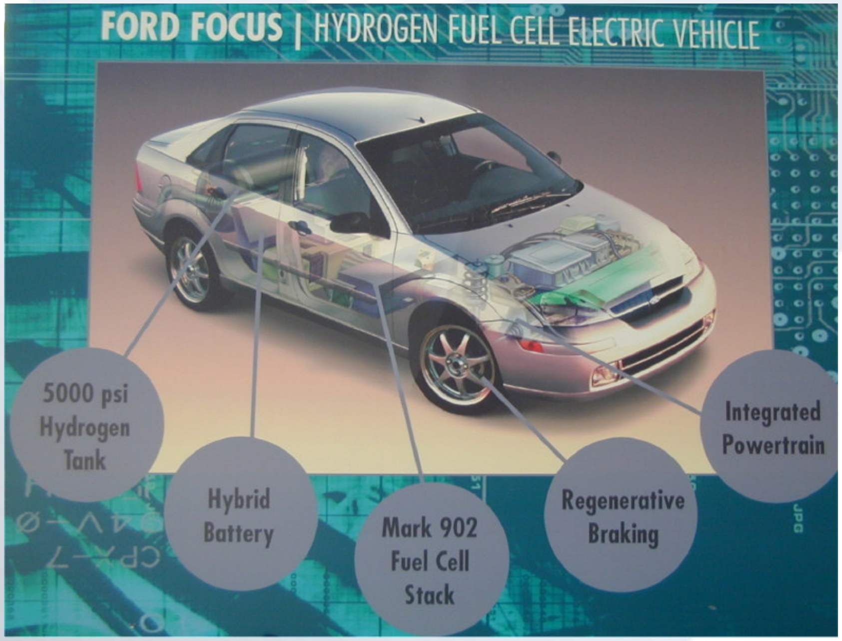


85kW (nominal)
~150kW (max.)
Weight: 96kg
Volume: 75L



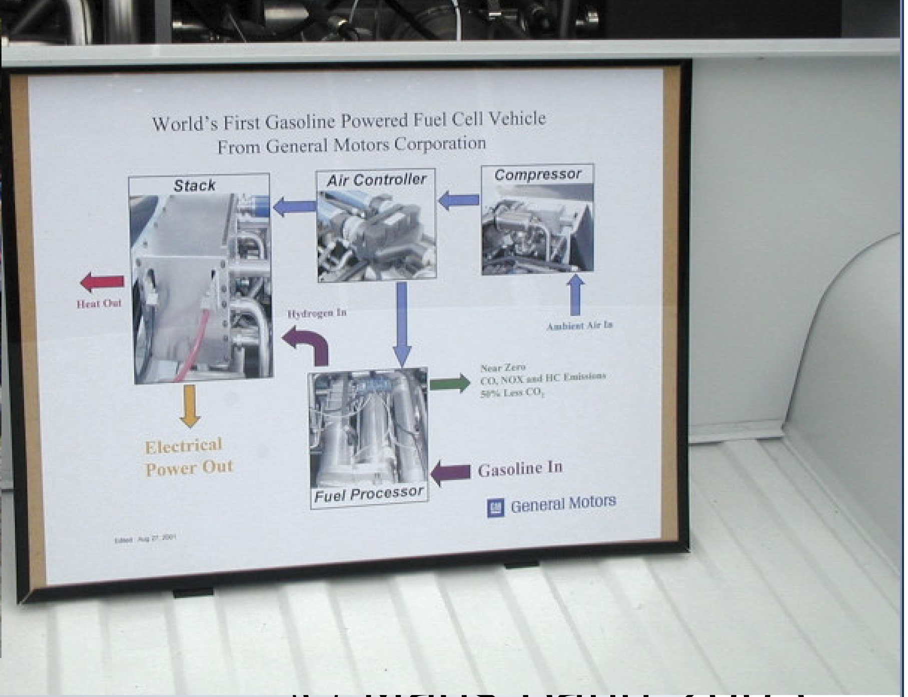
Automotive Applications





(Photos by Mads Pagh Nielsen)

Automotive Applications



World's First Gasoline Powered Fuel Cell Vehicle
From General Motors Corporation

Stack

Air Controller

Compressor

Heat Out

Hydrogen In

Ambient Air In

Near Zero
CO, NOX and HC Emissions
50% Less CO_2

Electrical
Power Out

Fuel Processor

Gasoline In

General Motors

Edited : Aug 27, 2001

(Photos by Mads Pagh Nielsen)

GM’s ”Autonomous Fuel Cell Vehicle”

Ballard Busses in Vancouver

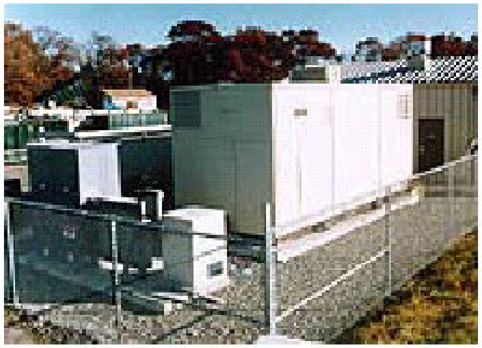
Stationary Power Production Applications

4.5 KW PEM – H Power

7 KW PEM – GE/Plug Power

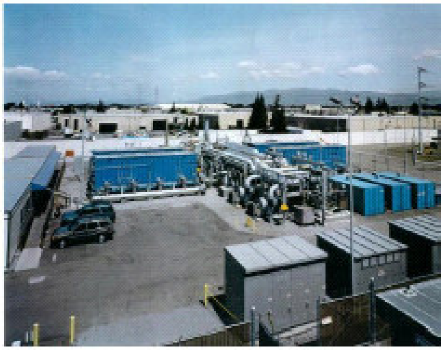
1-50 KW PEM – Nuvera

250 KW PEM -- Ballard



200 KW PAFC – Int'l Fuel Cells

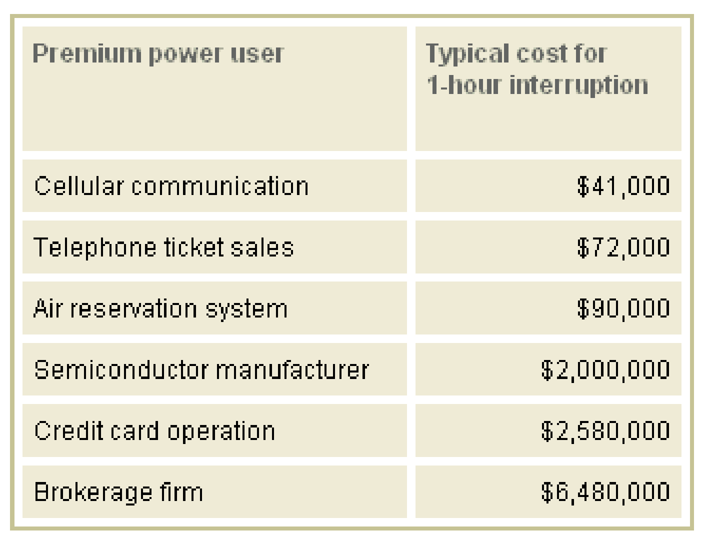
250 KW SOFC – Siemens Westinghouse



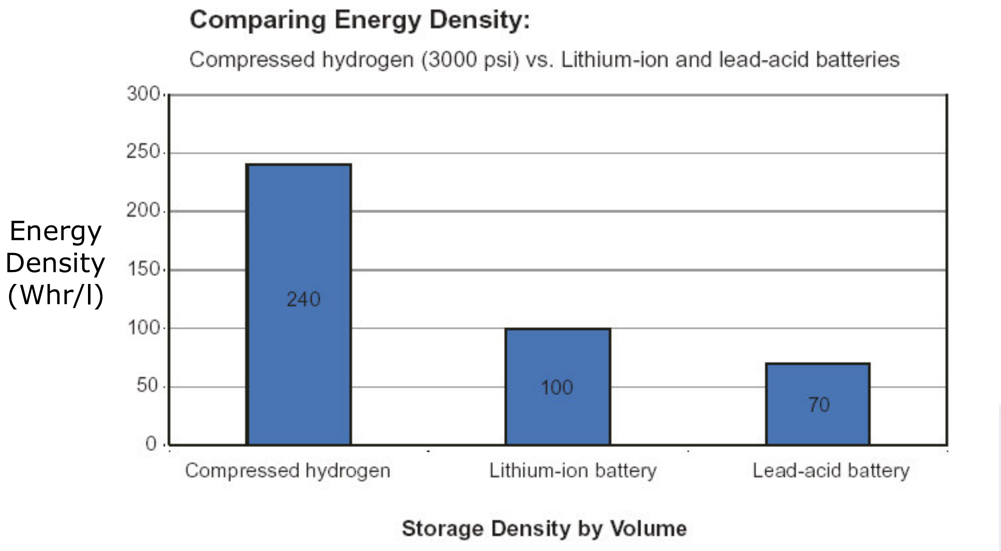
2000 KW MCFC – Fuel Cell Energy

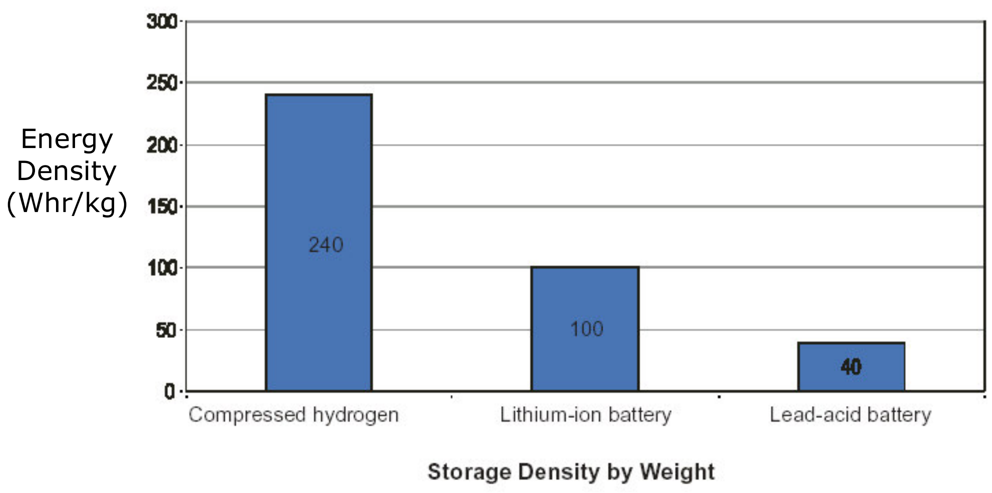
Premium Power (UPS-Applications)

Cost of power failures:



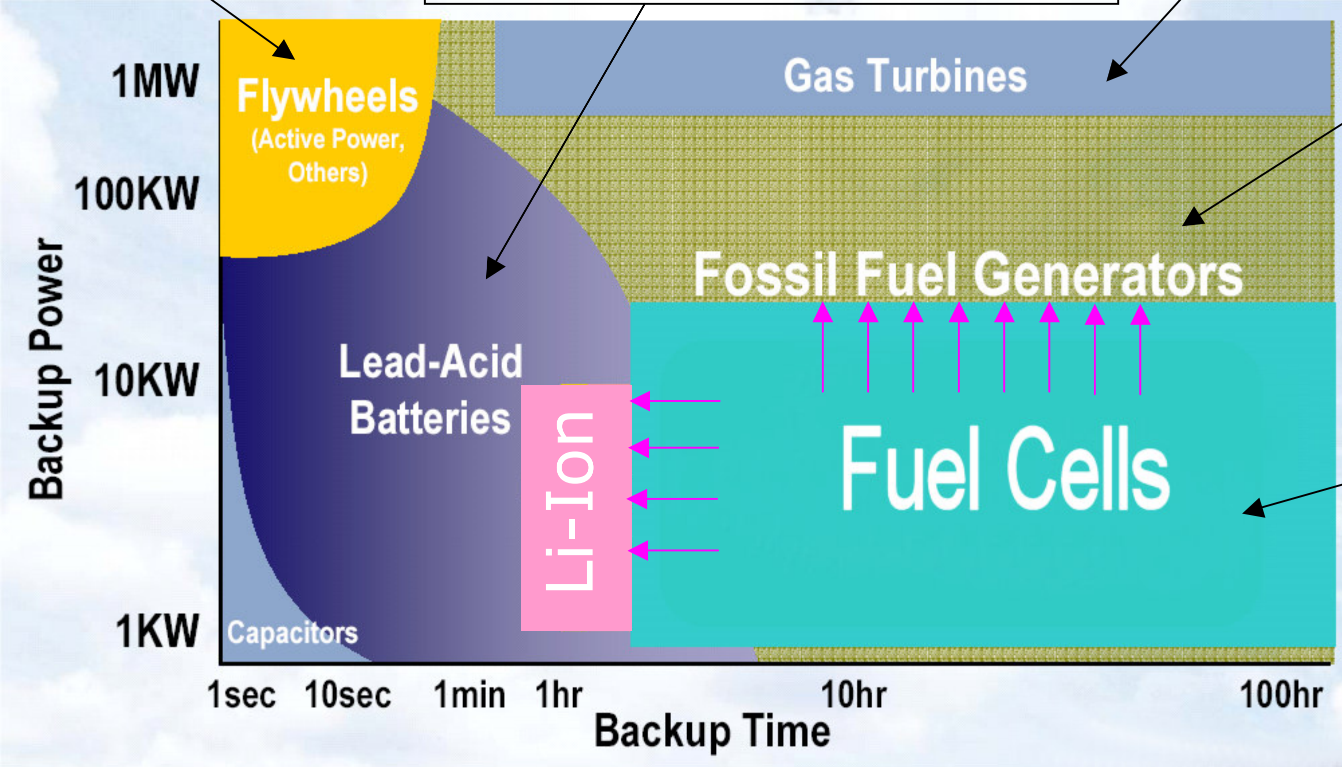
Premium power user	Typical cost for 1-hour interruption
Cellular communication	$41,000
Telephone ticket sales	$72,000
Air reservation system	$90,000
Semiconductor manufacturer	$2,000,000
Credit card operation	$2,580,000
Brokerage firm	$6,480,000





Source: GM electric, 2003

Premium Power (UPS-Applications)



Extremely high cost and space issues

Relative cost increases very much with size, limited backup time, recharging issues.

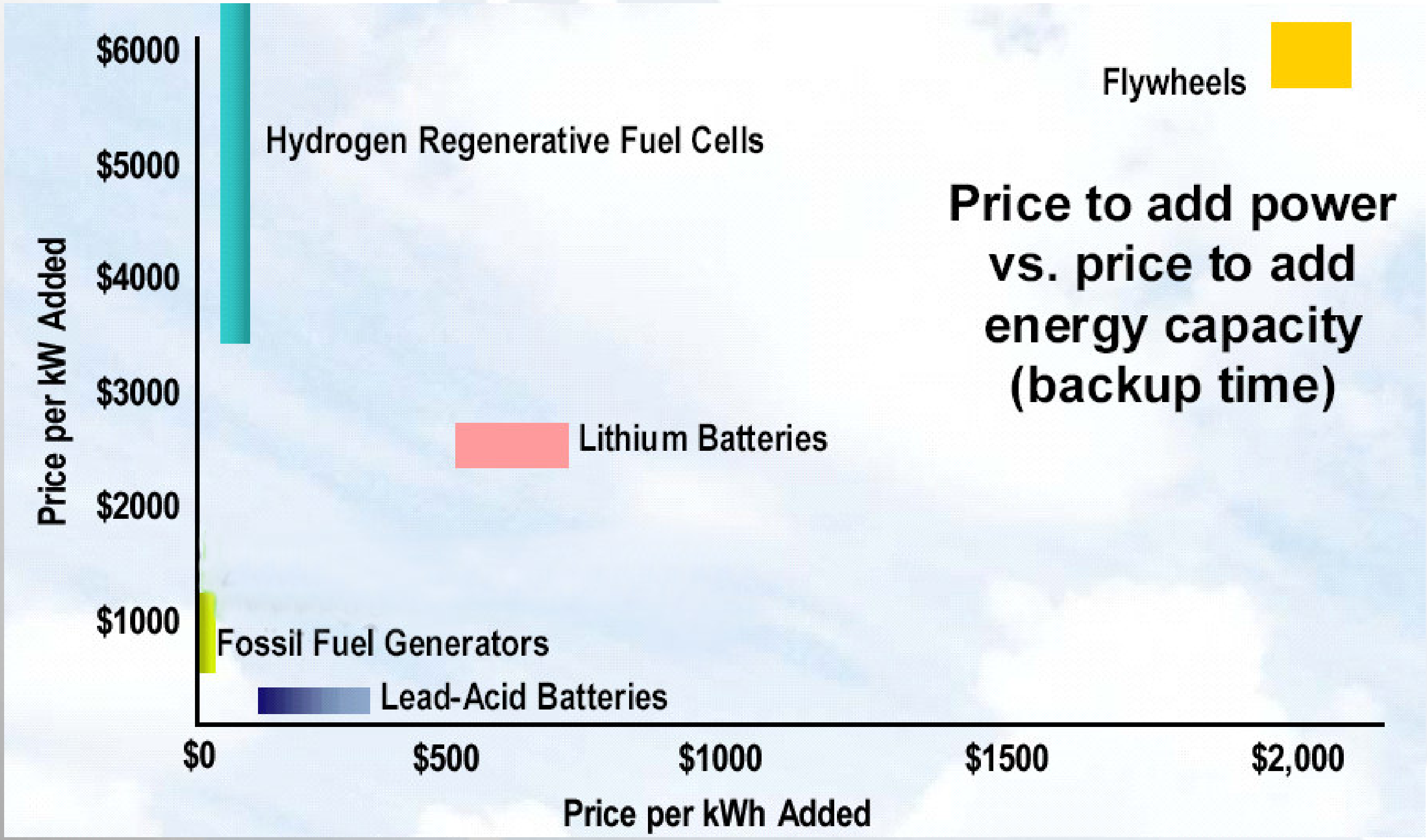
Limited to large plants

Cheaper than FC but relatively slow response (batteries unavoidable and pollution issues)

Very high investment cost but relative cost independent of size (scalability). No pollution issues. Can principally be used in entire diagram regime!

(Adapted from Metallic Power, INC. Presentation)

Premium Power (UPS Applications)

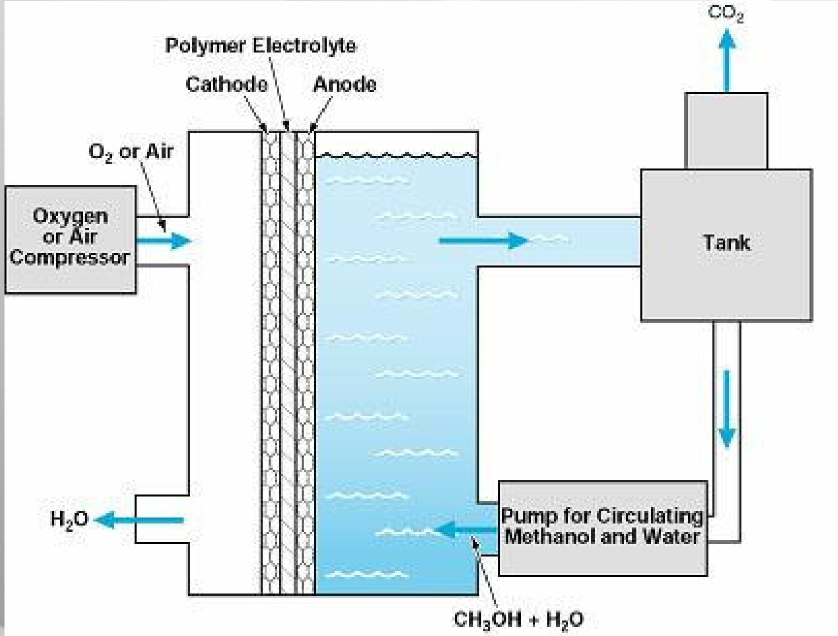


(Adapted from Metallic Power, INC. Presentation)

Consumer electronics (prototypes)

DMFC Laptop

DMFC Phone Recharger



Overall DMFC reaction:

$$CH_3OH + 3/2O_2 \rightarrow CO_2 + 2H_2O$$

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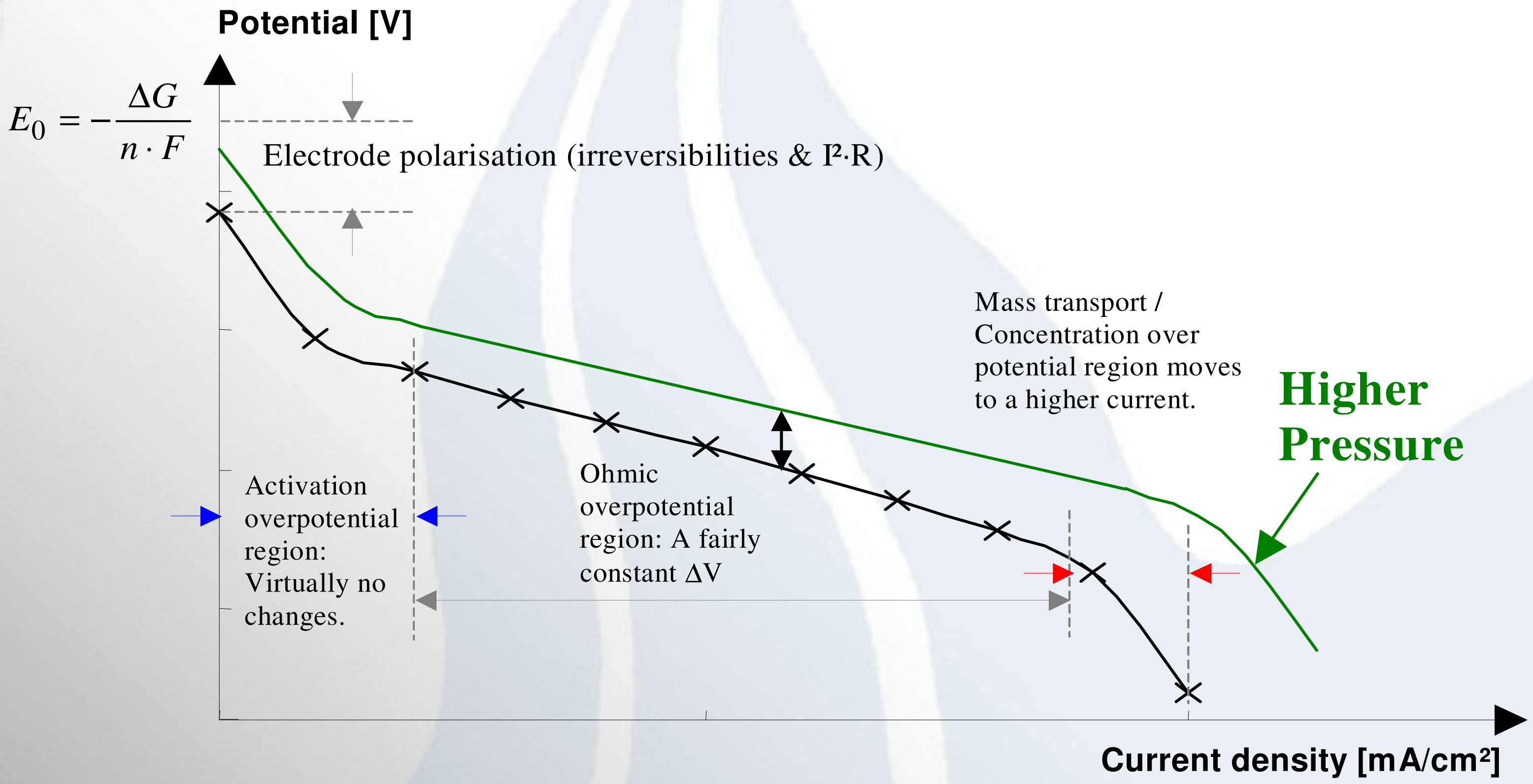
Only the imagination limits the range of applications…

(Photos by Mads Pagh Nielsen)

What happens when a PEM-fuel cell is applied a load?



Potential [V]

$E_0 = -\frac{\Delta G}{n \cdot F}$

Electrode polarisation (irreversibilities & $I^2 \cdot R$)

Mass transport / Concentration over potential region moves to a higher current.

Higher Pressure

Activation overpotential region: Virtually no changes.

Ohmic overpotential region: A fairly constant ΔV

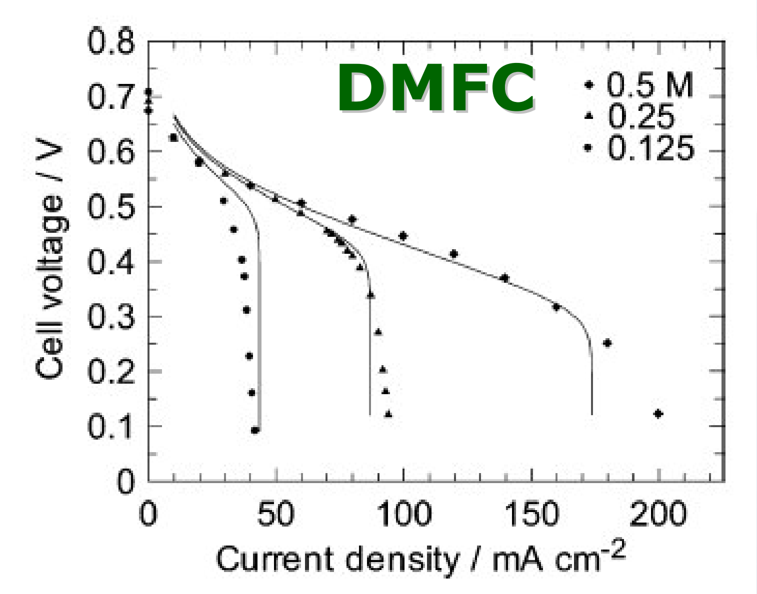
Current density [mA/cm²]

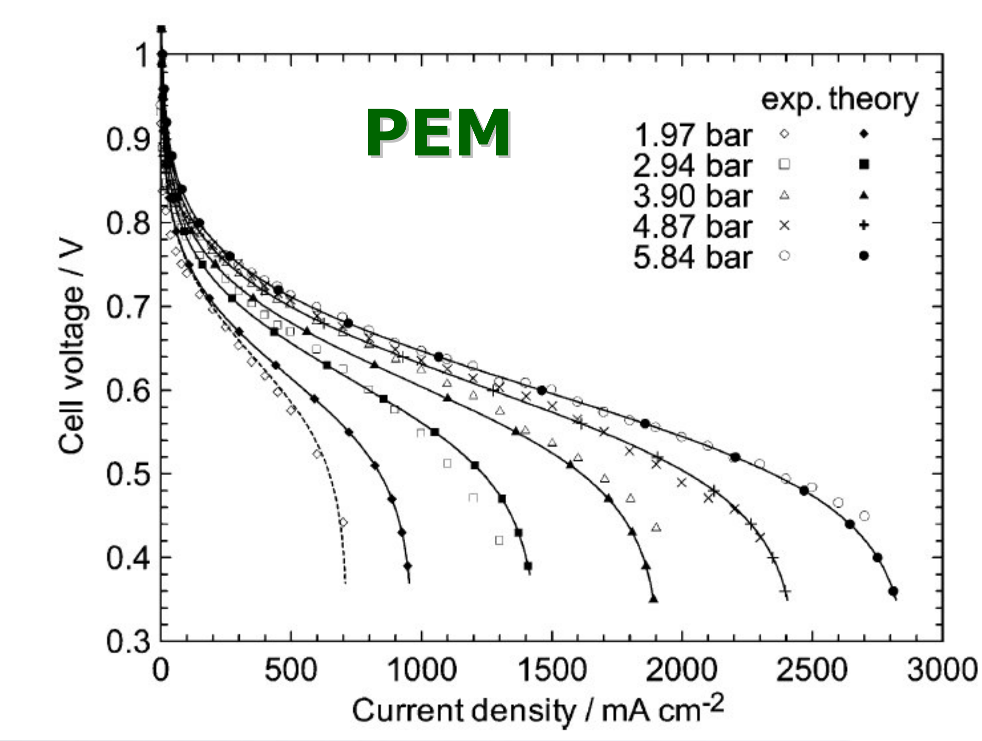
- Dependant mainly upon temperature, pressure and concentration of species and humidification at anode and cathode side.

- A battery has the same characteristic – only the load j_{cell} (the abscissa) should be replaced by the number of operation hours.

DMFC could be a serious contender to H_2 PEMFC’s

- Particularly for small-scale applications (consumer electronics)
- Maybe also large scale applications (?)





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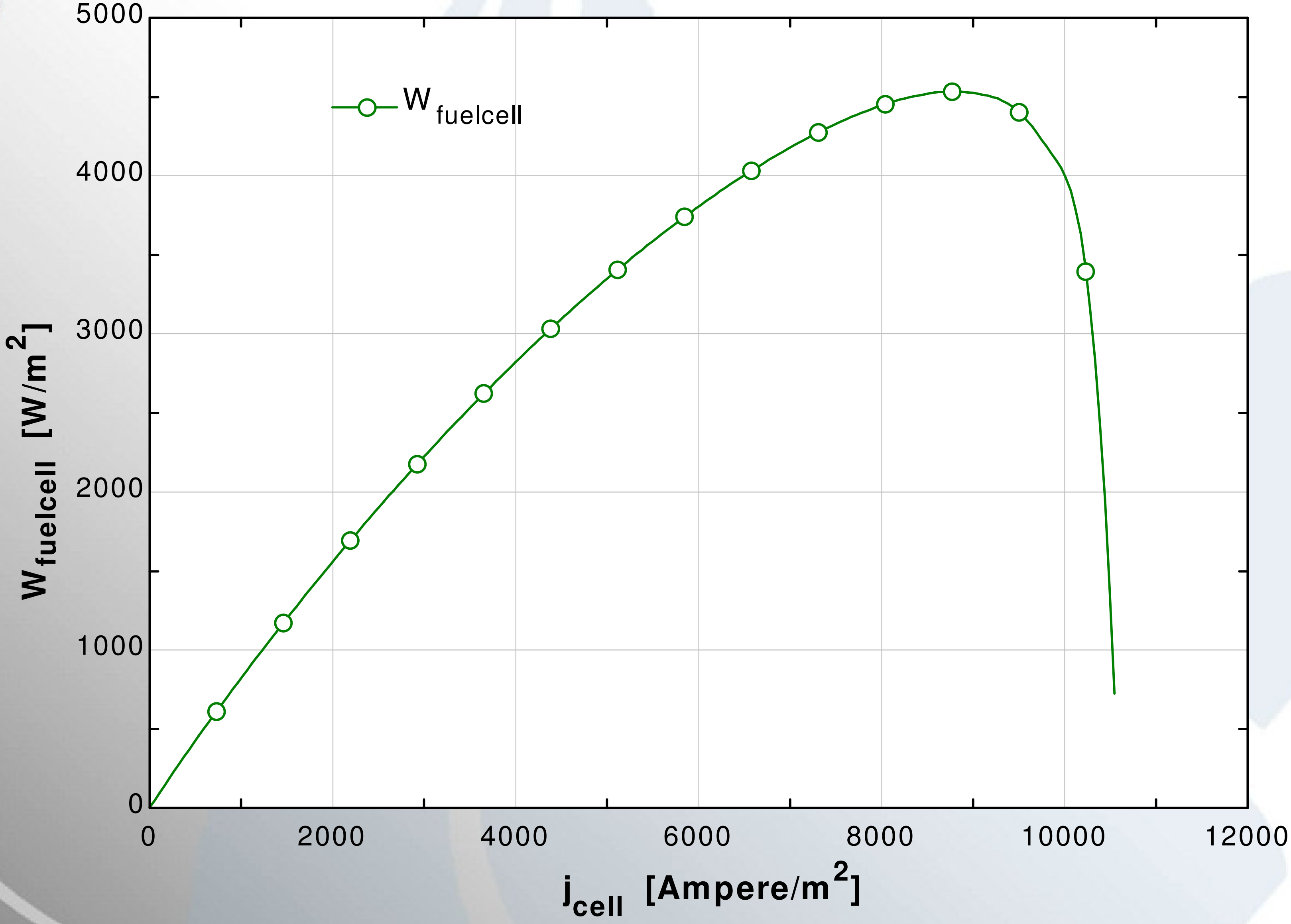
Power Characteristic

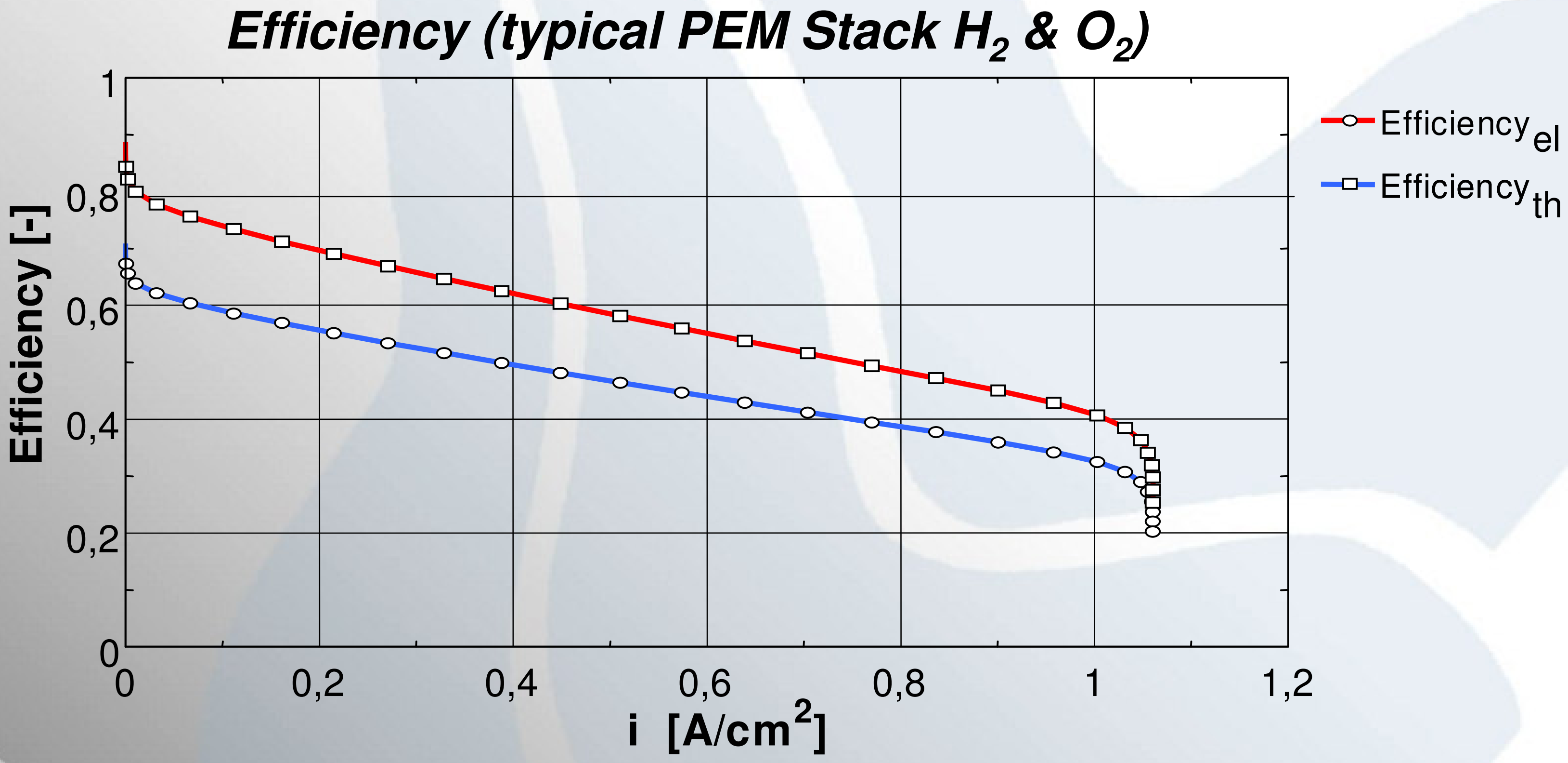


Two Efficiency Definitions (!)

Electrical: $\eta_{el} = \frac{V}{EMF}$

Thermal: $\eta_{thermal} = \frac{W_{el}}{\Delta H_{HHV}}$

$$\eta_{thermodynamic,max} = \frac{\Delta g}{\Delta h} = \frac{-237\frac{kJ}{mol}}{-286\frac{kJ}{mol}} \approx 83\%$$



Heating values an important issue when comparing various technologies:

- Two heating values:
  - Higher Heating Value *(HHV)*: used when all water formed by combustion is a *liquid (physically correct reference based on enthalpies of formation)*
  - Lower heating value *(LHV)*: when all water formed by combustion is a *vapor (Convention developed because evaporation of vapor does not contribute to heat production in a boiler or heat engine)*

Technology	**Fuel**	**LHV based efficiency (peak)**	**HHV based efficiency (peak)**
Power Plant	Coal	50%	48.9%
----"''----	Natural Gas	60%	53.8%
Condensing Boiler	Natural Gas	105% (unphysical!)	94.1%
IC engine (Car)	Gasoline	25%	22.8%
Fuel Cell Car	Hydrogen	45%	38.1%

(Reported state-of-the-art values)

Conclusion: It is very hard to compare efficiencies!
Be extremely careful out there ☺!

Thermodynamics also apply to fuel cells (!):

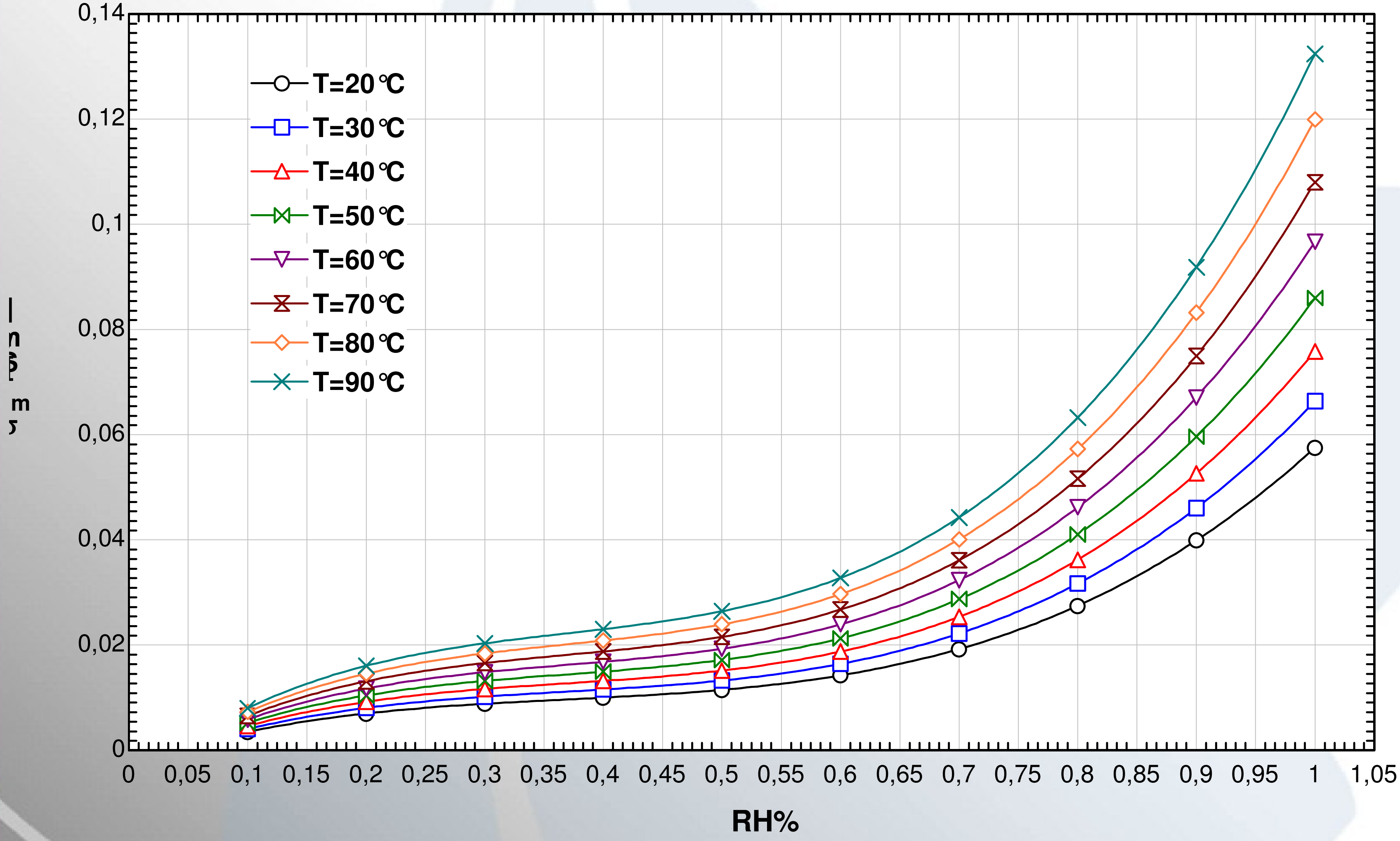
It is a common mistake to state that “fuel cells are not limited by the Carnot efficiency” (the theoretical upper limiting efficiency found using 2nd law of thermodynamics on a perfect heat engine).

However, a heat engine must absorb heat at the flame temperature (1500-2000K) and reject at 298K whereas a fuel cell can utilize energy at a much lower temperature.

Therefore, heat engines are forced to accept operating losses that fuel cells, operating at a much lower temperature, can avoid.

The Necessity of Humidification

(Assuming that the membrane is homogeneously humidified)



Proton conductivity of a Nafion 115 membrane aau

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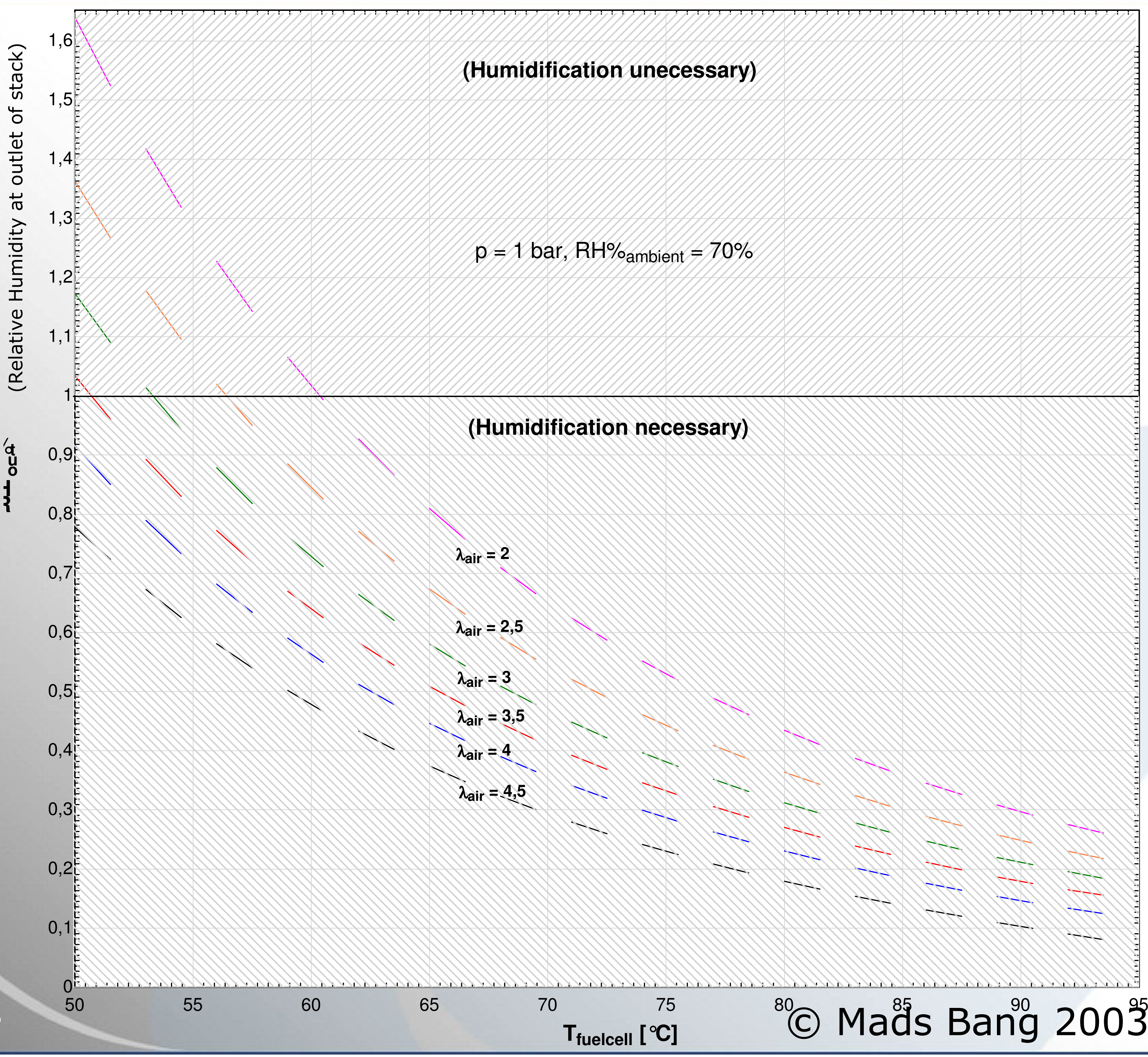
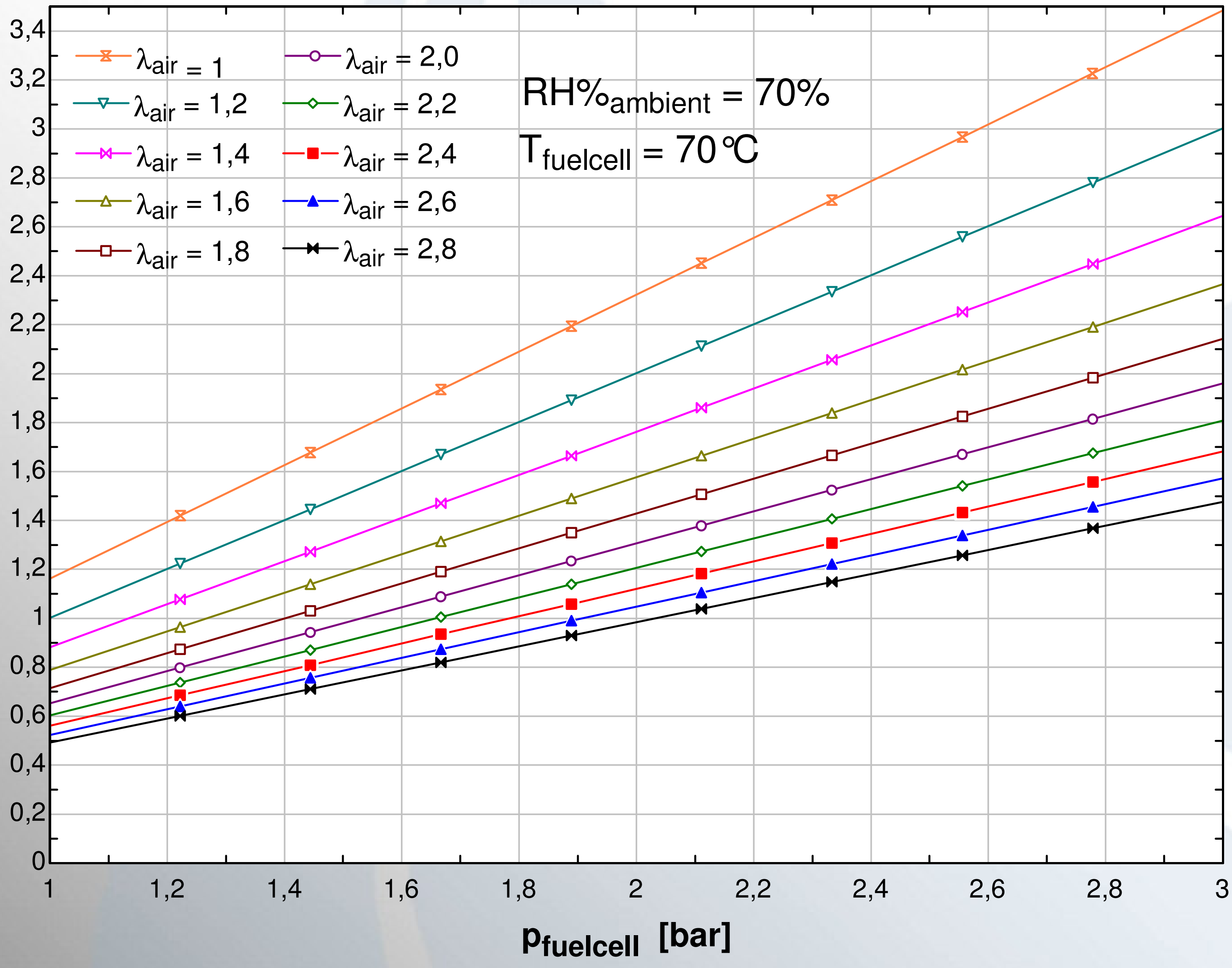
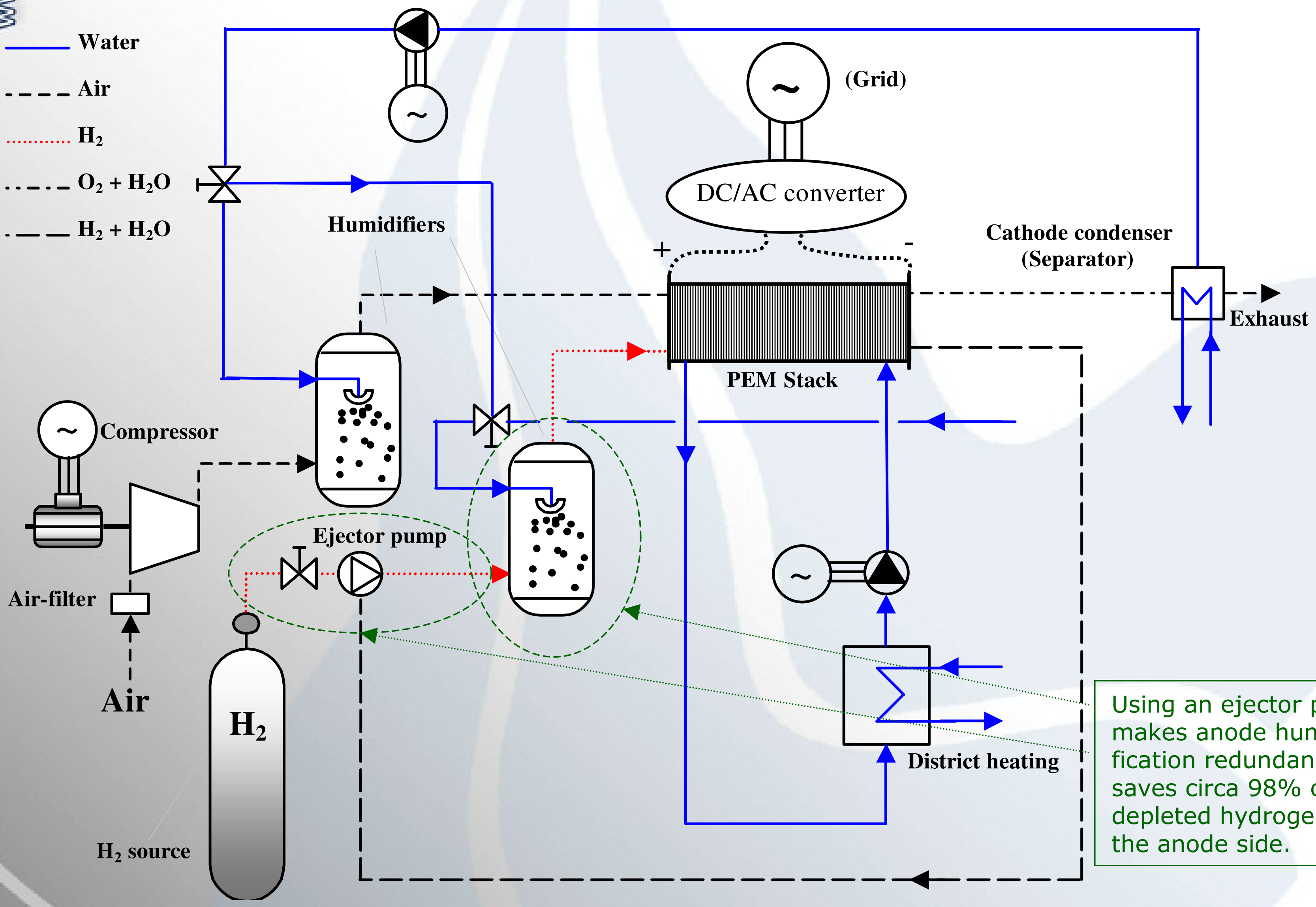


The effect of increasing stack pressure (PEMFC)



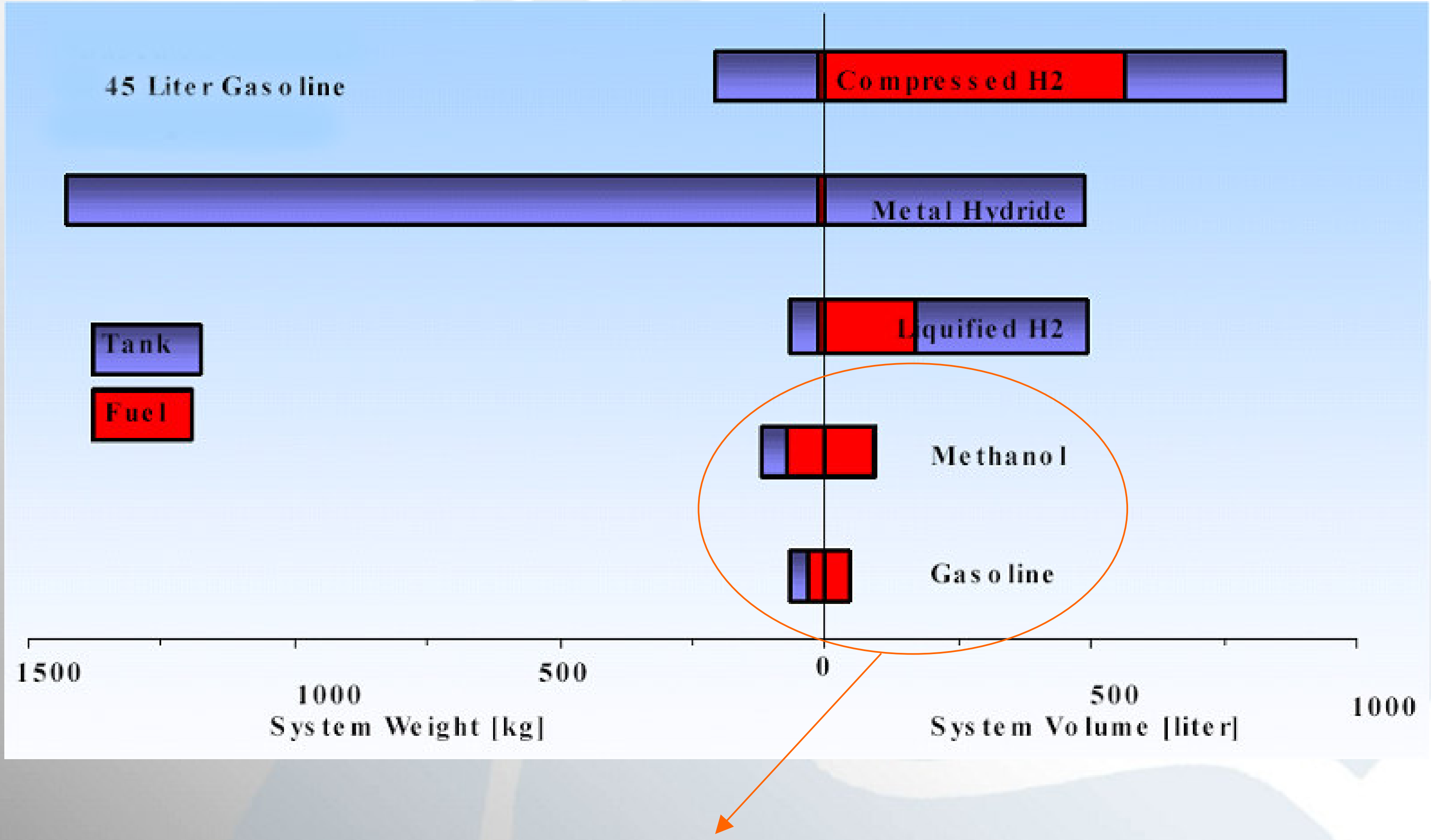
Basic Hydrogen Fuel Cell ***System***

Fuel Cell Stack is sensitive to pollution by metal ions =>
Material considerations and use of demineralized water and airfiltering.



Using an ejector pump makes anode humidification redundant and saves circa 98% of the depleted hydrogen at the anode side.

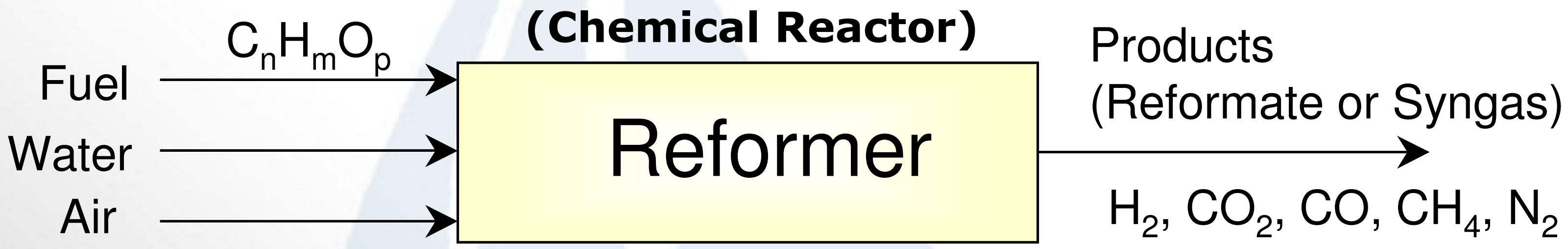
Where to get the hydrogen? Storage issues:



- Storage Issues & Fuel Production/Transportation Infrastructure

(Source: Johnson Matthey Fuel Cell Inc., 2002)

The Reforming Process:



General Reforming Reaction (Developed By Argonne National Laboratory):

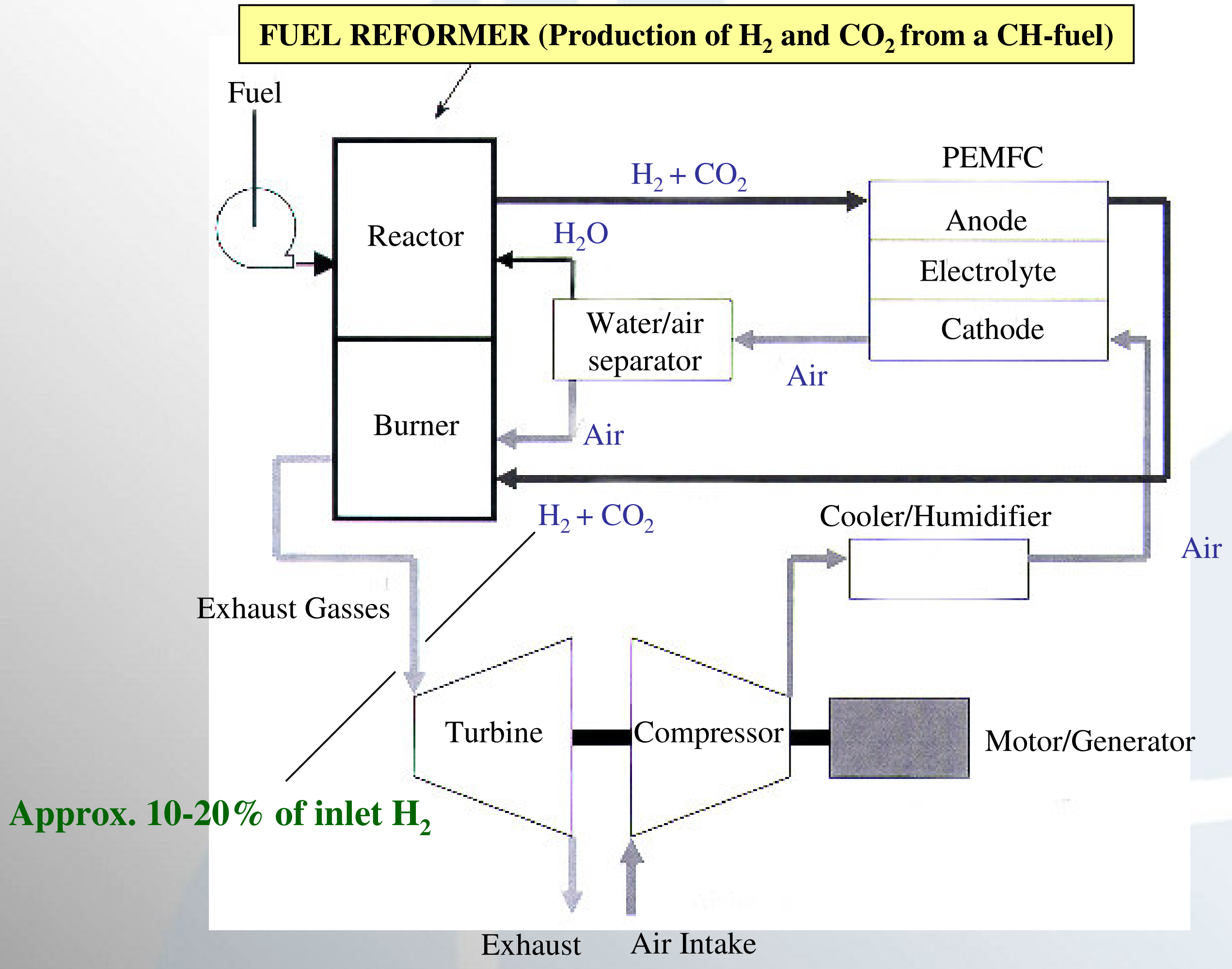
$$C_nH_mO_p + xO_2 + (2n-2x-p)H_2O = nCO_2 + (2n-2x-p+m/2)H_2$$

Enthalpy of Reaction:

$$-\Delta H_r = n\Delta H_{CO2} - (2n-2x-p)\Delta H_{H2O} - \Delta H_{fuel}$$

Definition of Reforming: *The process of converting liquid or gaseous hydrocarbon fuels into a gas consisting of mainly hydrogen and carbon monoxide.*

System with reforming



FUEL REFORMER (Production of H_2 and CO_2 from a CH-fuel)

Fuel

Reactor

Burner

$H_2 + CO_2$

PEMFC

Anode

Electrolyte

Cathode

H_2O

Water/air separator

Air

Air

$H_2 + CO_2$

Cooler/Humidifier

Air

Exhaust Gasses

Turbine

Compressor

Motor/Generator

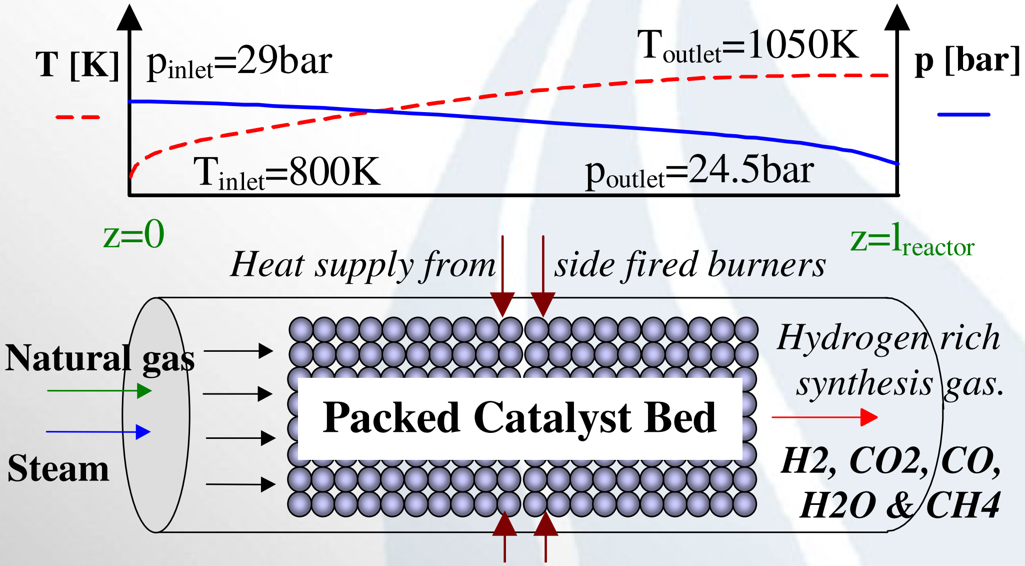
Approx. 10-20% of inlet H_2

Exhaust

Air Intake

Thermodynamic Equilibrium Of The Steam Reforming Process

(Reacting natural gas or methane with steam over a catalyst)



T [K] p_{inlet}=29bar

T_{outlet}=1050K p [bar]

T_{inlet}=800K p_{outlet}=24.5bar

z=0 z=$l_{reactor}$

Heat supply from side fired burners

Natural gas

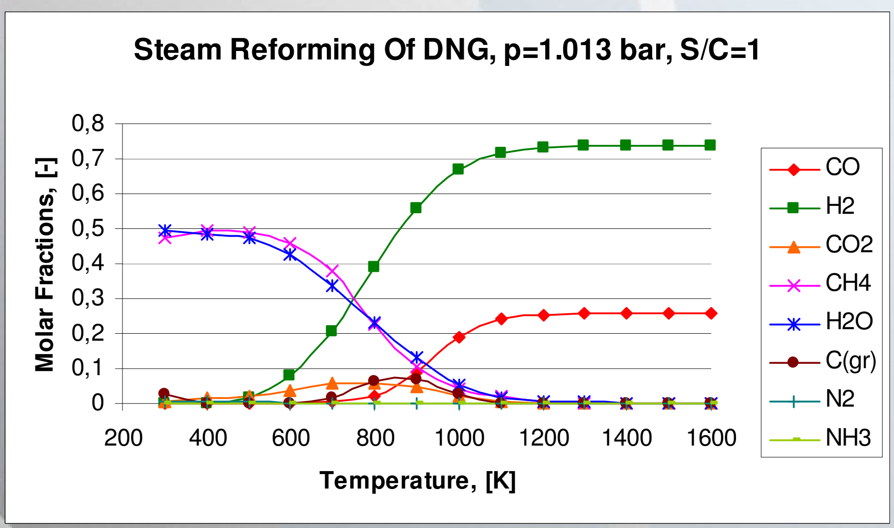
Steam

Packed Catalyst Bed

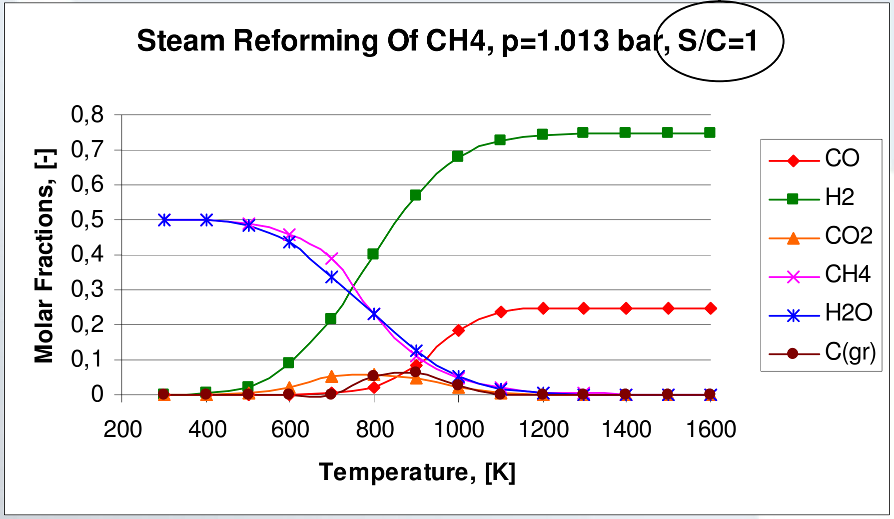
Hydrogen rich synthesis gas.

H2, CO2, CO, H2O & CH4

”Steam To Carbon Ratio”



Steam Reforming Of DNG, p=1.013 bar, S/C=1

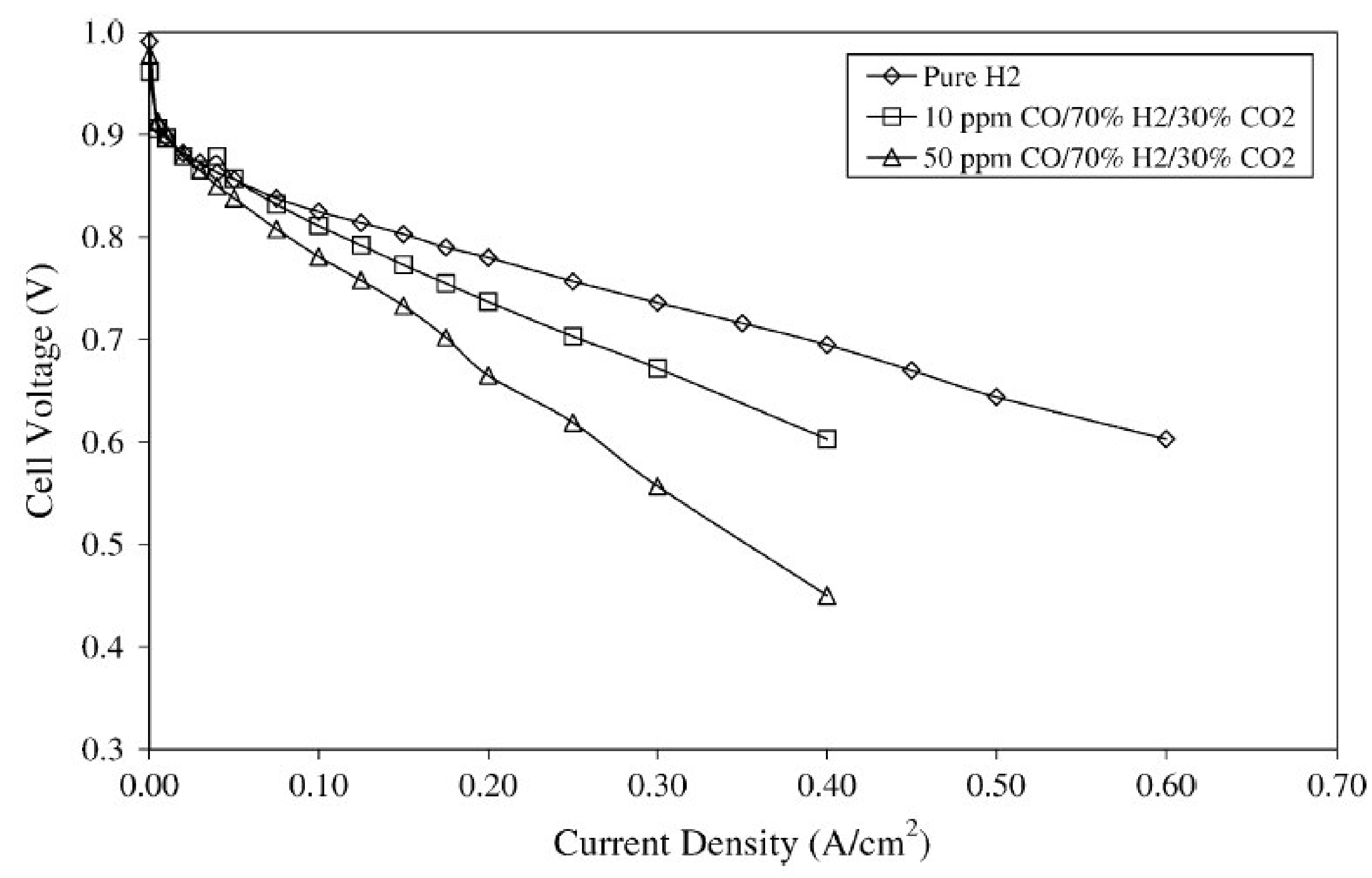


Steam Reforming Of CH4, p=1.013 bar, S/C=1

Gibbs minimization done with
The NASA-Lewis code:
http://www.grc.nasa.gov/WWW/CEAWeb/

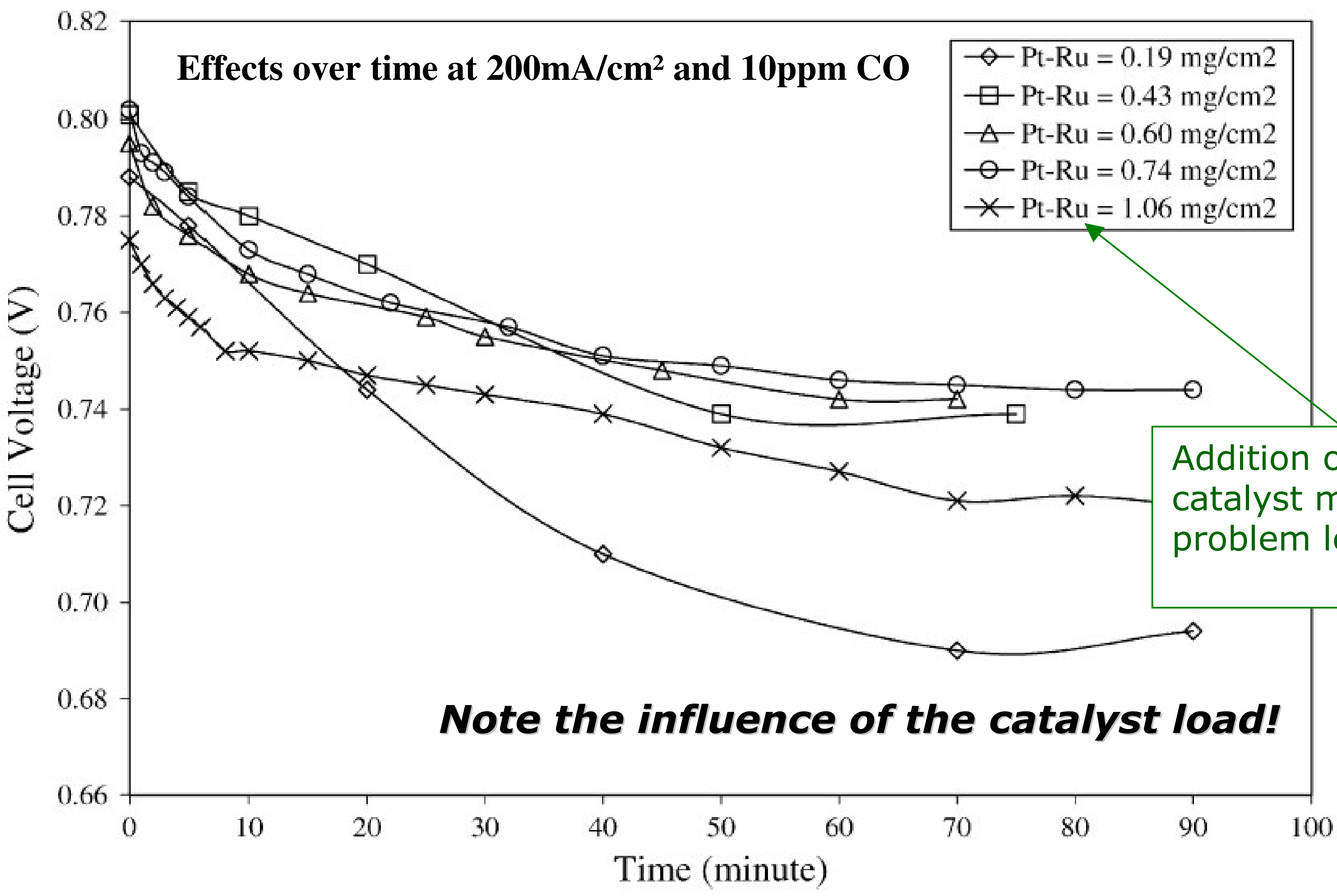
CO results in severe losses in PEM stacks:

Polarization Curves:



The CO effect is *temporary* and changes over time

(Stack fully regenerates over time when operated on pure hydrogen
– no permanent damage)



Effects over time at 200mA/cm² and 10ppm CO

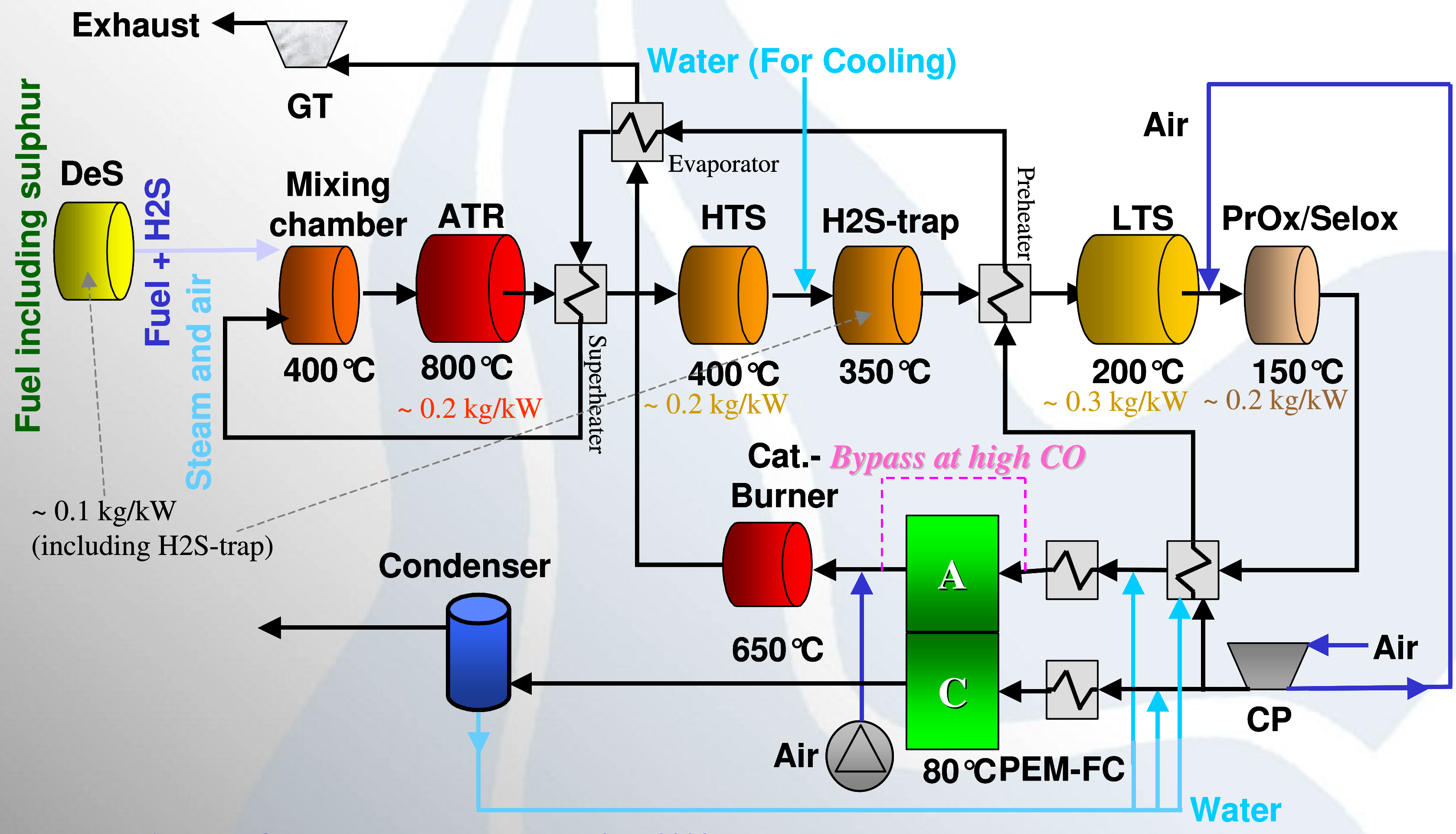
Note the influence of the catalyst load!

Addition of Ruthenium catalyst makes the problem less significant.

In high temperature PEM's the problem is absent (i.e. 120°C)

Automotive PEM-System Operated On Gasoline

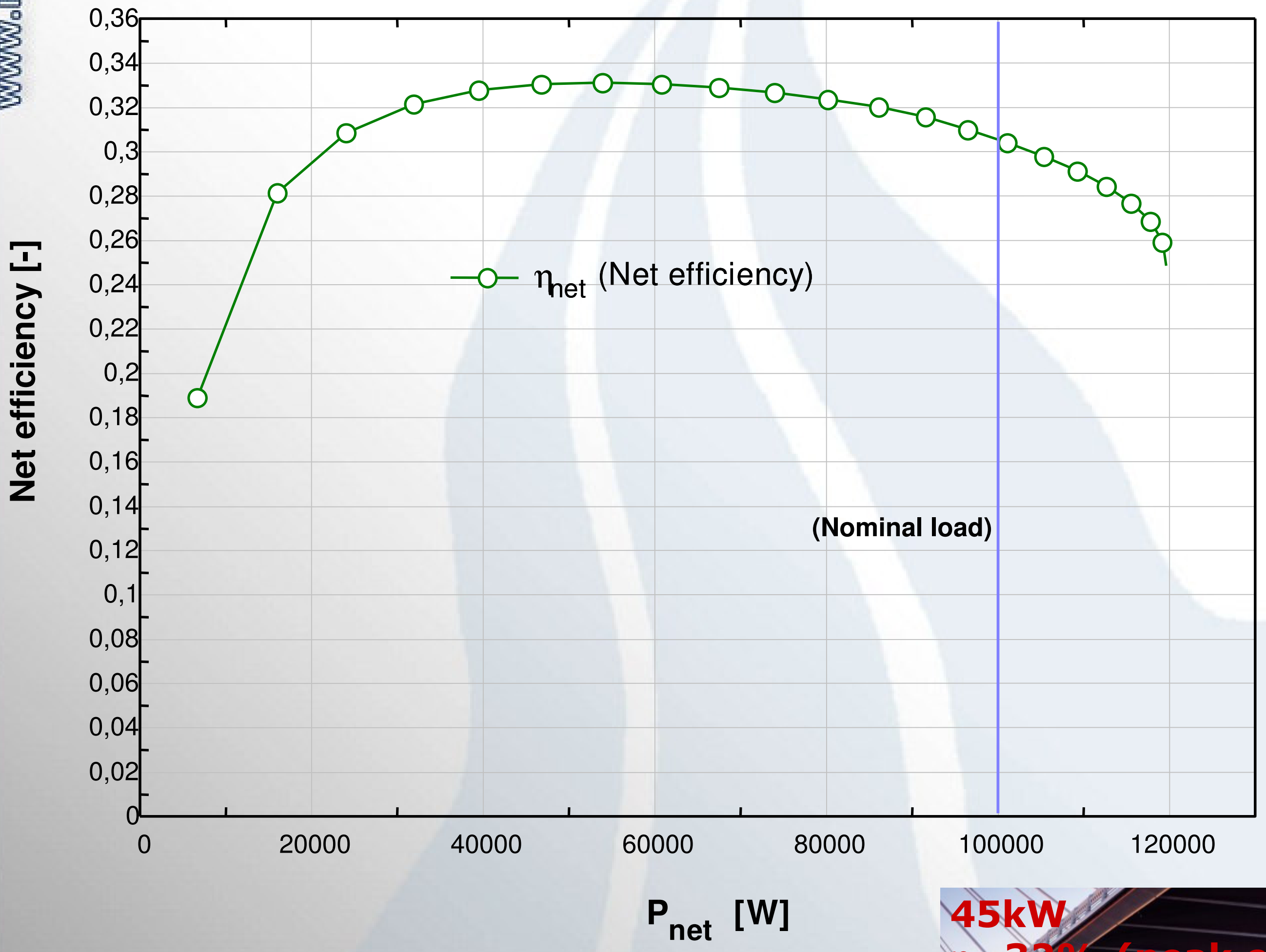
PEM's are poisoned by Sulfur, Ammonia compounds and CO:



Adapted from Volkswagen presentation, 2002

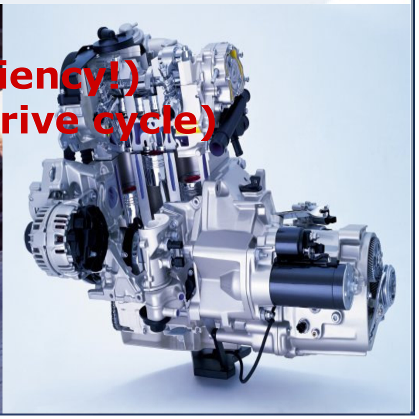
Power densities are set assuming automotive targets are met ~ 1kg/kW.

Projected Automotive 100kW Diesel Reforming system



45kW
η~32% (peak efficiency!)
η~24% (average drive cycle)

3L Lupo TDi



Conclusion

- Fuel cells are being rapidly developed and constantly improved and the cost is getting lower.
- Dedicated development of single components and reactors is necessary.
- Focus should mainly be on Process Integration (system design) and Material Science, which both plays a major role in commercialization.
- Development of hydrogen production and storage methods is of great importance.
- Volume production necessary before economically feasible. For comparison, a conventional ICE cost approximately ***30$ per kW*** (everything included!).

Thank You For Your Attention!

Fuel Cell Stack Design and Development

Mads Bang
IRD Fuel Cells A/S
Institute of Energy Technology

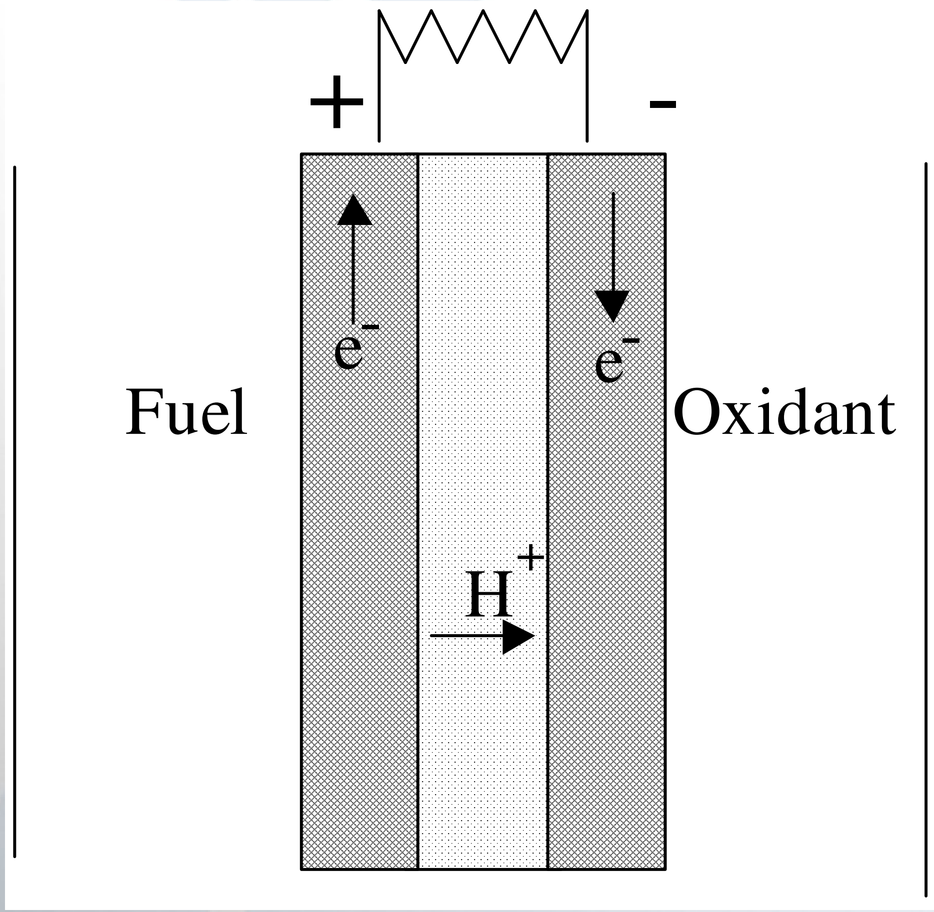
Outline

- The basics -How does a fuel cell look like, and what does it consist of?
- Operational characteristics of a FC - Tracing the losses
- Modelling the processes –Improving understanding and performance

The basics
-How does a fuel cell look like, and what does it consist of?

Fuel cell Schematics-The MEA

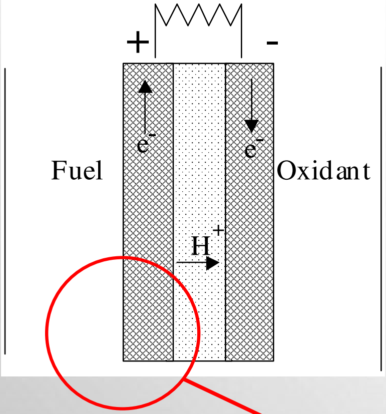
(Membrane Electrode Assembly)



$$Fuel \Rightarrow Product + H^{+} + e^{-}$$

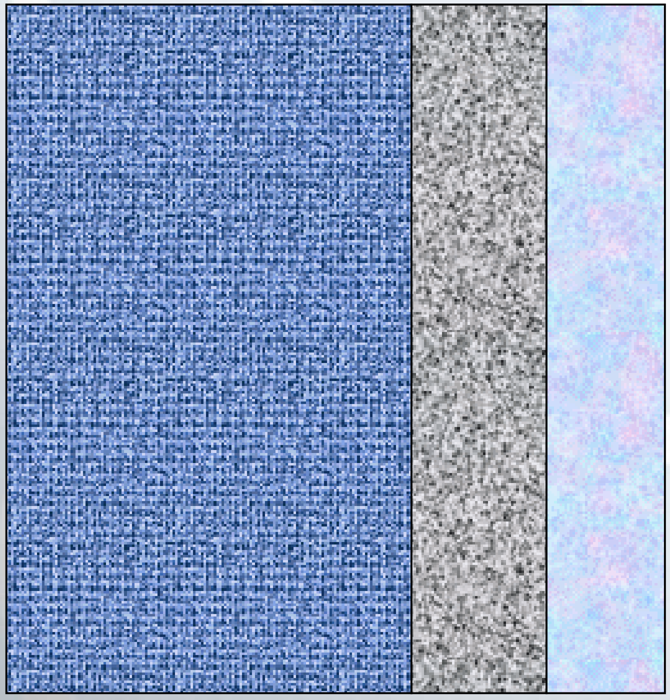
$$Oxidant + H^{+} + e^{-} \Rightarrow Product$$

The diffusion layer & electrode



Electrode/catalyst

Porous catalyst
Electric conductive
Protonic conductive



Membrane

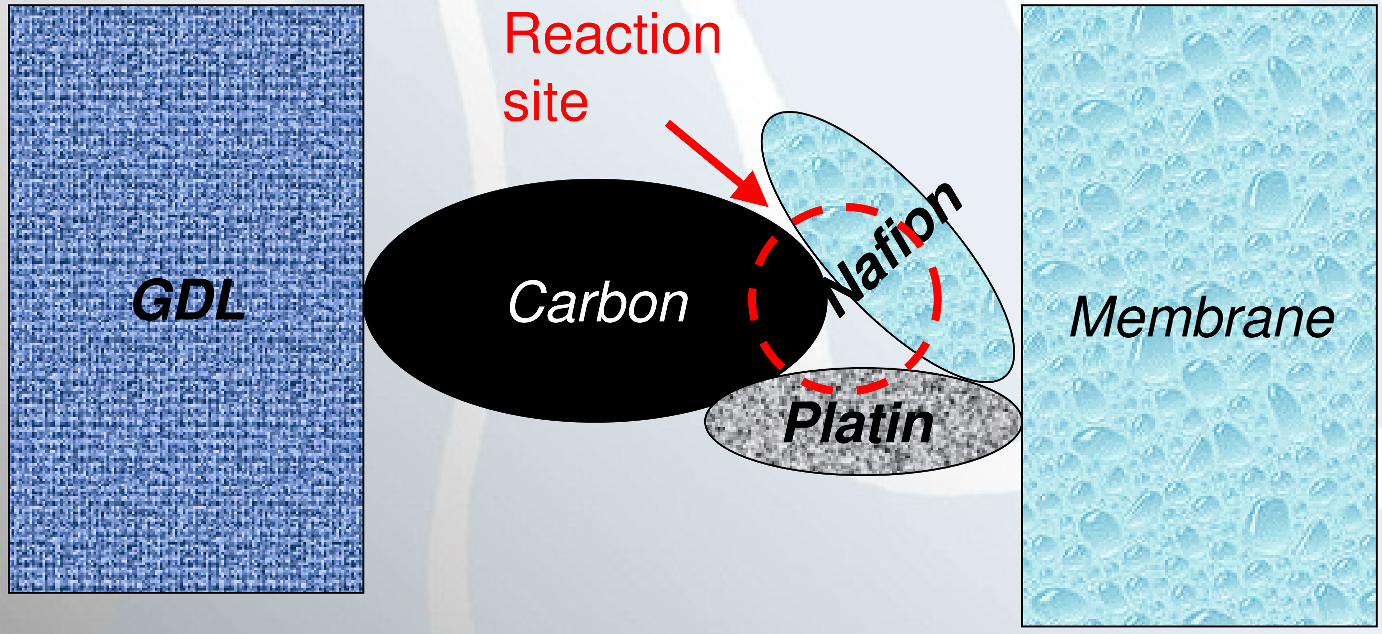
GDL
(Gas diffusion Layer)

Hydrophobic &
Electric conductive

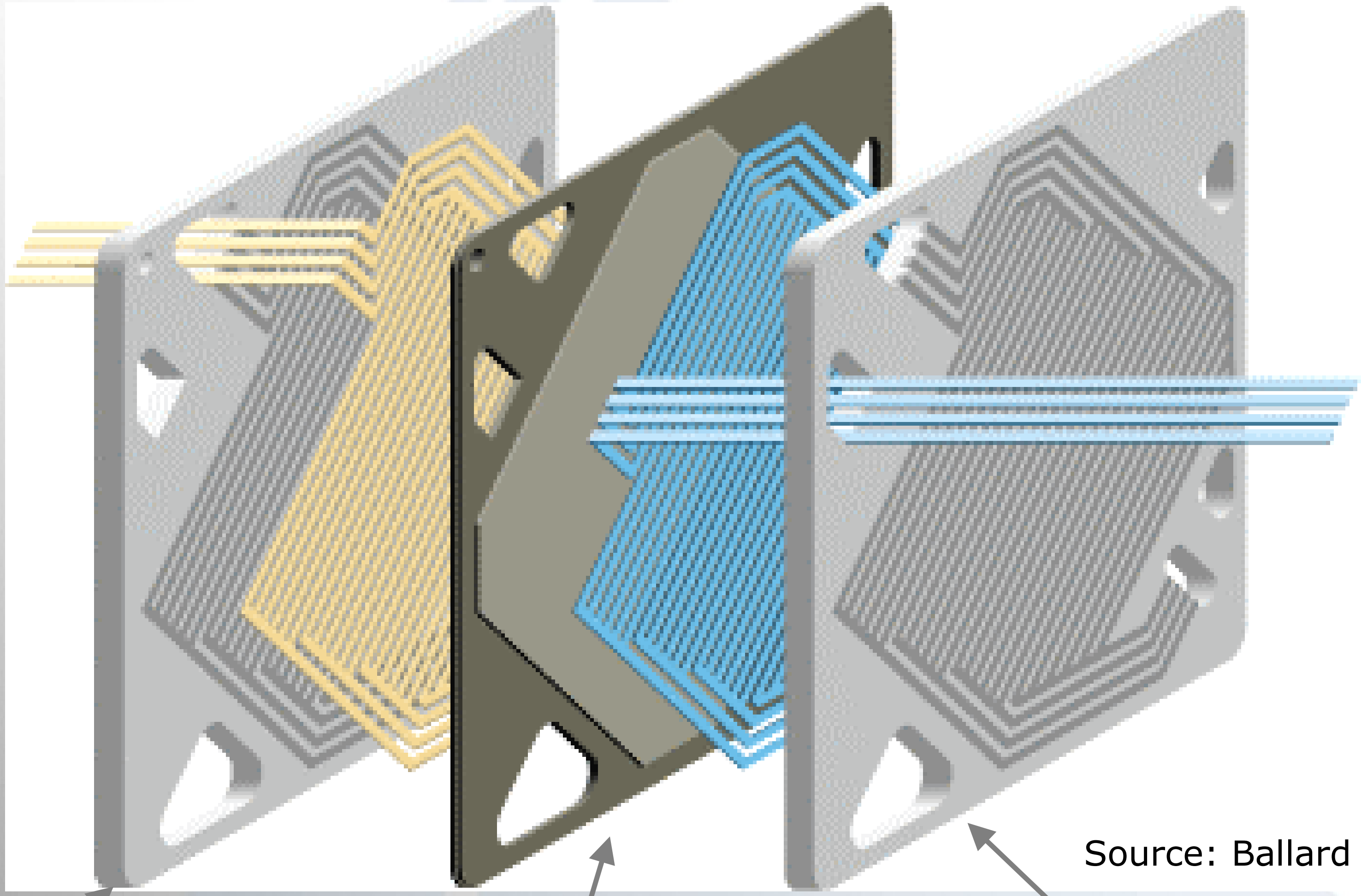
Protonic
conductive

The catalyst layer (the wholly trinity)

- Carbon (electrical conductivity)
- Nafion (protonic conductivity)
- Reaction catalytic material (e.g. Pt,Ru)



Fuel cell Schematics-Single Cell



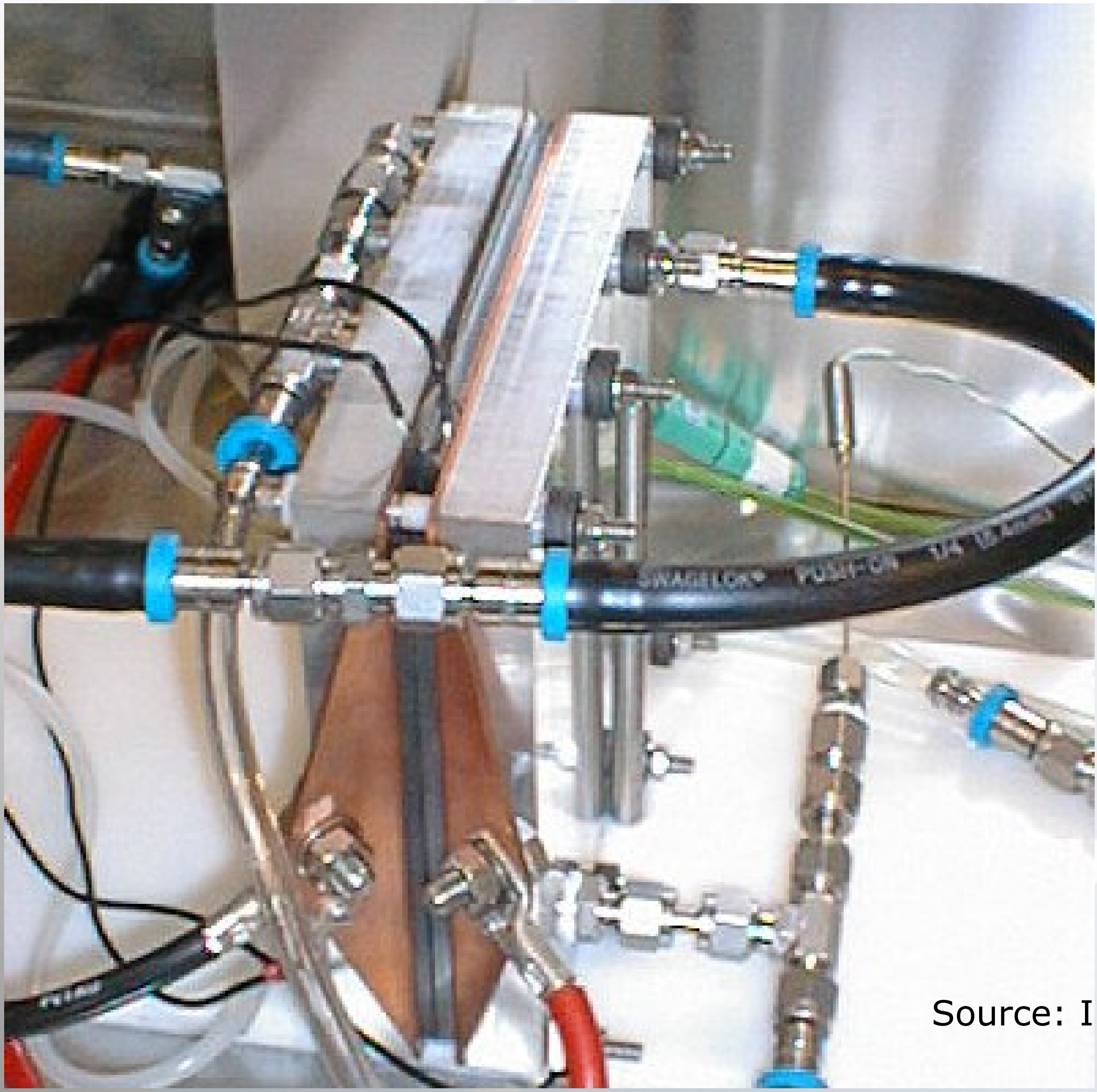
Source: Ballard

Bipolar plate

MEA

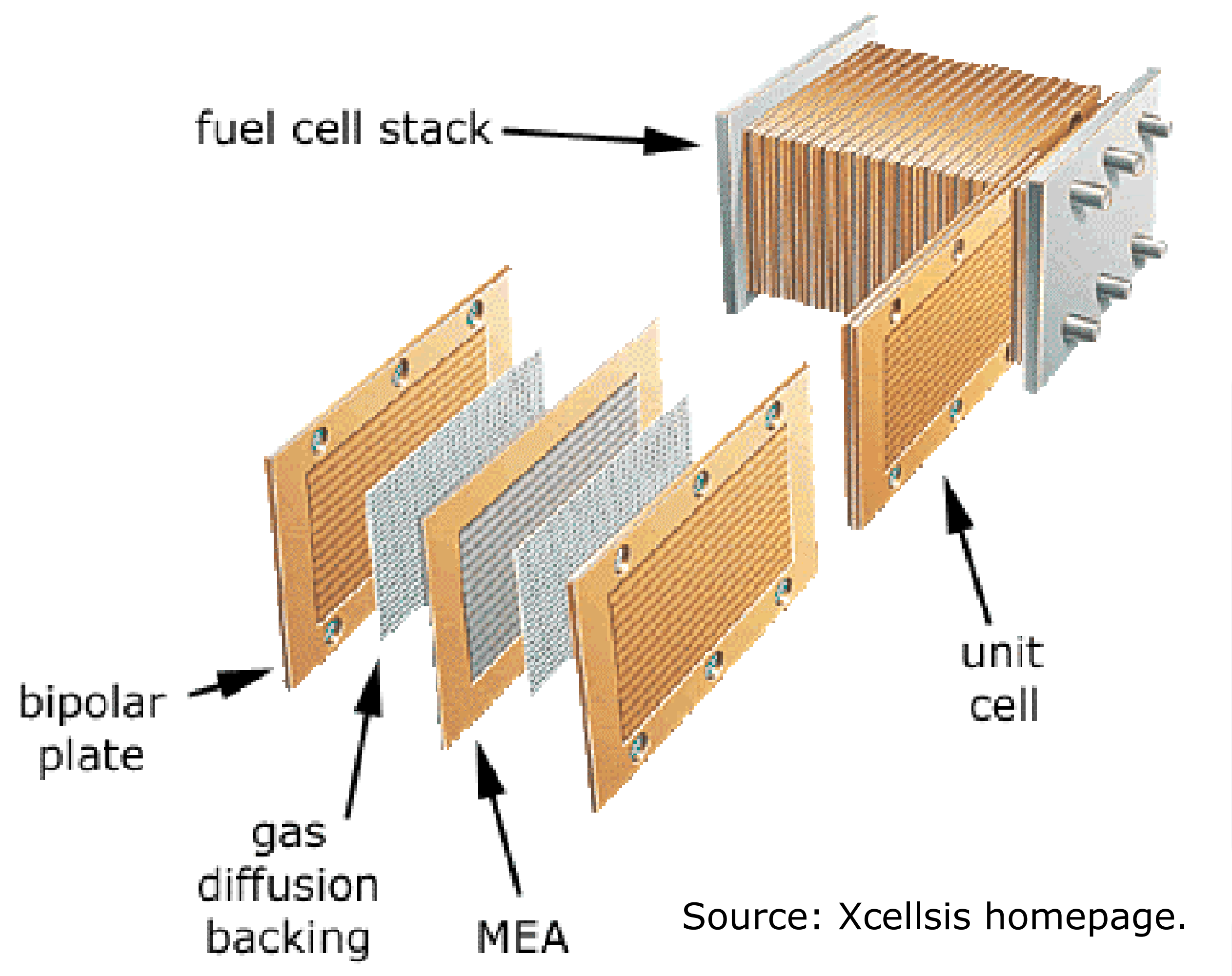
Bipolar plate

Real PEM fuel cells-single cells



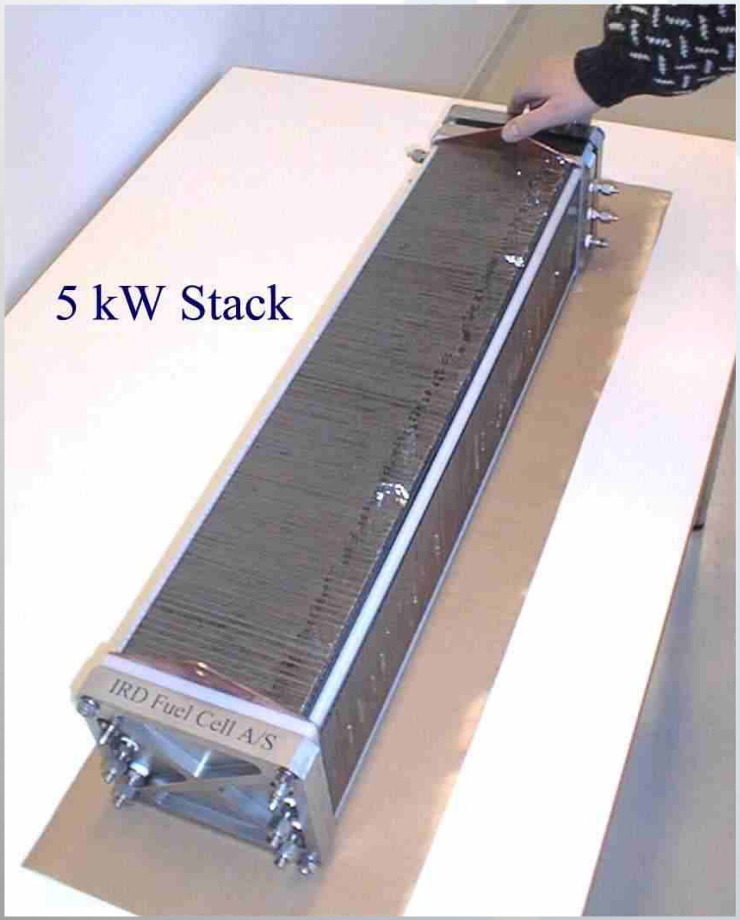
Source: IRD Fuel Cells

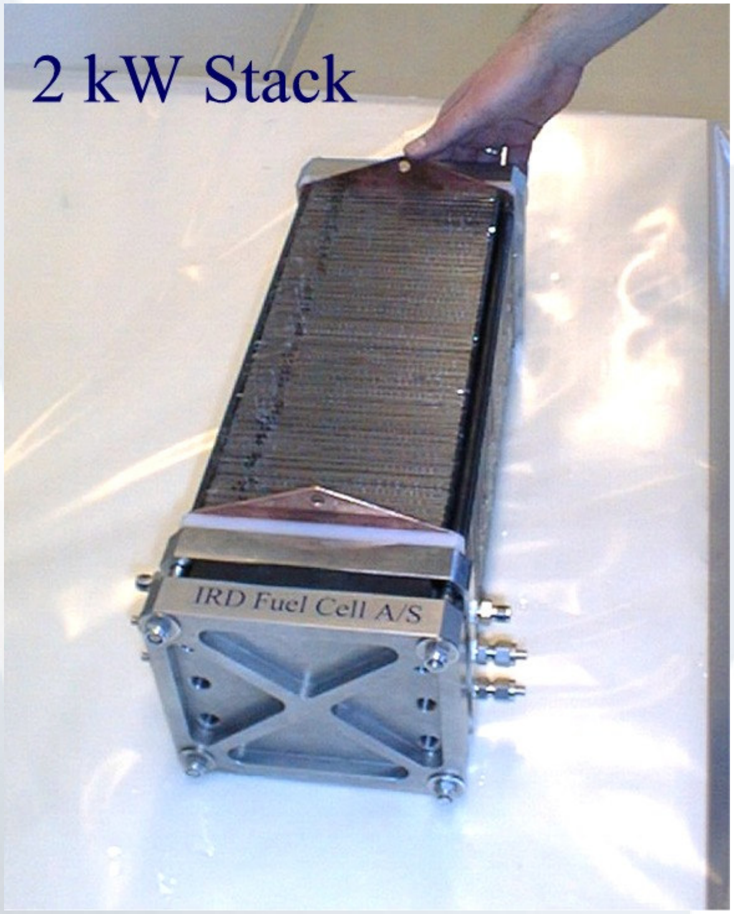
Fuel cell Schematics-Stacking

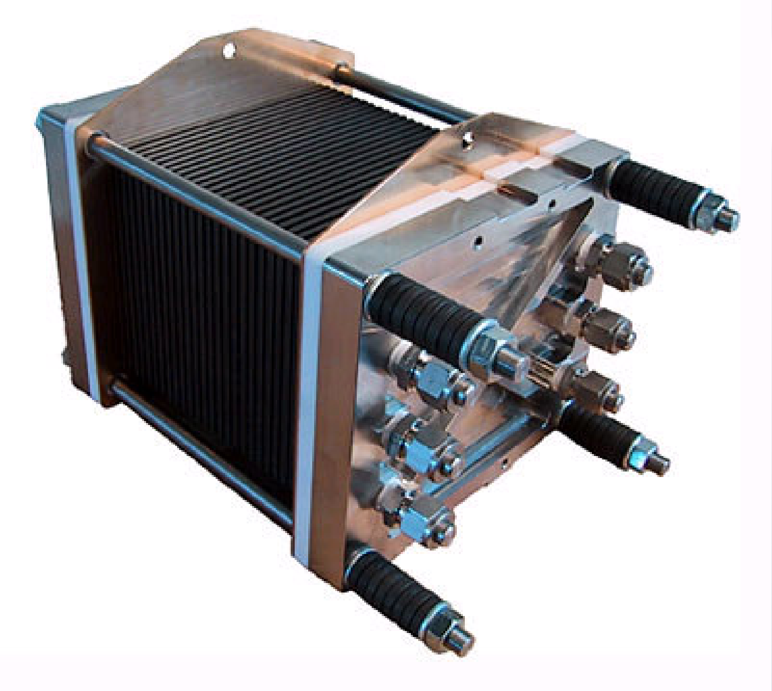


Source: Xcellsis homepage.

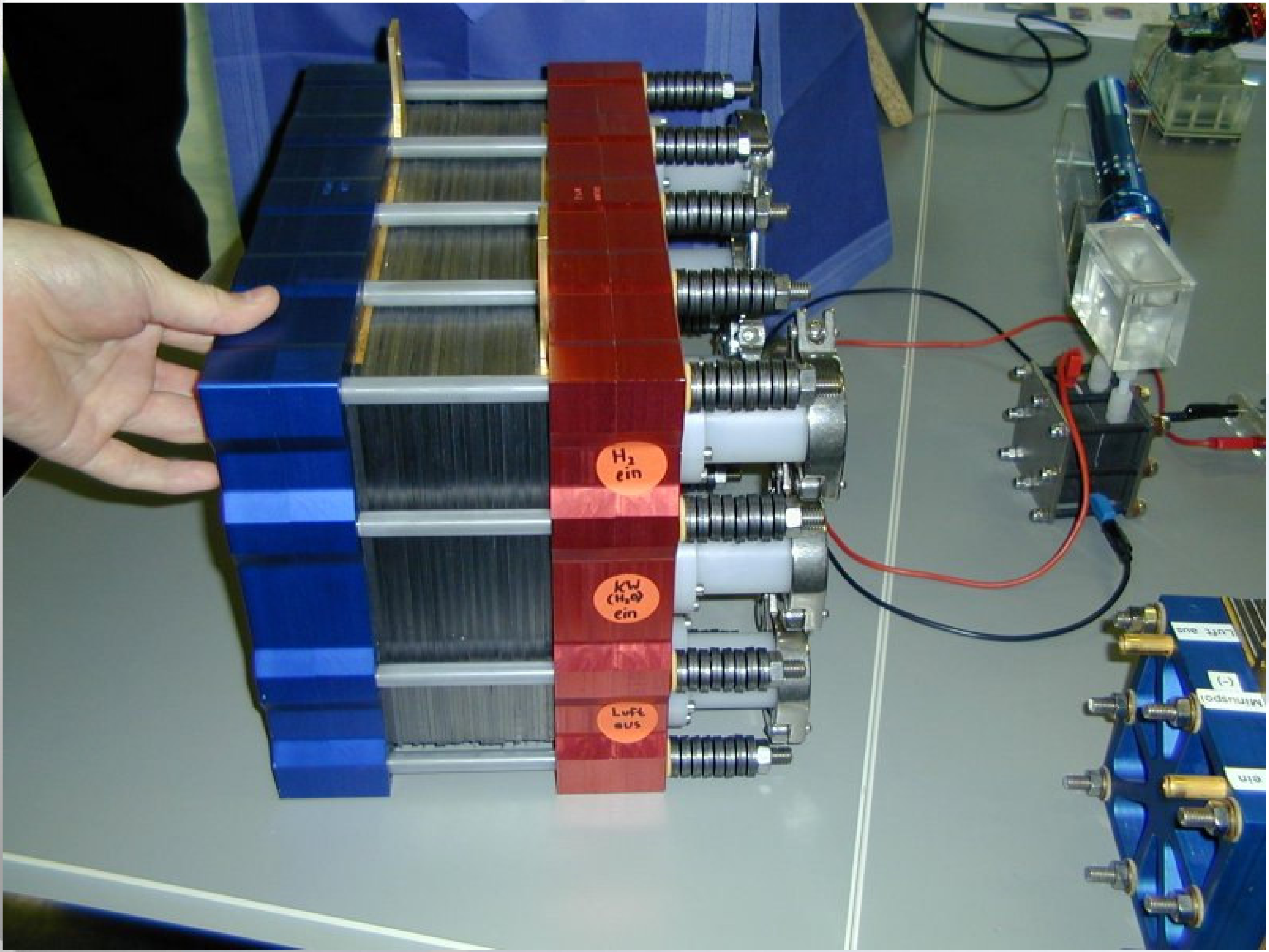
Real PEM fuel cells-stacks(size does matter)

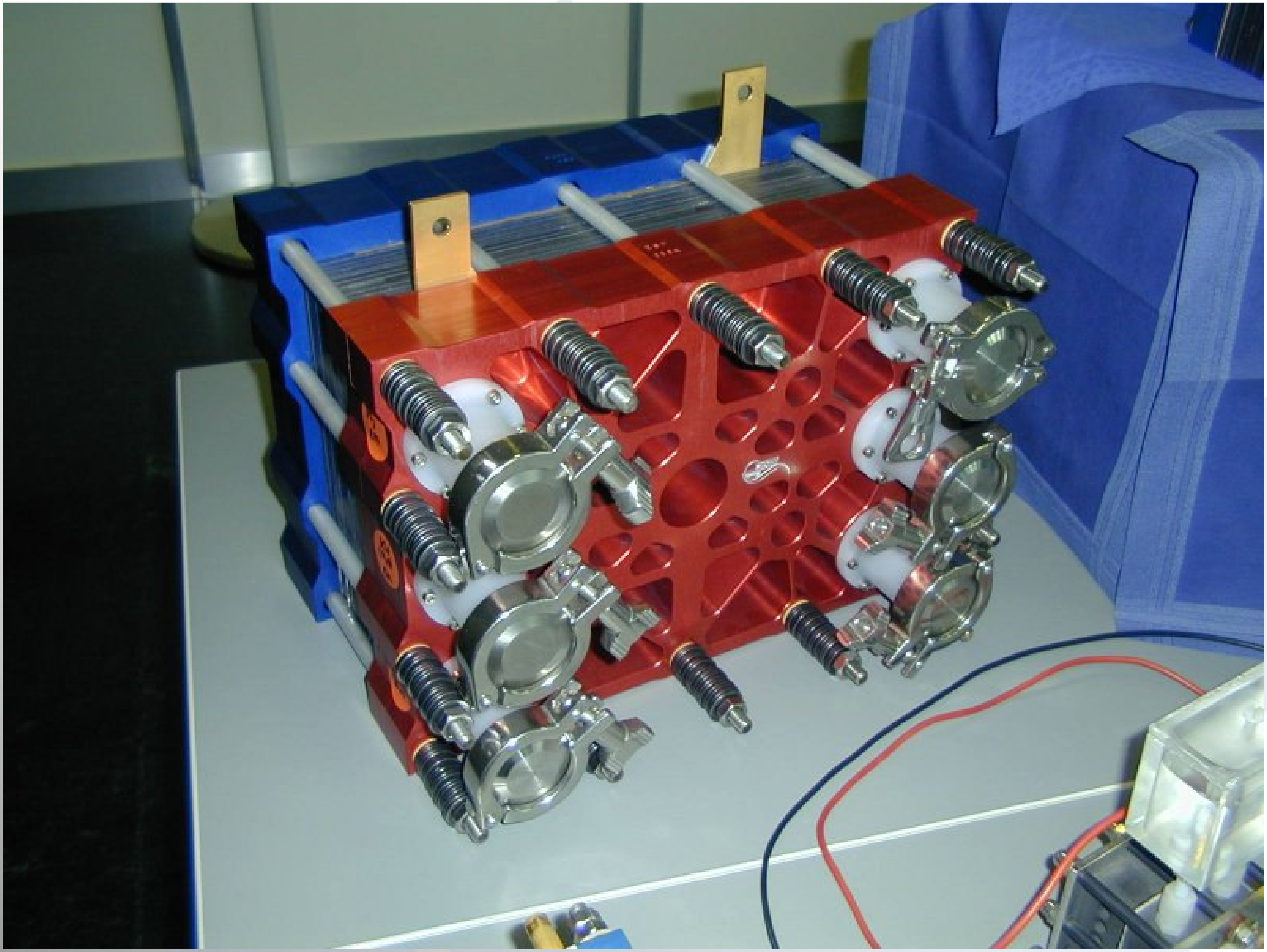






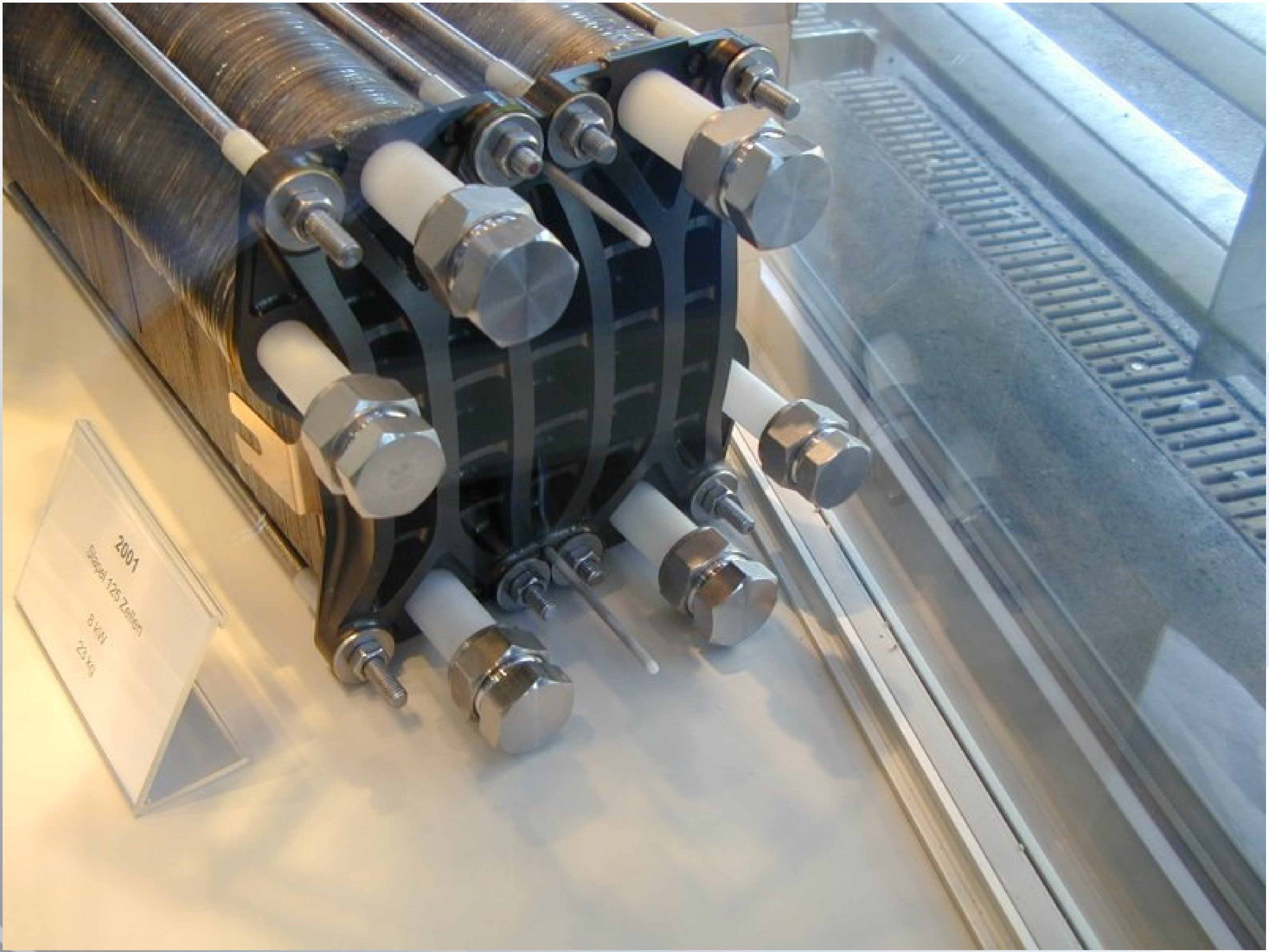

IRD Fuel Cells A/S
C+
Air
Water
H₂


H2 ein
KW (H2O) ein
Luft aus
Luft aus
(-)
Minuspol
ein




BALLARD
BALLARD


2001
Stapel 125 Zellen
8 kW
23 kg


2001
Stapel 125 Zellen
8 kW
20 kg

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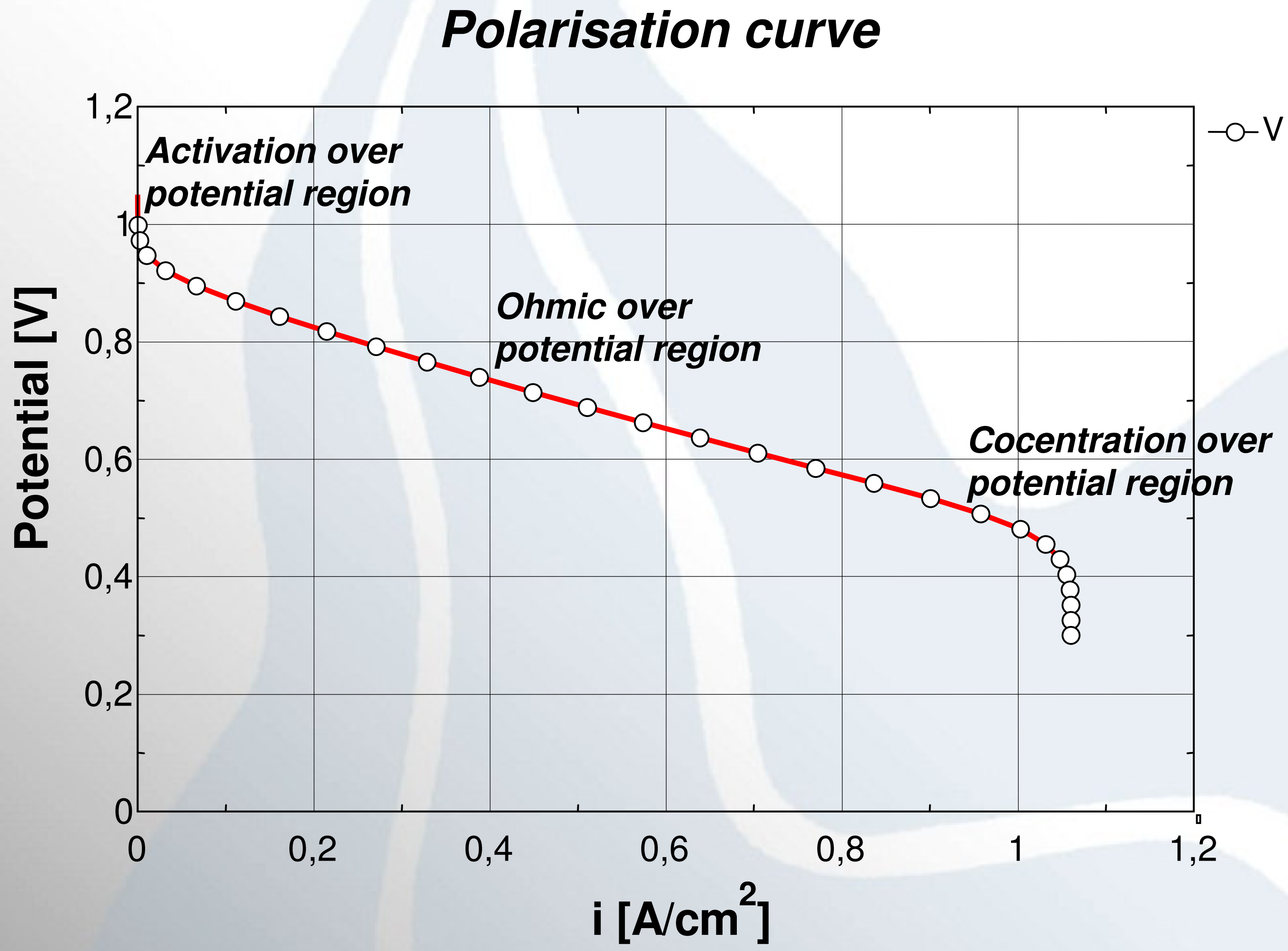
Operational characteristics of a FC -Tracing the losses

What happens when a fuel cell is applied a load?

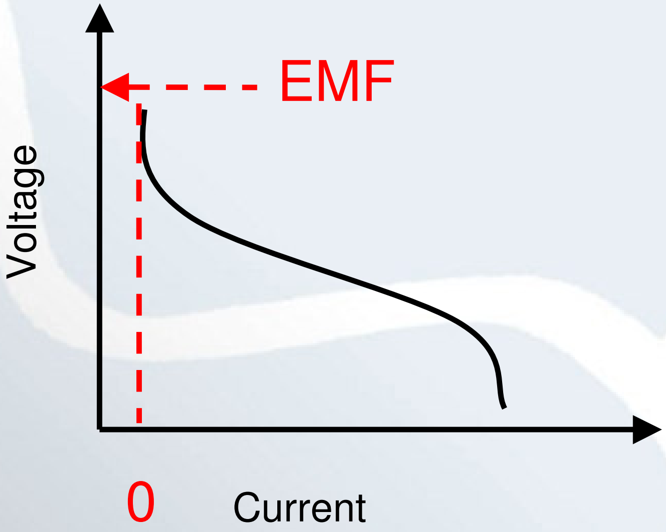


- Dependant mainly upon temperature, pressure and concentration of species.

The electrochemical potential

- The potential of the reaction, at zero reaction rate, gives the cells EMF (electromotive force)

$$EMF = \frac{\Delta g}{zF}$$

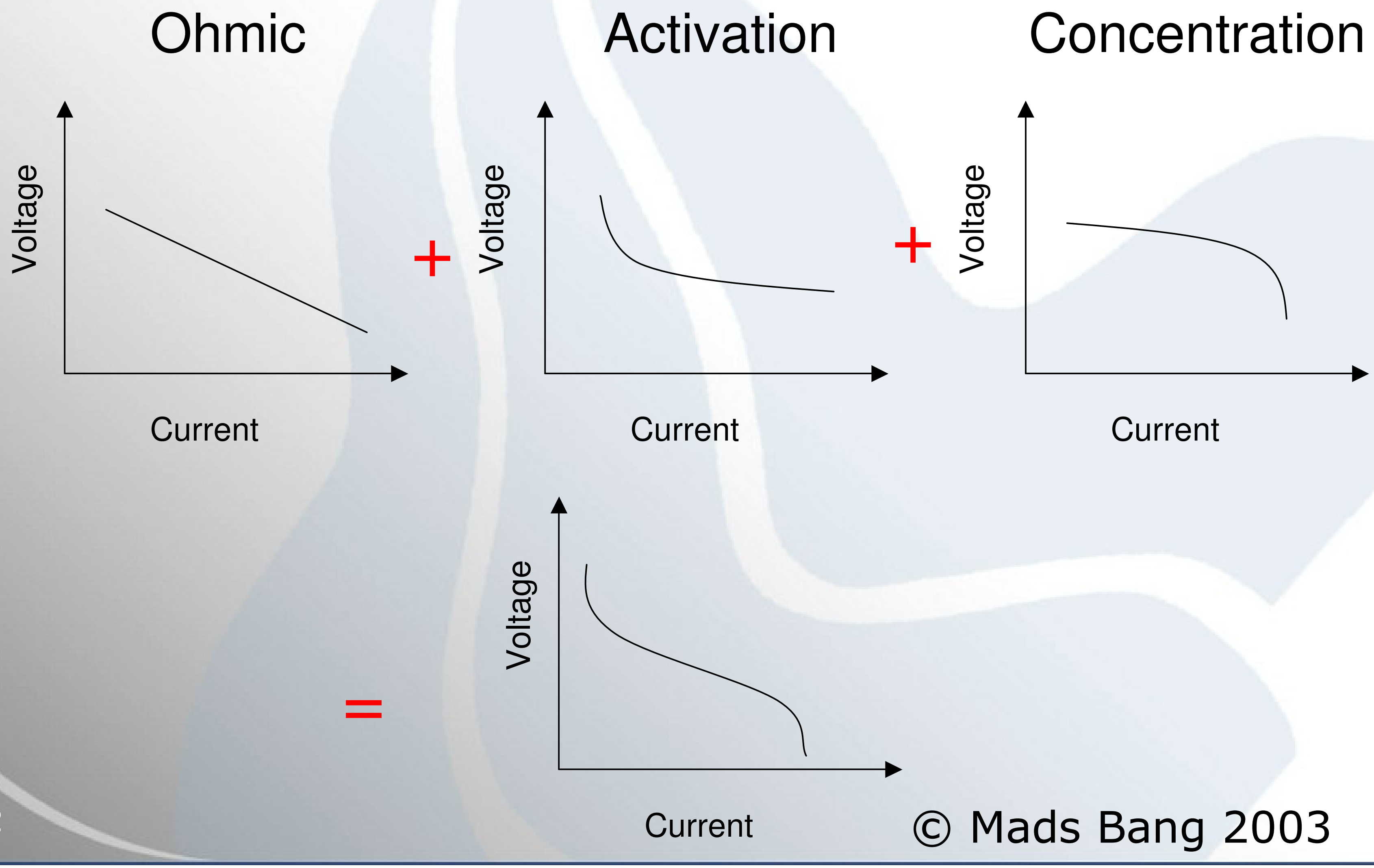


Operating potential

- The operating potential of the fuel cell is the EMF minus the various potential losses.

$$V = EMF - \eta_{conc} - \eta_{ohmic} - \eta_{act}$$

Operating potential-Superposition



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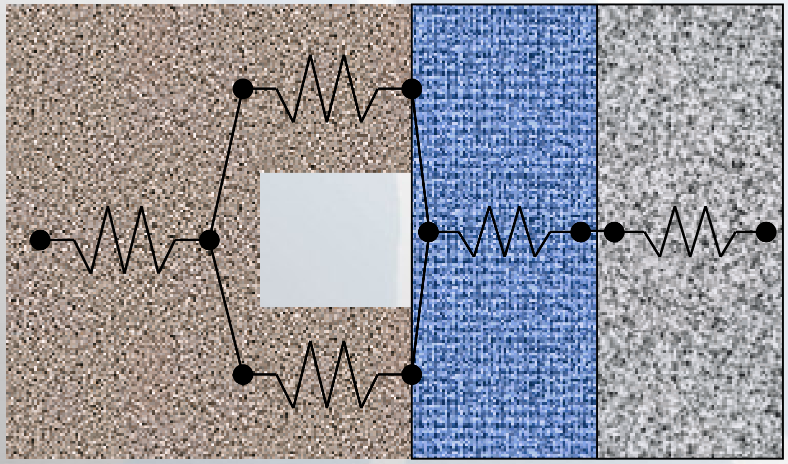
Potential losses-Ohmic

- The ohmic loses is the summation of all linear loses
  - Membrane conductivity (protonic)
    - Humidification level & temperature dependent
  - Diffusion layer conductivity
  - Bipolar plate conductivity
  - Etc.

$$\eta_{ohm} = \sum R \cdot I$$

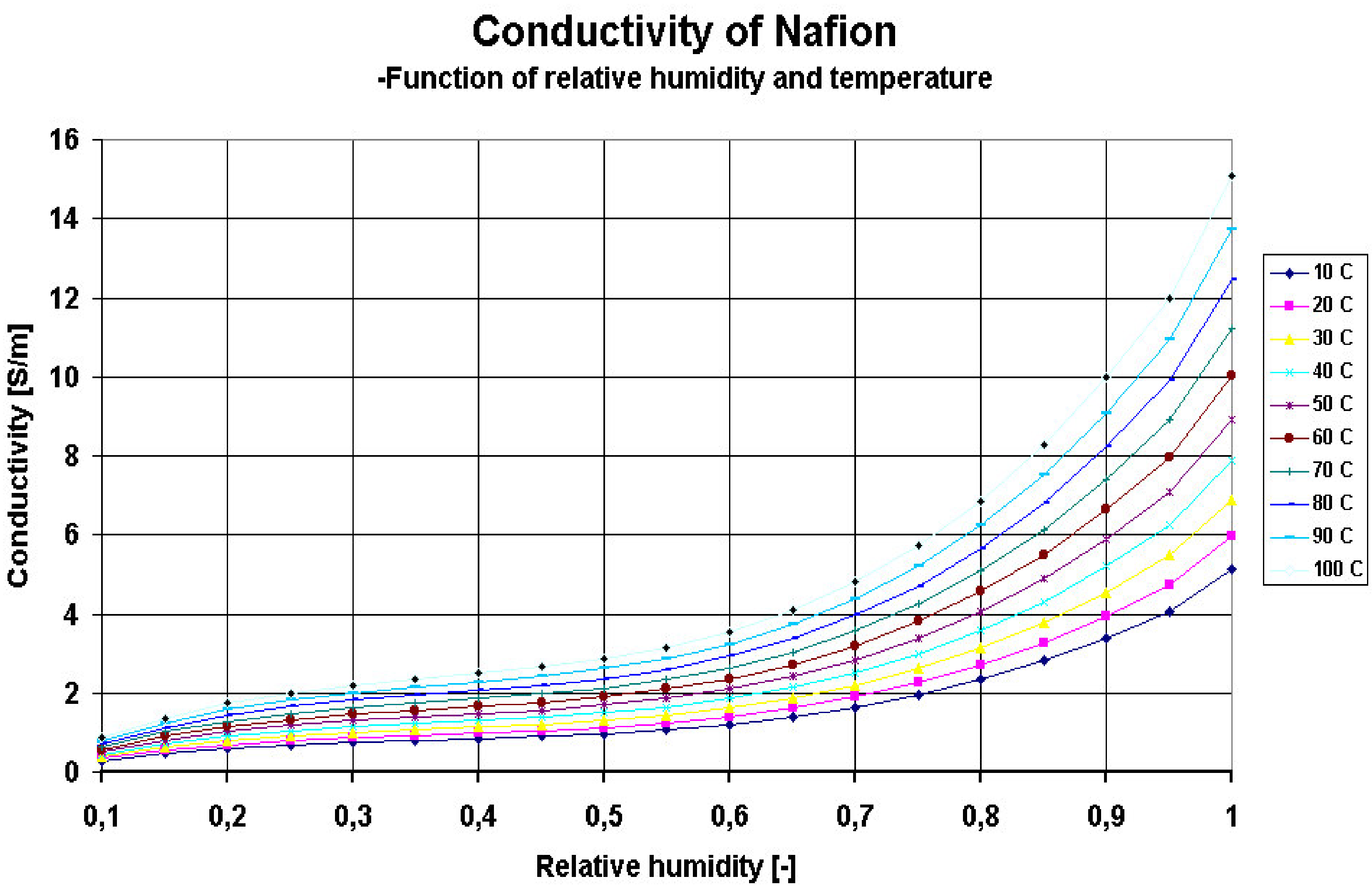
Potential losses-Ohmic -3

- Illustration of origination of potential ohmic loses



NB: Measurements indicates that many of the major ohmic losses are caused by contact resistance between the different layers

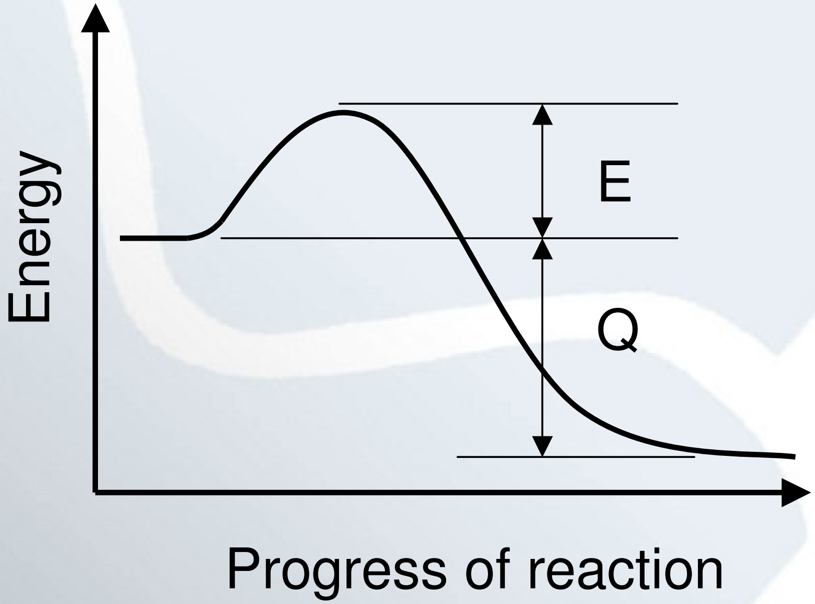
Potential losses -Ohmic -2



Potential losses activation

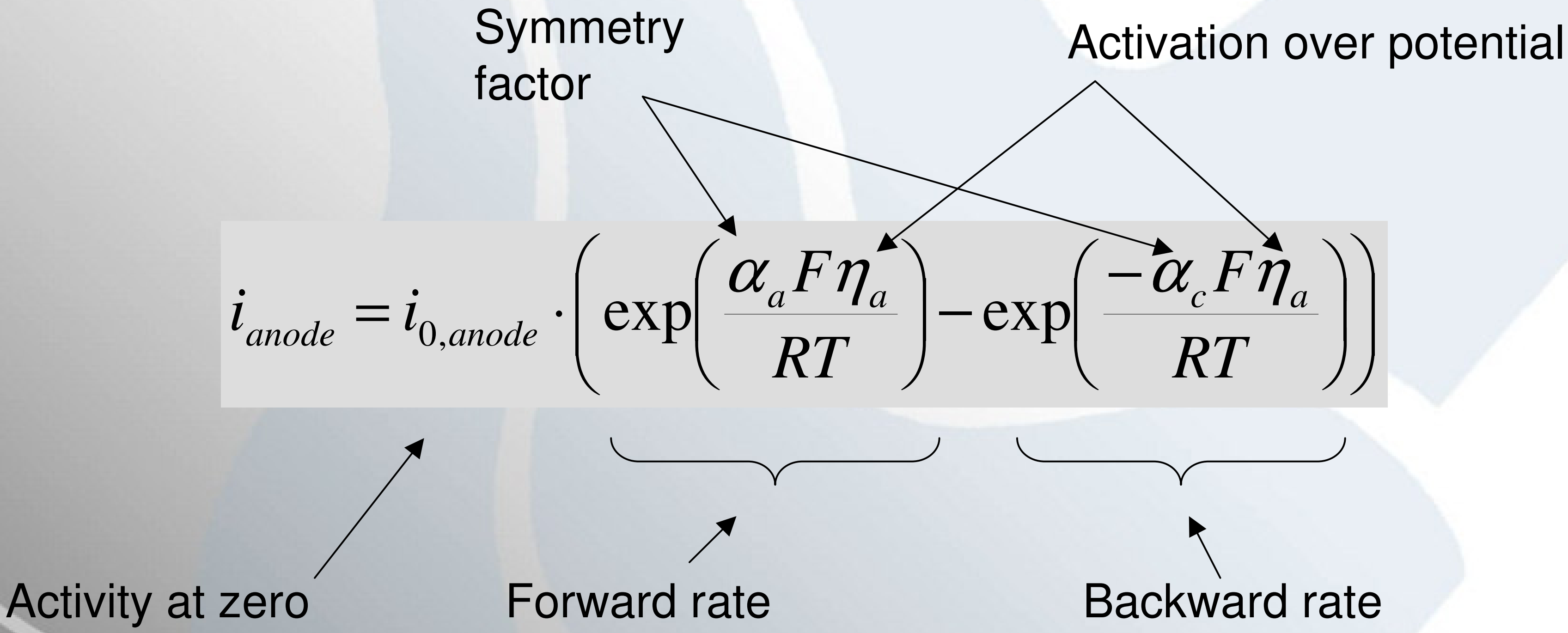
- The reaction rate of the electrochemical reaction can be modelled via a Arhenius type equation:

$$\frac{dn}{dt} = Ae^{-E/RT}$$



Potential losses-Activation

- The electrochemical reaction rate can be modelled via the Butler-Volmer equation.



Symmetry factor

Activation over potential

$$i_{anode} = i_{0,anode} \cdot \left(\underbrace{\exp\left(\frac{\alpha_a F \eta_a}{RT}\right)}_{\text{Forward rate}} - \underbrace{\exp\left(\frac{-\alpha_c F \eta_a}{RT}\right)}_{\text{Backward rate}} \right)$$

Activity at zero current

Forward rate

Backward rate

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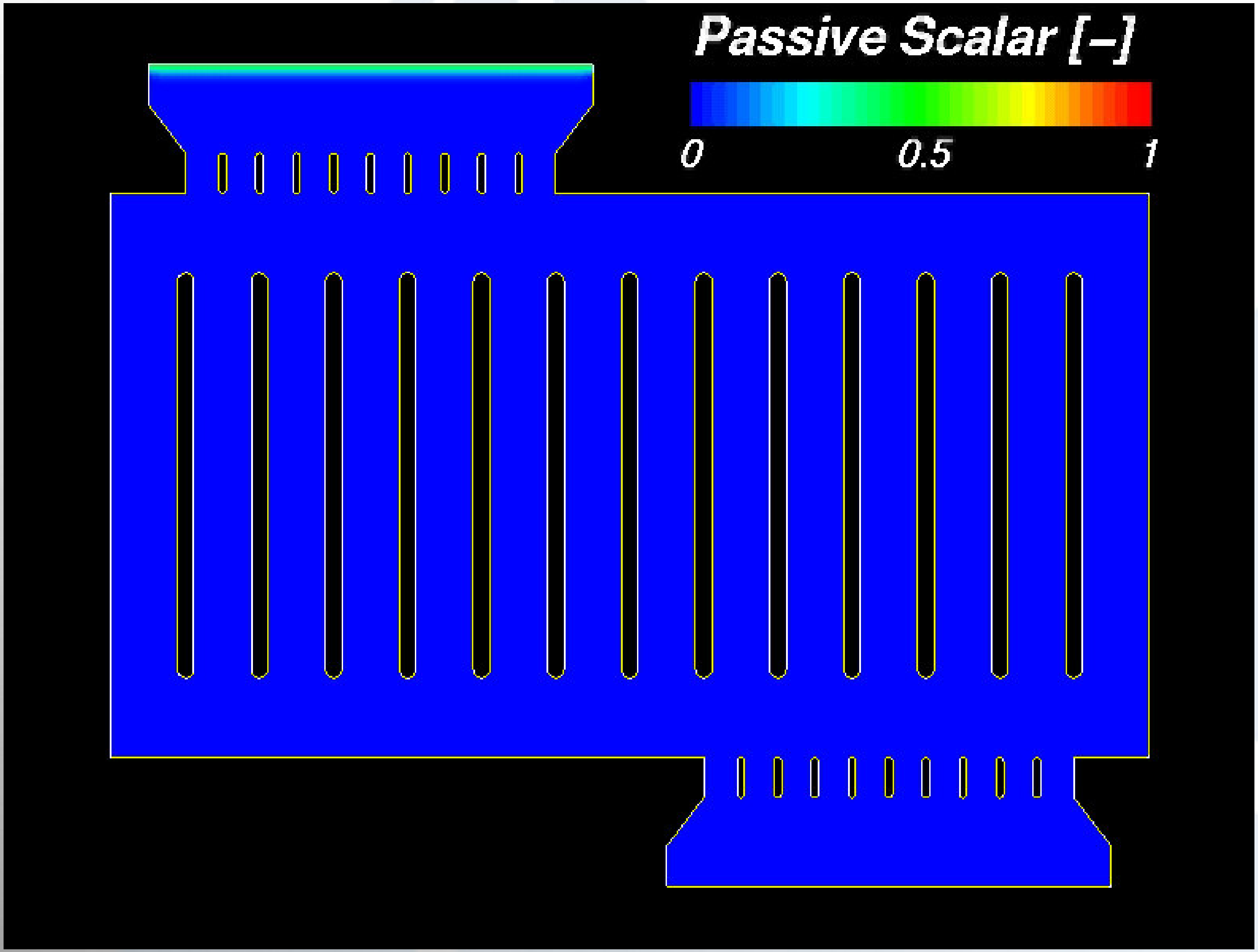
Potential losses-Concentration

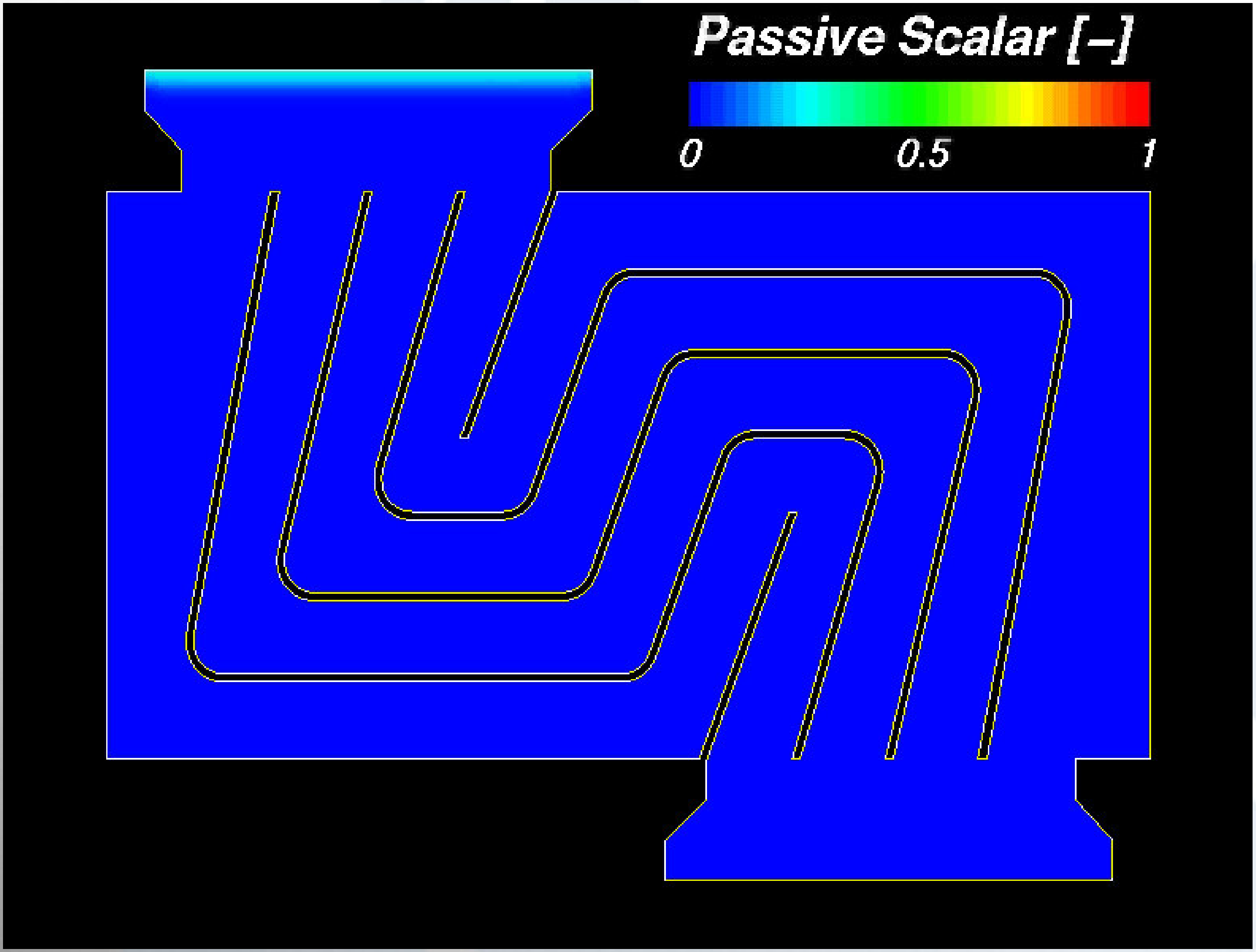
- The concentration over potential is governed by the concentration of reactants in the catalyst layer.

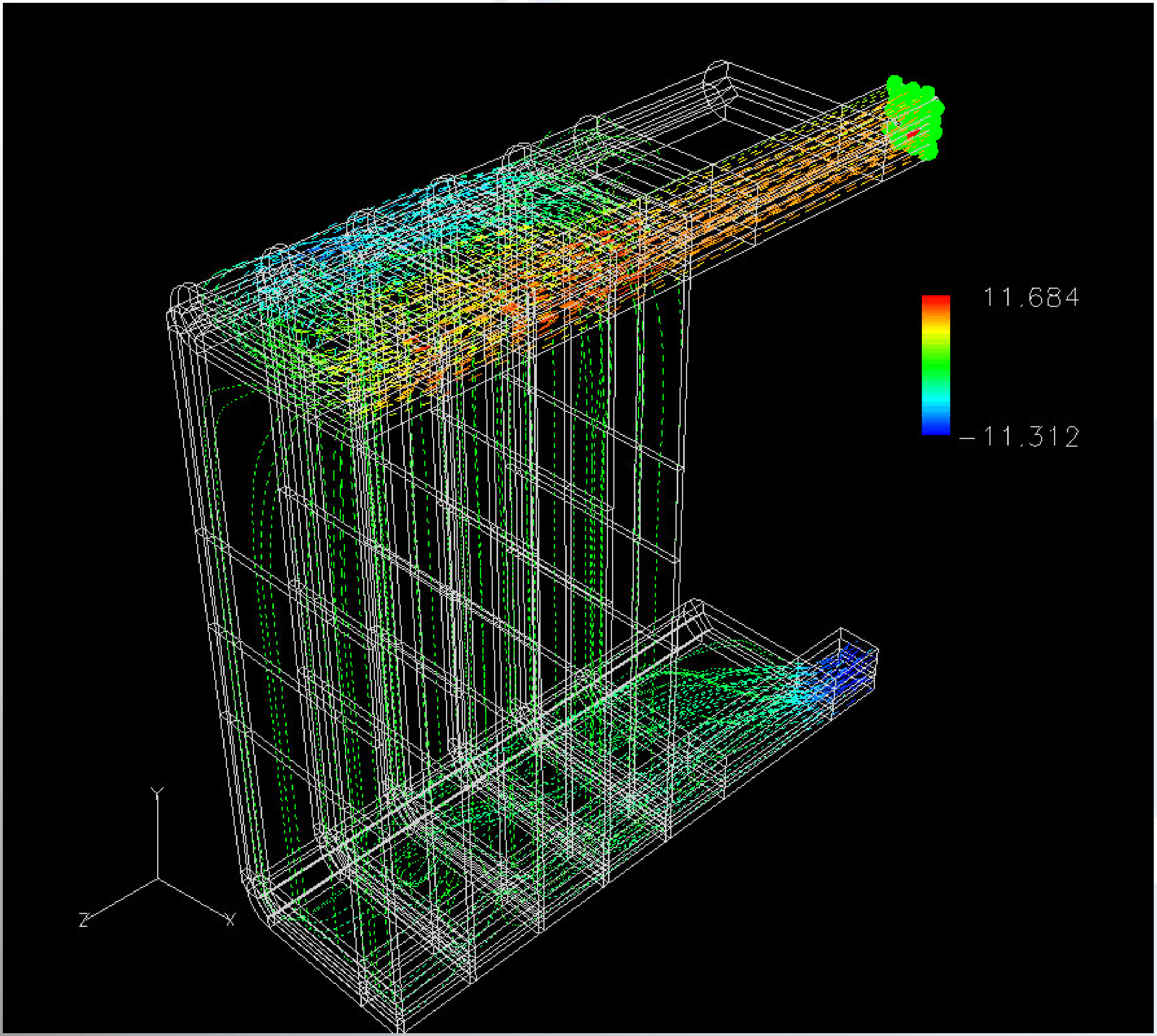
$$\eta_{conc} = \frac{RT}{2F} \cdot \ln\left(\frac{p_{H_2} \cdot p_{O_2}^{1/2}}{p_{H_2O}} \right)$$

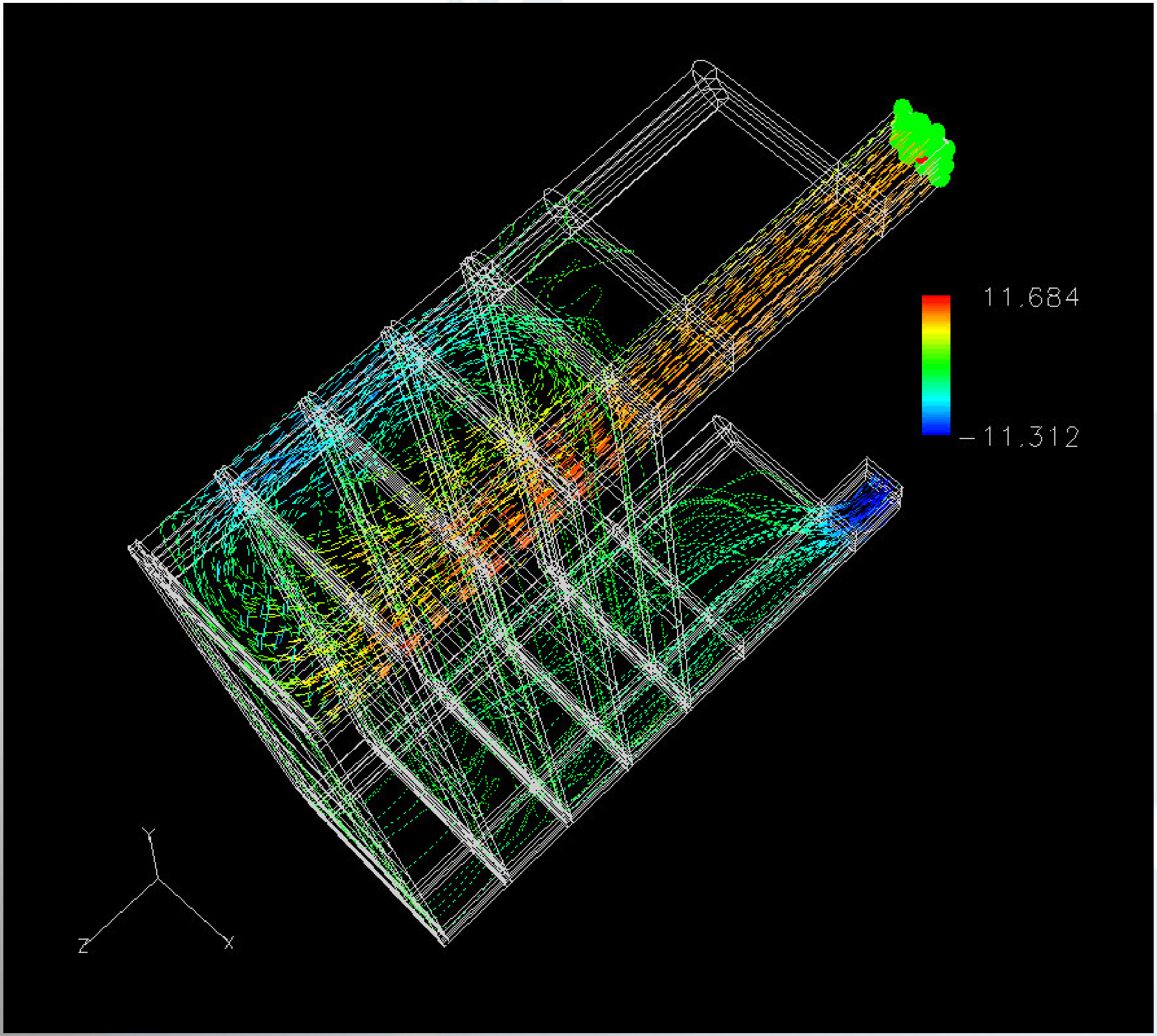
NB: The concentration over potential is ***negative*** if the concentration of reactants are less than unity and ***positive*** if the concentration is above unity e.g. a pressurised cell

Modelling the processes –Improving understanding and performance

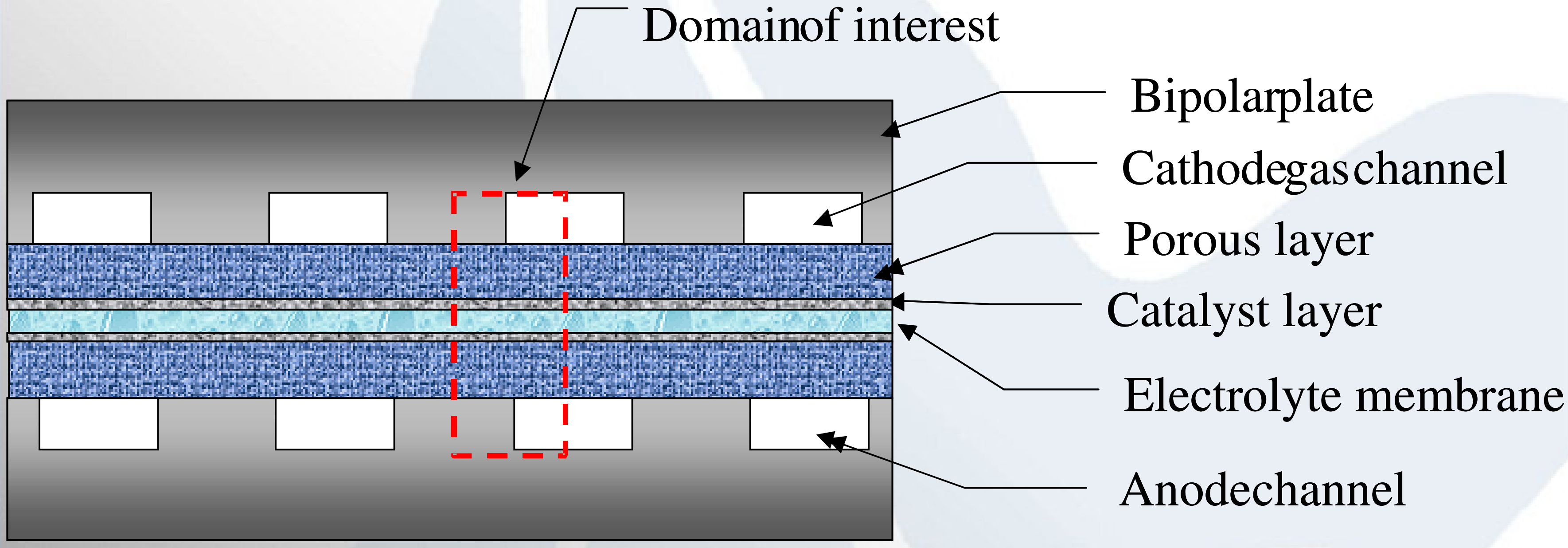

Passive Scalar [-]
0
0.5
1


Passive Scalar [-]
0
0.5
1


11.684
-11.312
Y
Z
X


11.684
-11.312
Y
Z
X

Fuel cell Topology



Domainof interest

Bipolarplate

Cathodegaschannel

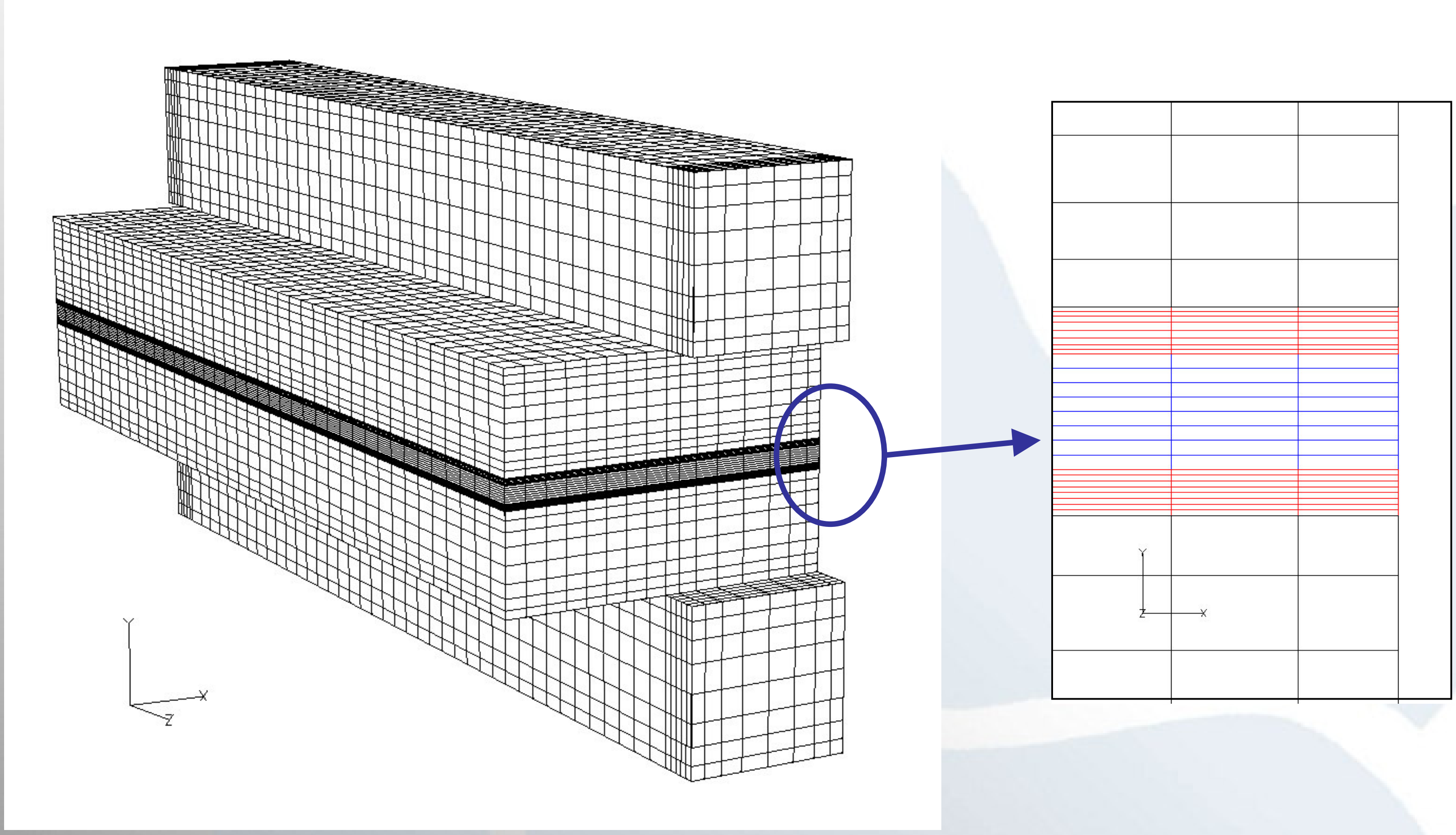
Porous layer

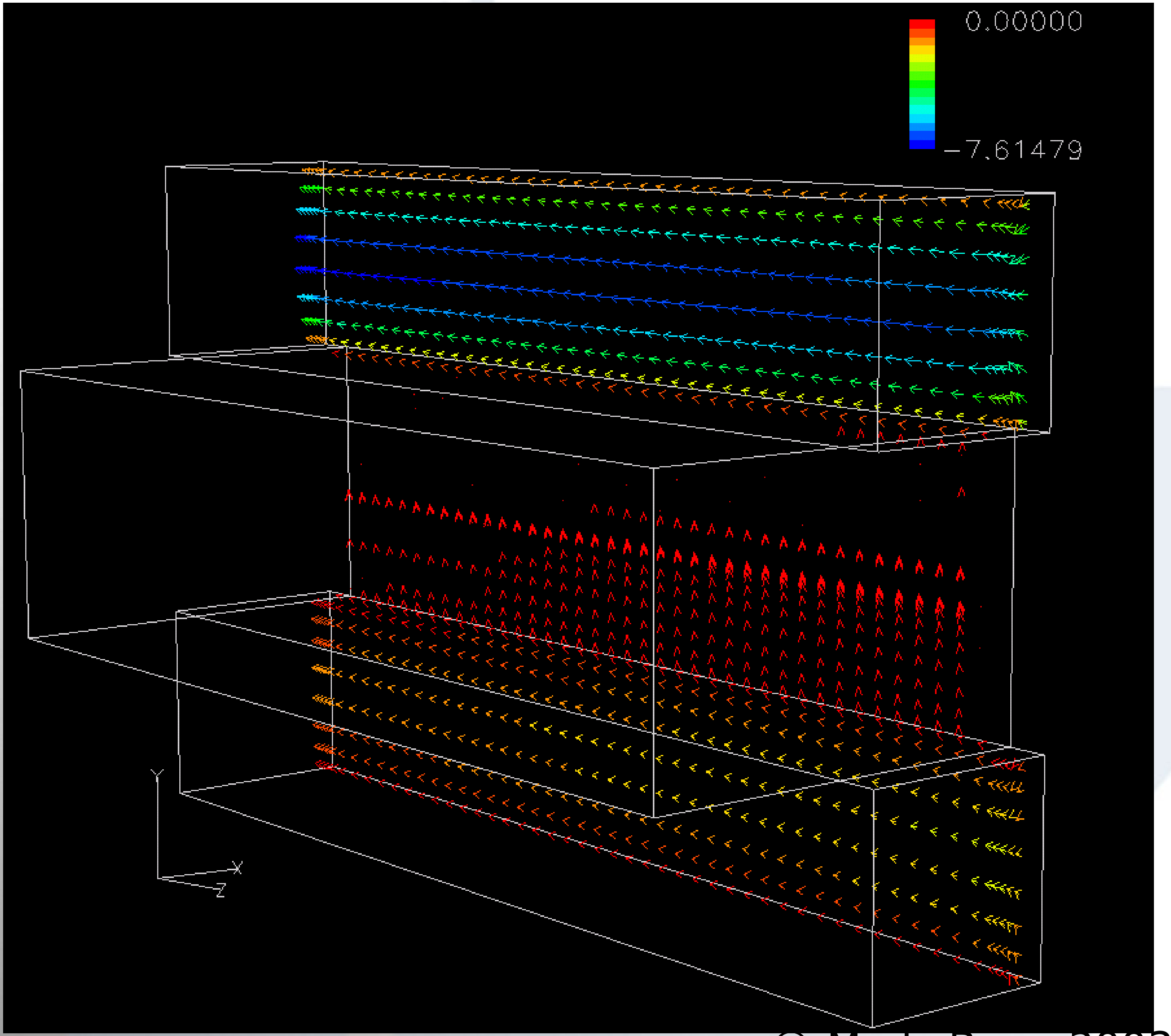
Catalyst layer

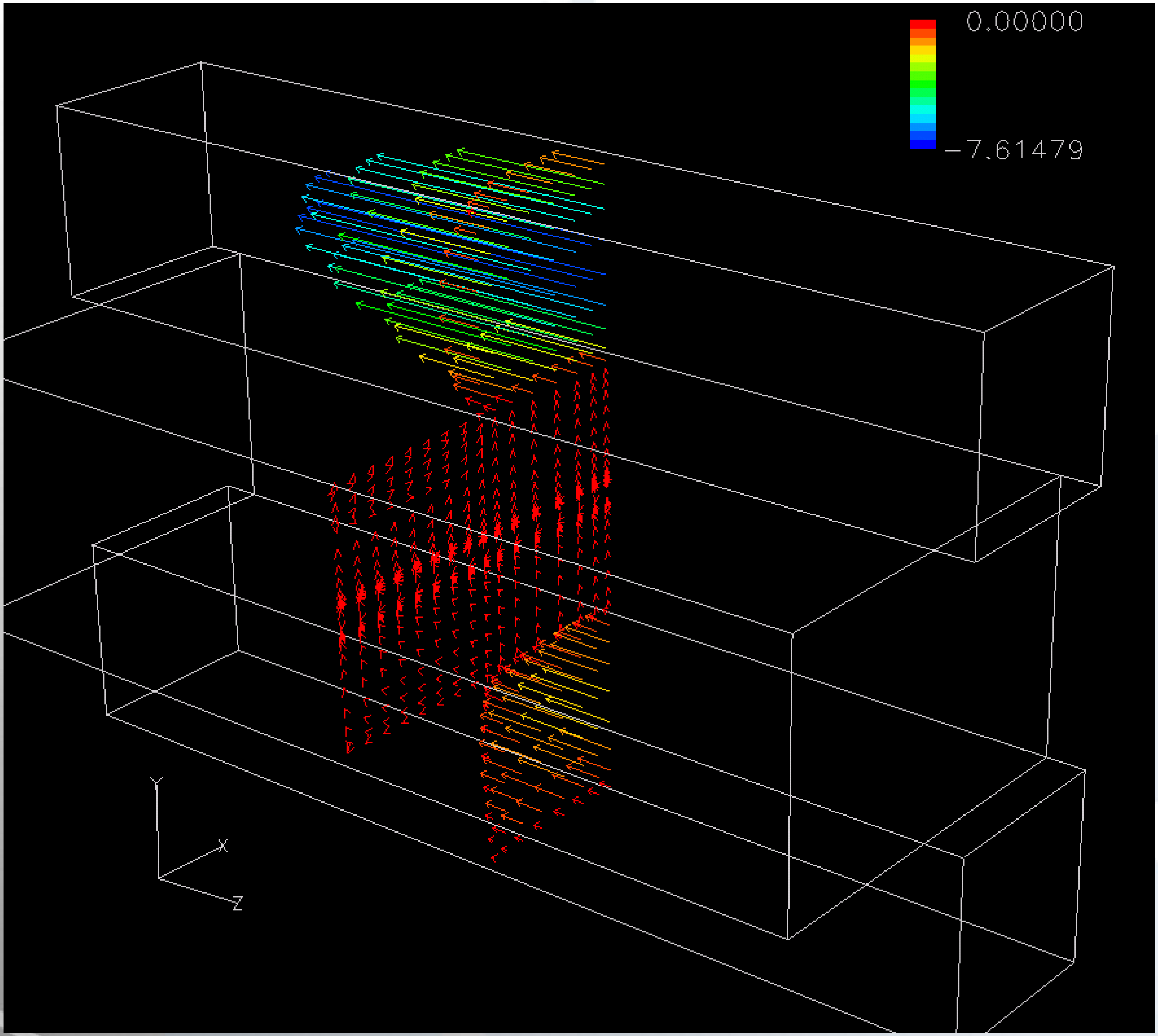
Electrolyte membrane

Anodechannel

Computational Domain

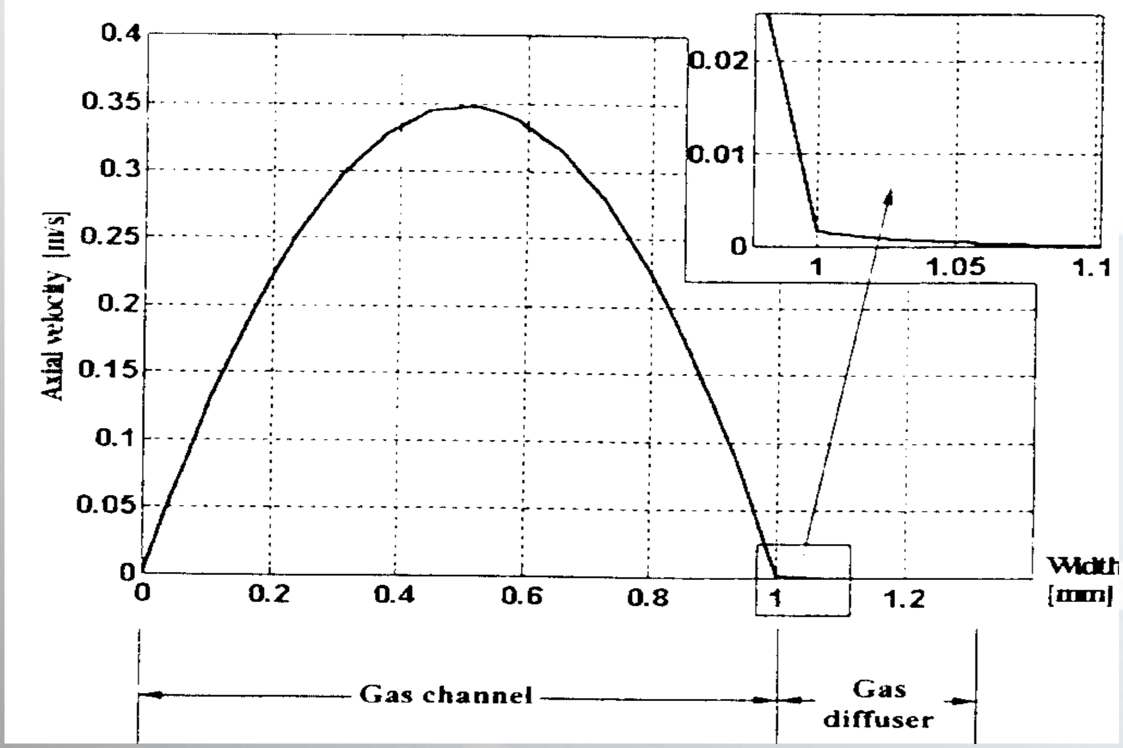



0.00000
-7.61479
Y
X
Z


0.00000
-7.61479
Y
X
Z

Transport of species in the channels

- The flow regime is normally LAMINAR (Re < 2300) which means that diffusion plays an important role.



Gurau et al. 1998

Maximum reaction rate

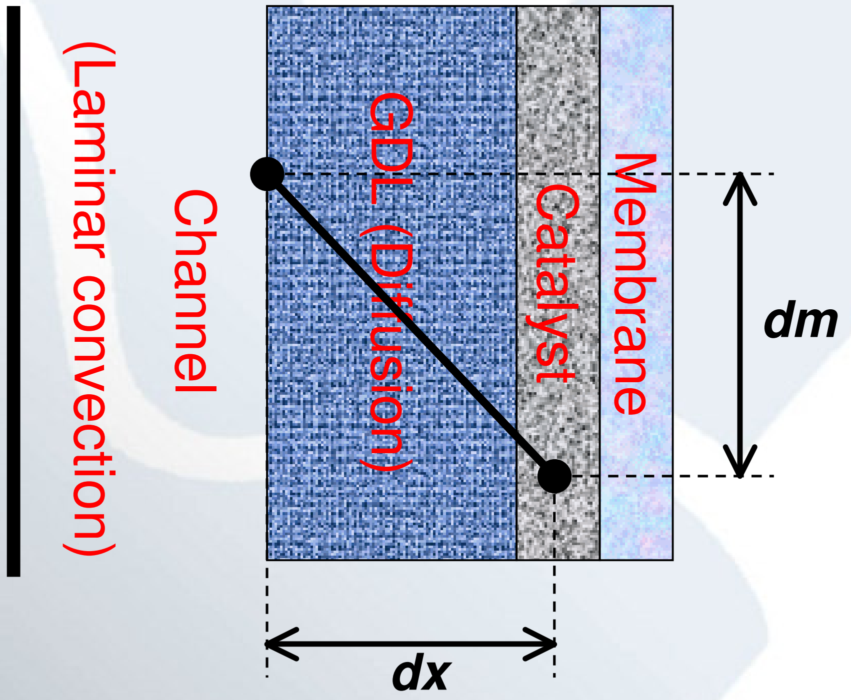
- At maximum current density, the reaction rate is diffusion controlled

Diffusion rate:

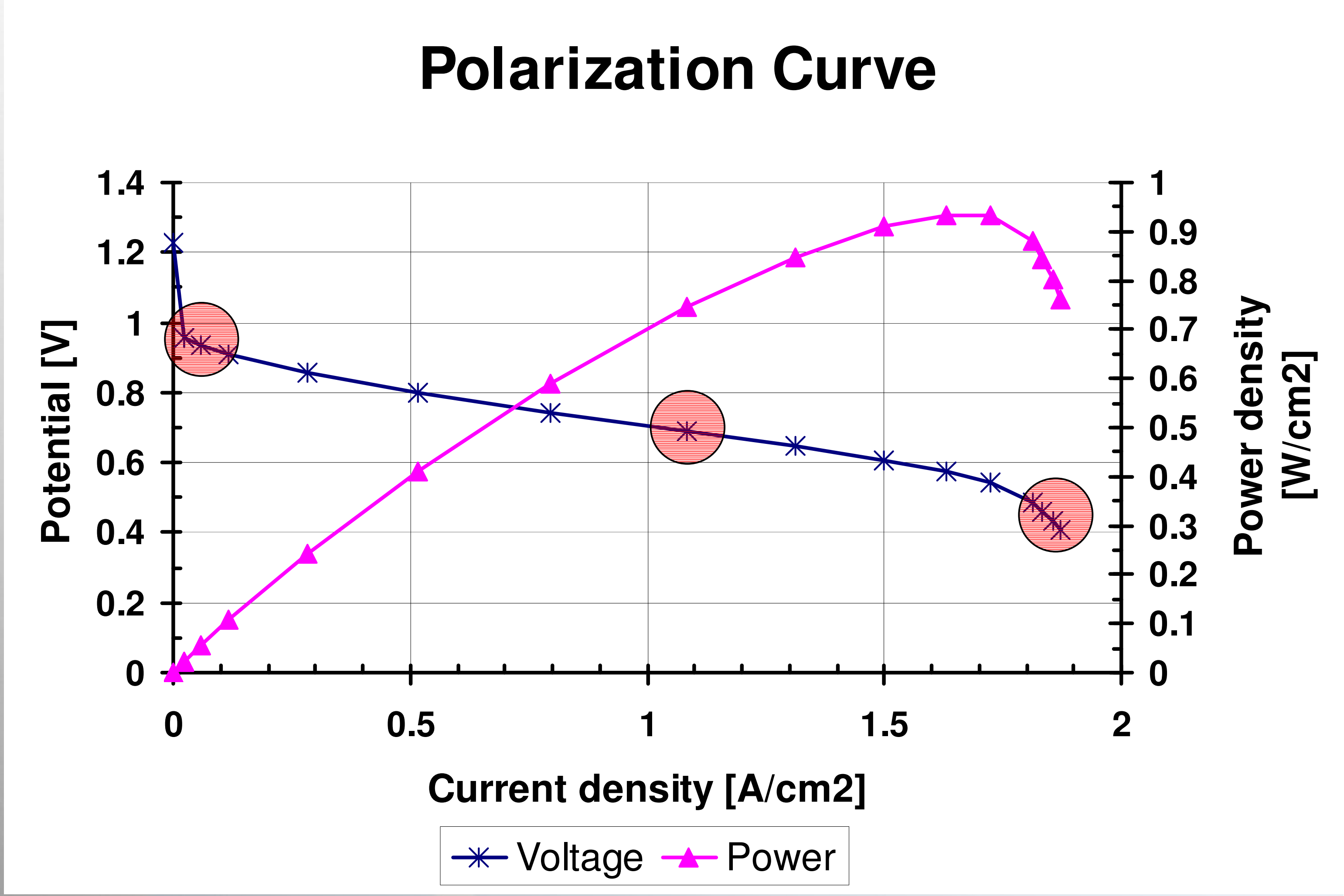
$$\boxed{\frac{\partial m}{\partial t} = A \cdot \rho \cdot D_{eff} \cdot \frac{\partial m}{dx}}$$

Reaction rate:

$$\boxed{\frac{\partial m}{\partial t} = M \frac{1}{Z} \frac{i_{face} \cdot A_{face}}{F}}$$



Cases selection

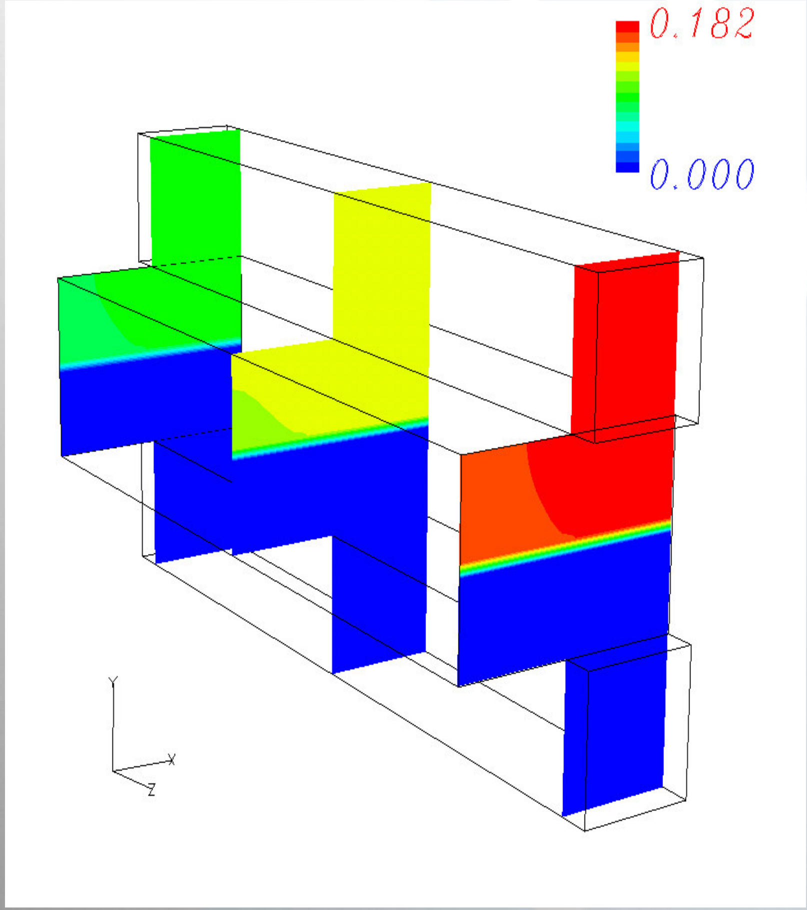


Cases

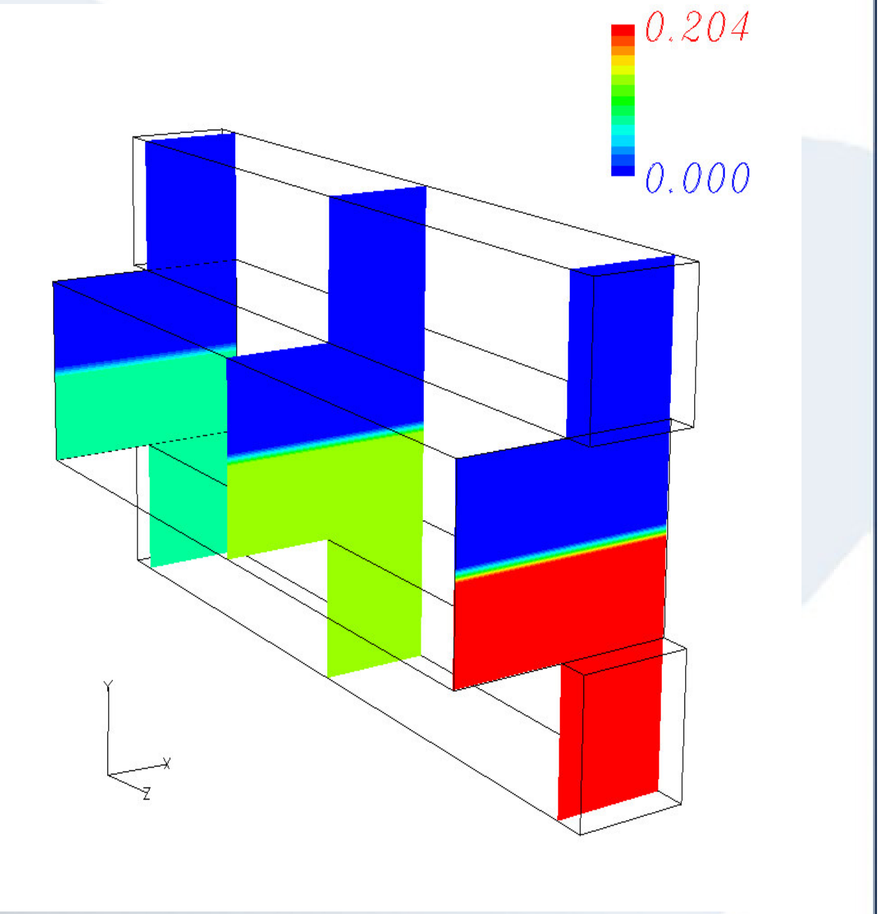
1. **low load**	**0.12 A/cm2 and 0.91V**
2. **Medium Load**	**1.1 A/cm2 and 0.69V**
3. **High load**	**1.9 A/cm2 and 0.41V**

Concentrations low load

Oxygen mass fractions

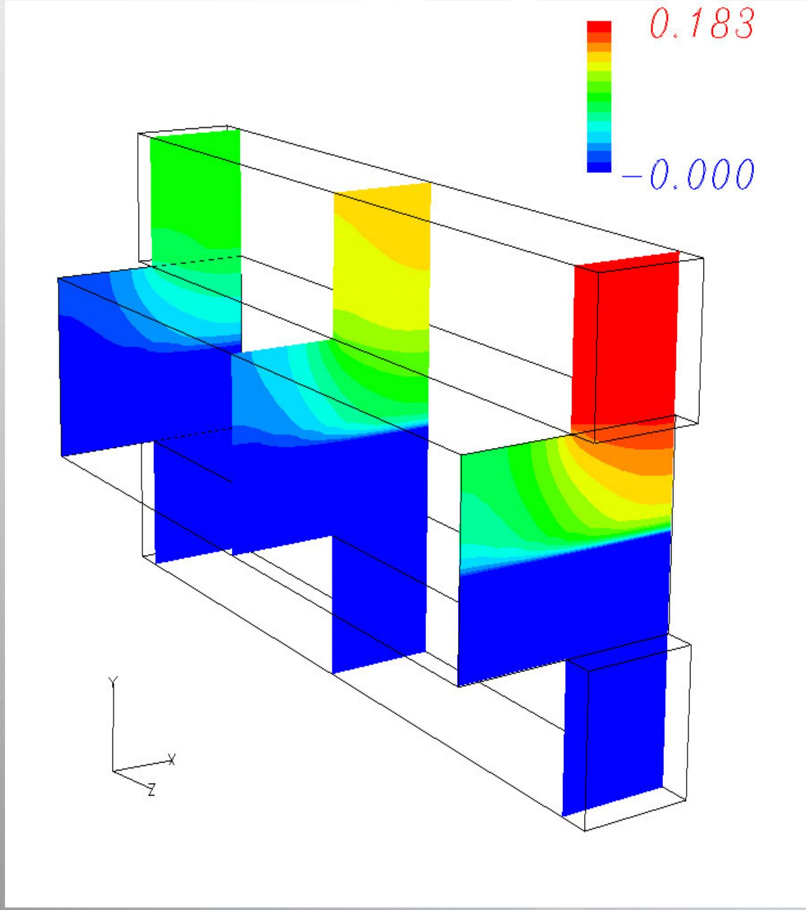


Hydrogen mass fractions

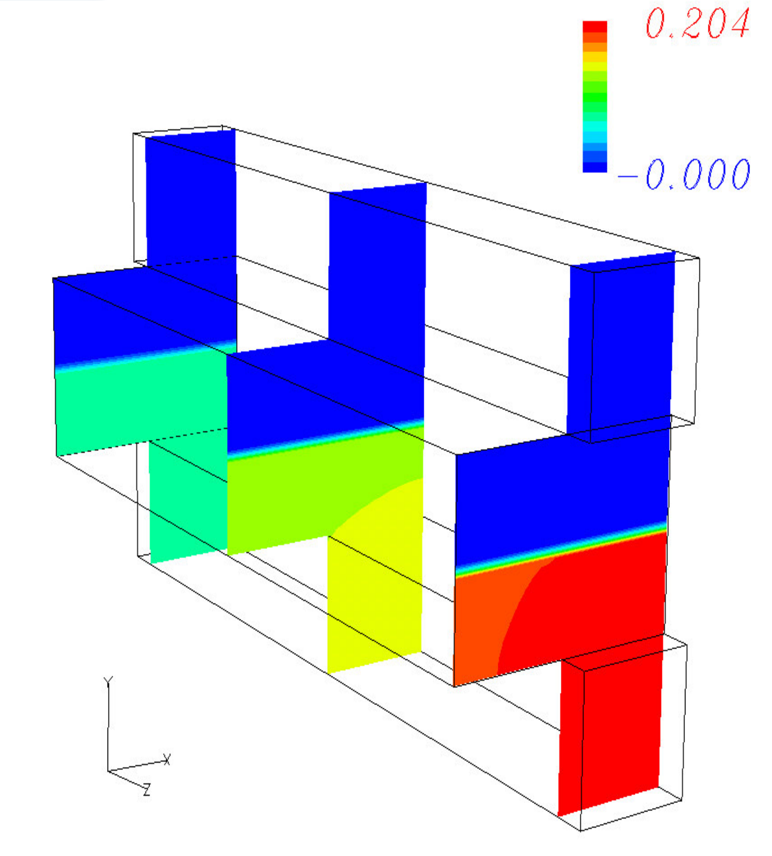


Concentrations med load

Oxygen mass fractions

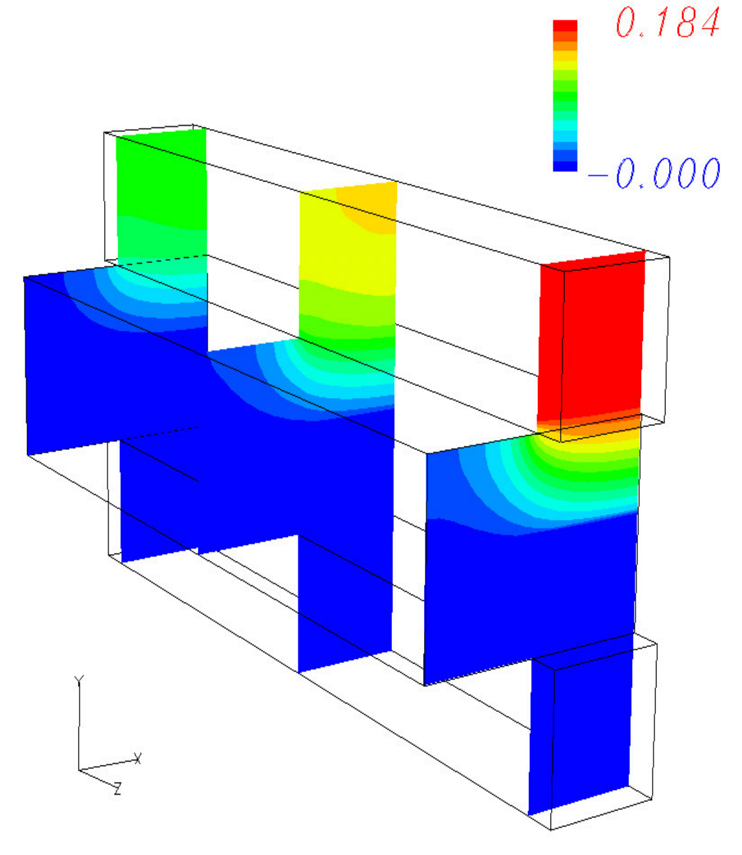


Hydrogen mass fractions

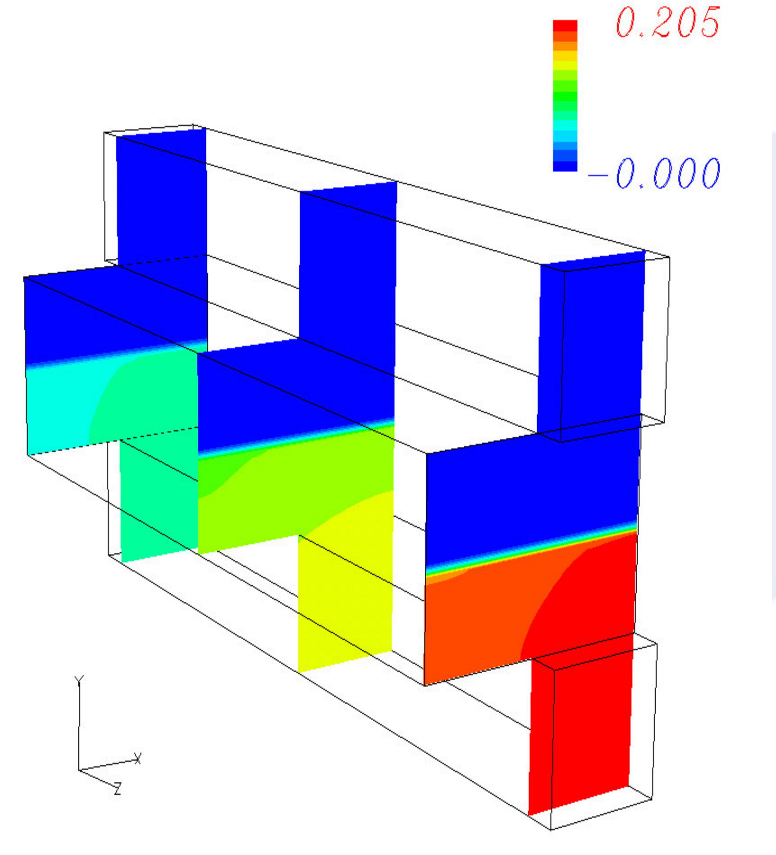


Concentrations high load

Oxygen mass fractions

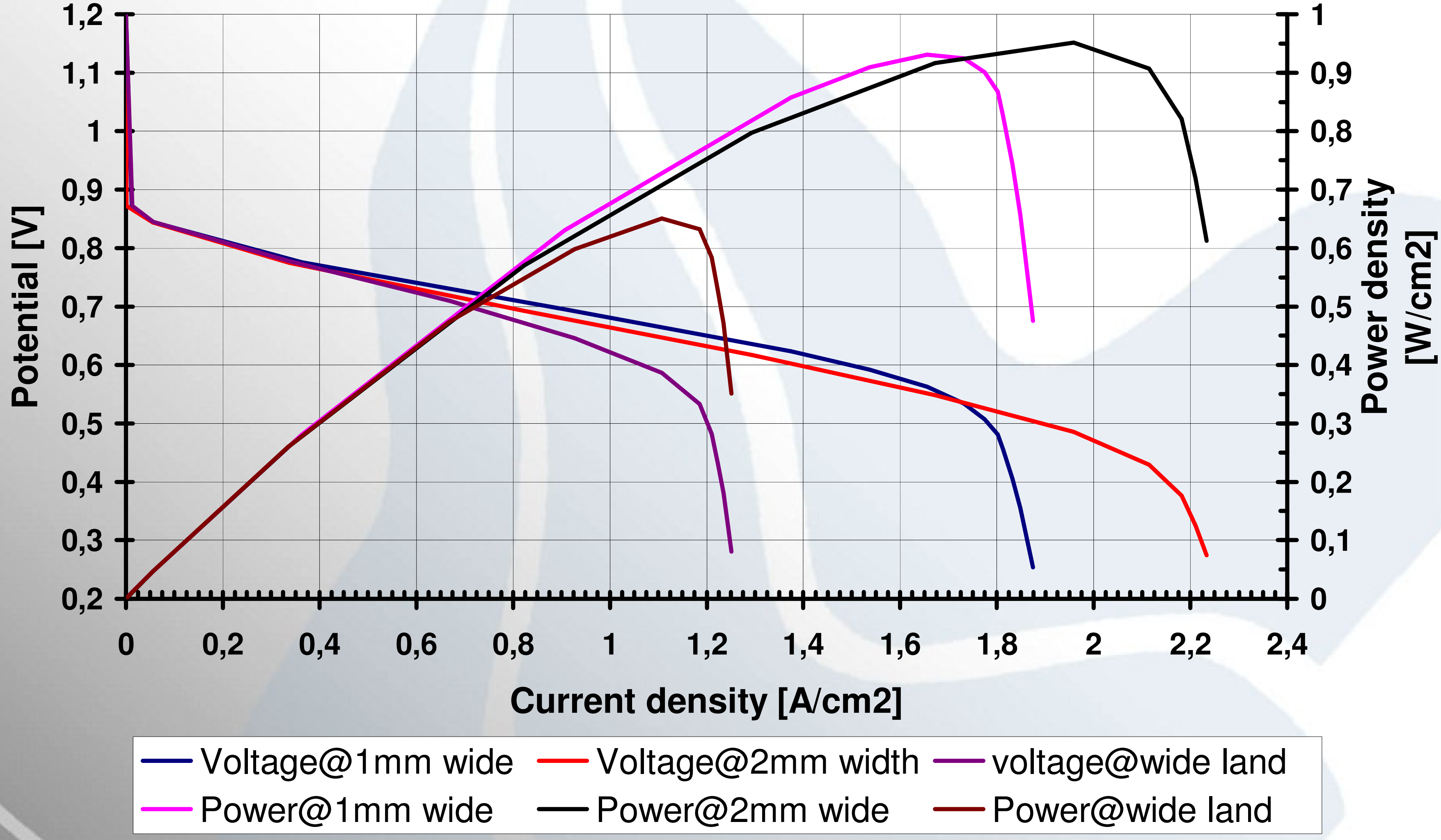


Hydrogen mass fractions

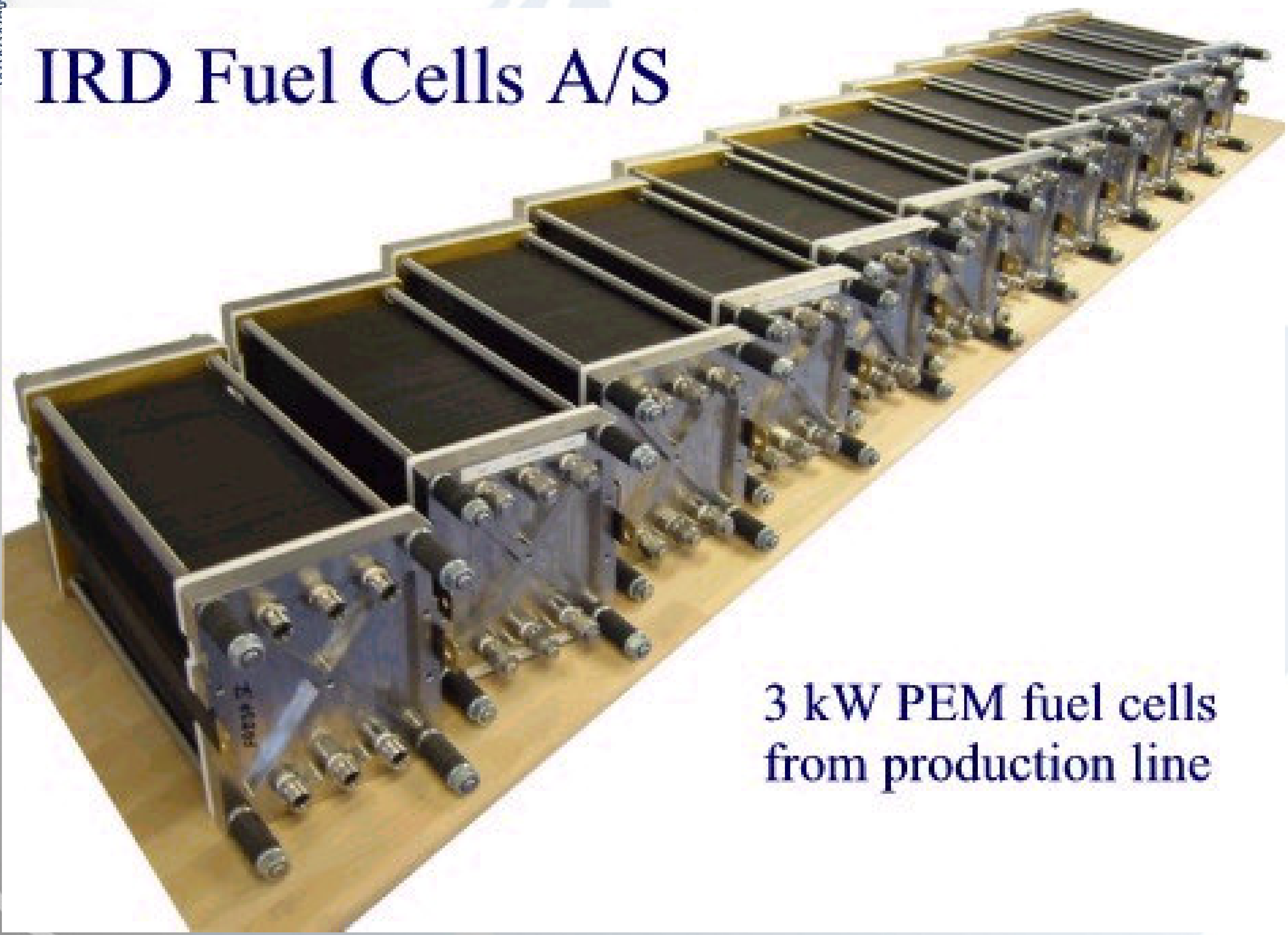


Polarization Curve

Varying channel width



IRD Fuel Cells A/S



3 kW PEM fuel cells
from production line

Thank You For Your Attention!

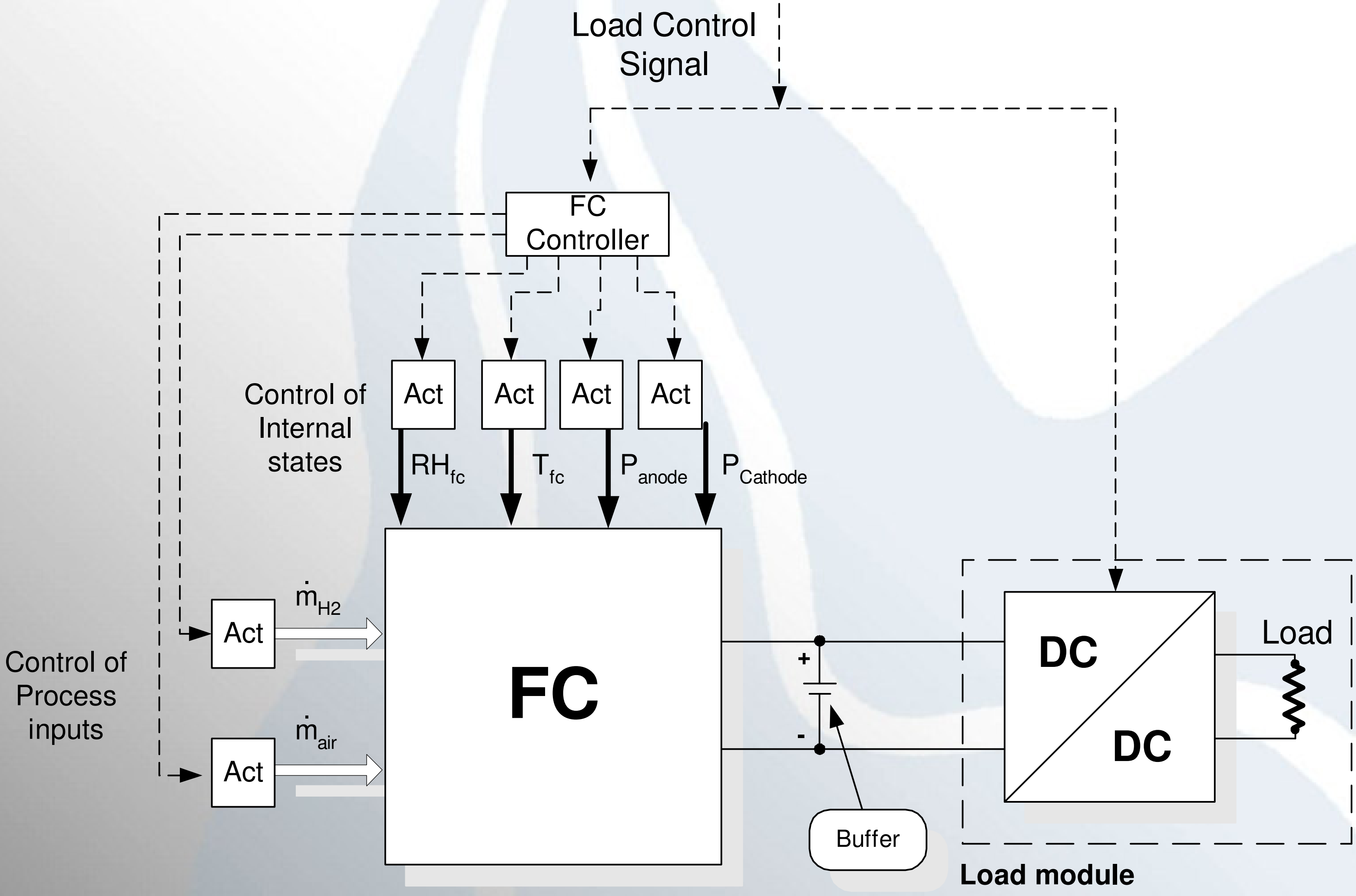
Fuel Cells Systems – Design & Control

Anders Korsgaard (ark@iet.auc.dk)

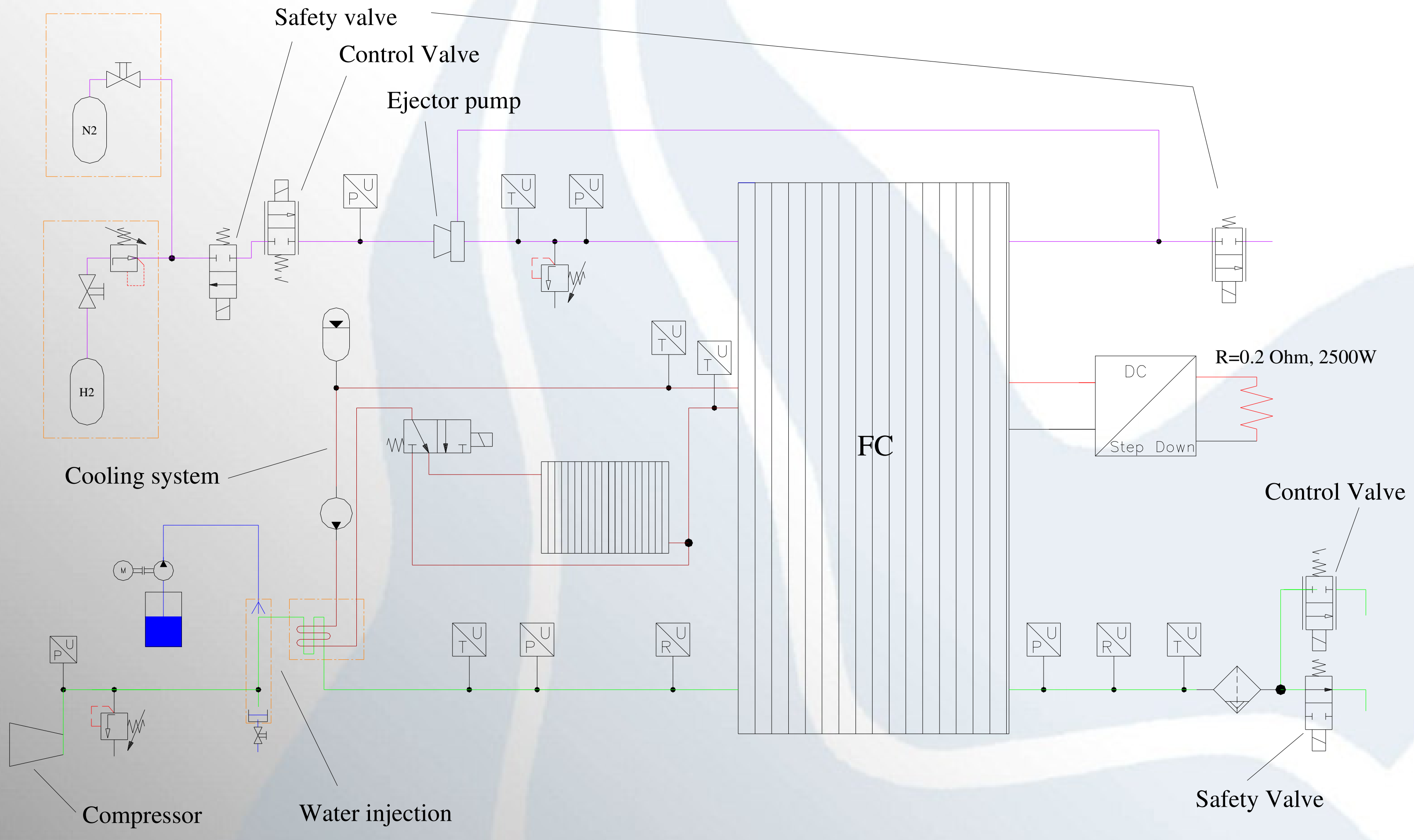
Overview

- Current laboratory facility – H2 Fuel Cell
- Control of facillity
- Efficiency of test facillity
- Future laboratory facillities
- Research activities within the control area

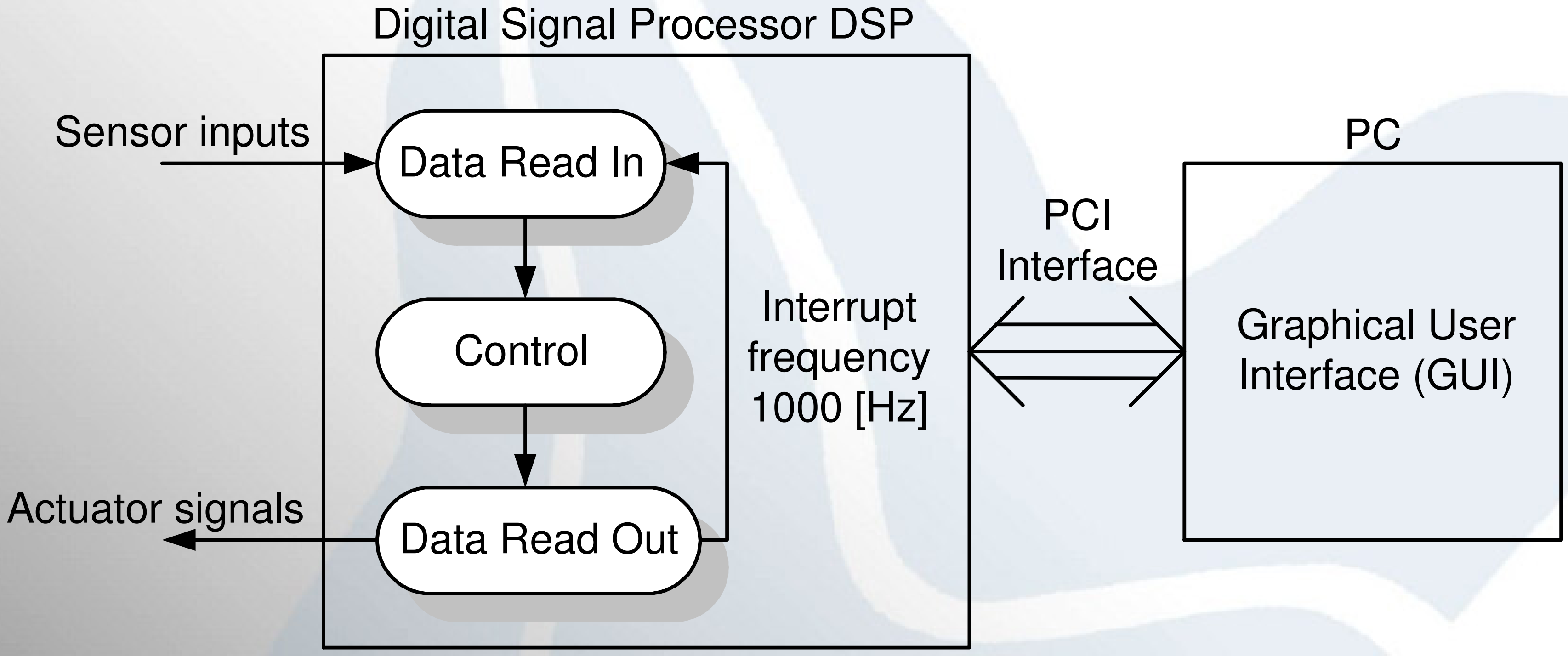
States to Control in FC-system



Laboratory facillity – H2 Fuel Cell



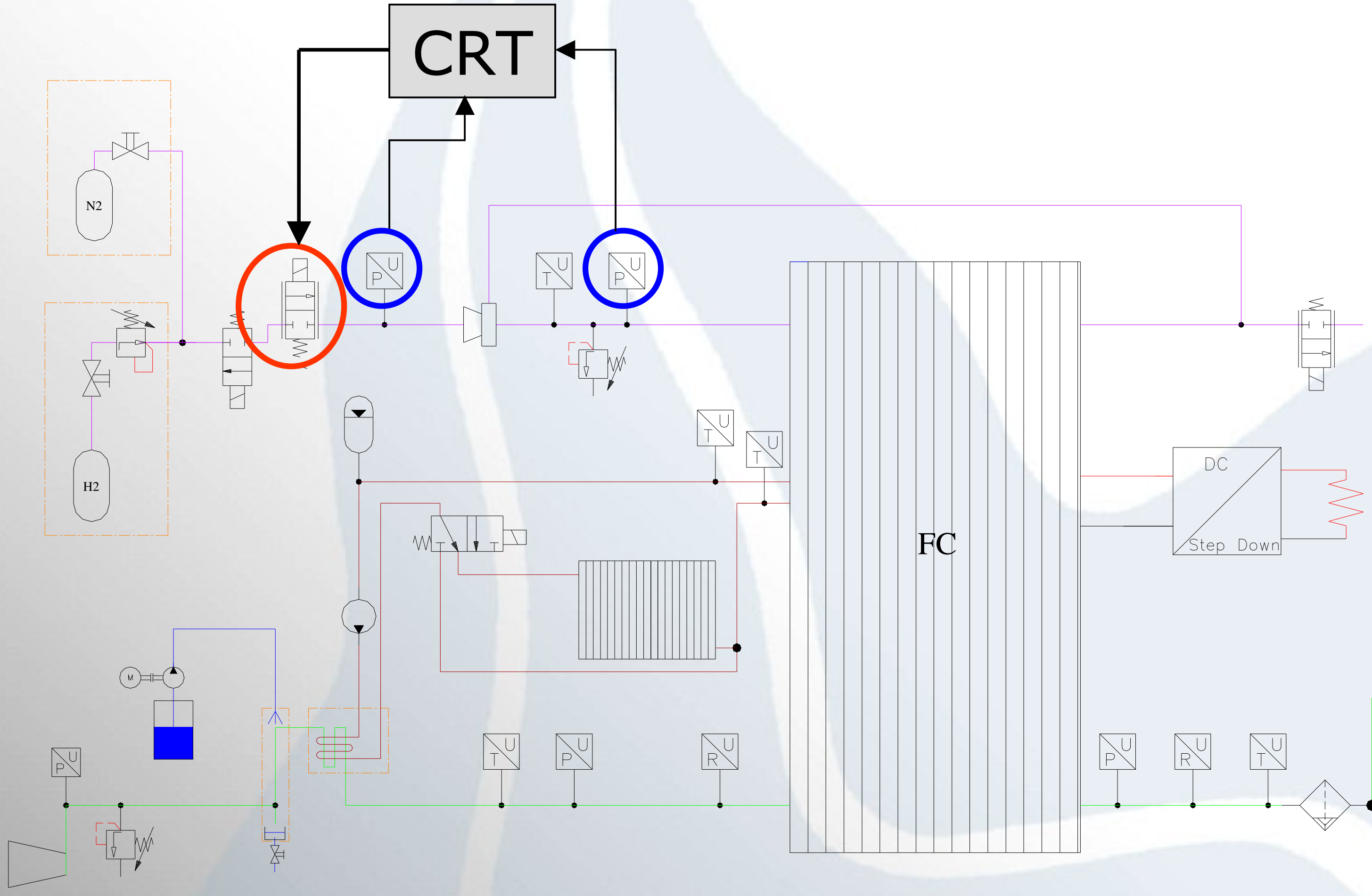
Control Hardware



Control Strategies

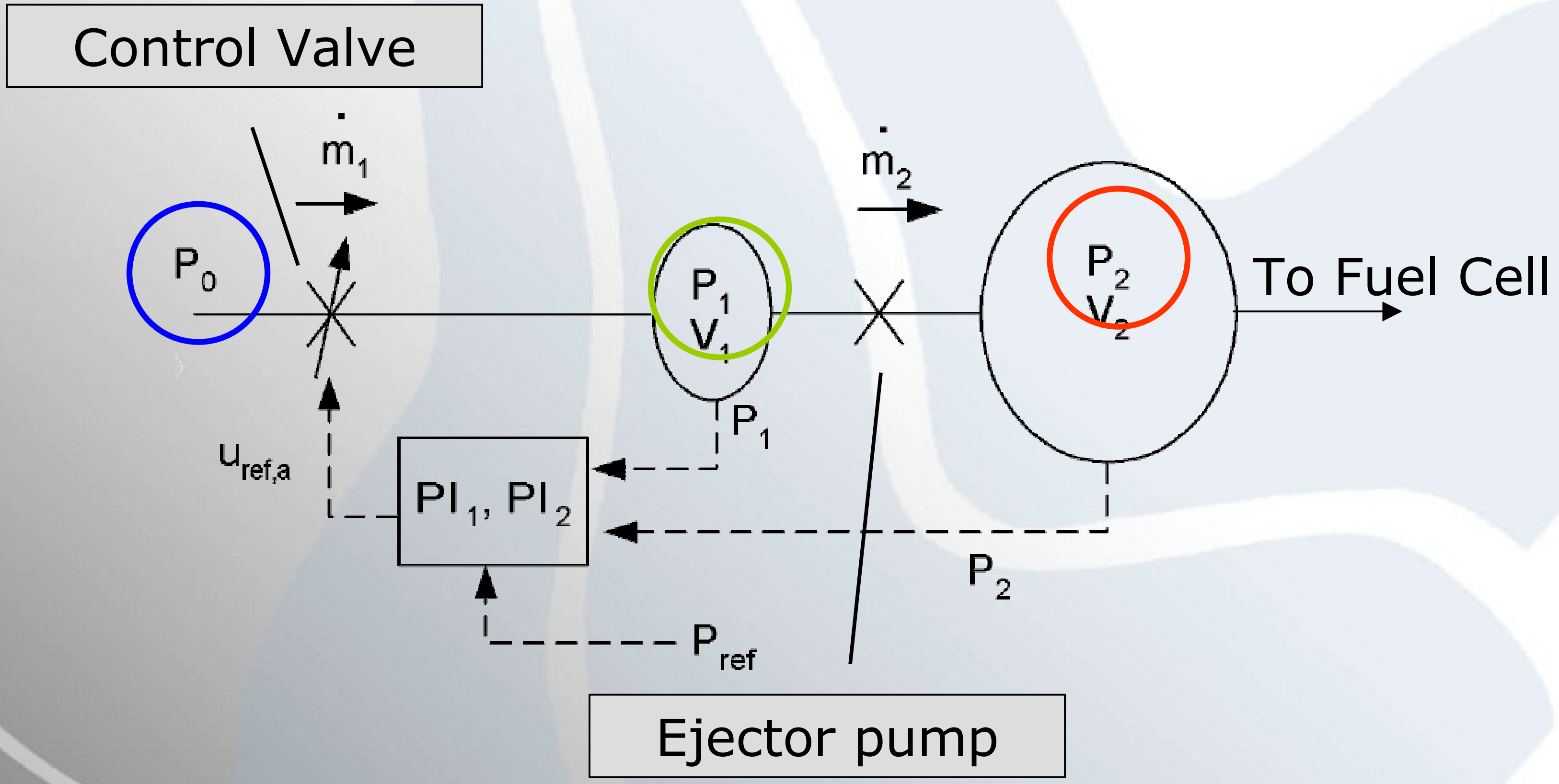
- Anode side pressure
    - Is kept constant
- Cathode side Flow
    - Should follow the current drawn: $m_{air} = k\ i_{load}$
- Cathode side Pressure
    - Is kept constant
- Control of Load
    - Is varied according to a load scenario
- Temperature
    - Is increase upto appr. 70 degrees
- Humidity
    - Is varied according to the humidity of the membrane

Control Strategies – Anode Pressure



Control Strategies – Anode Pressure

- Anode Side – cascade control



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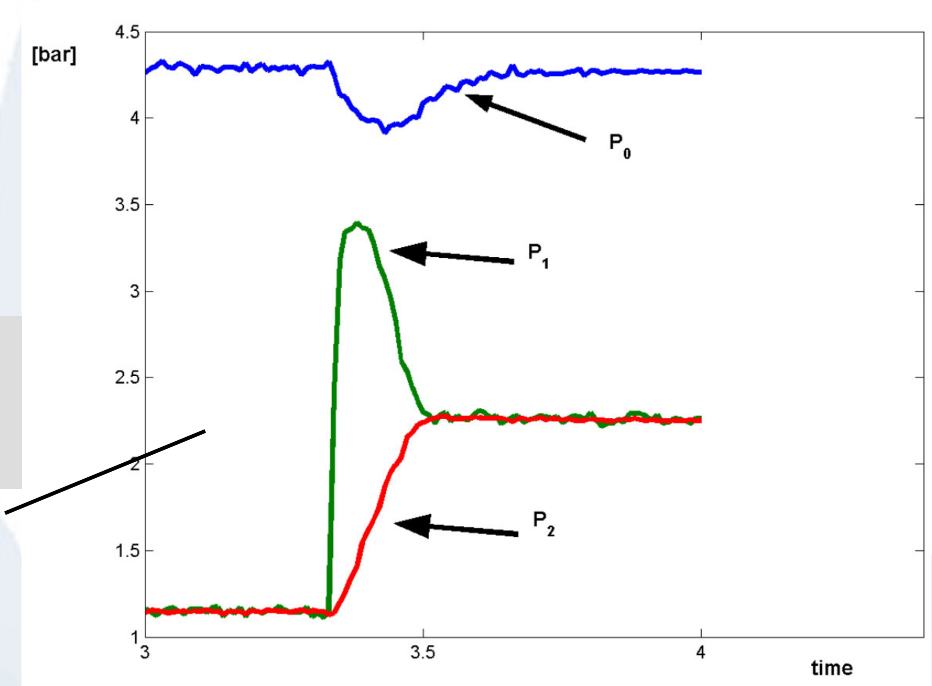
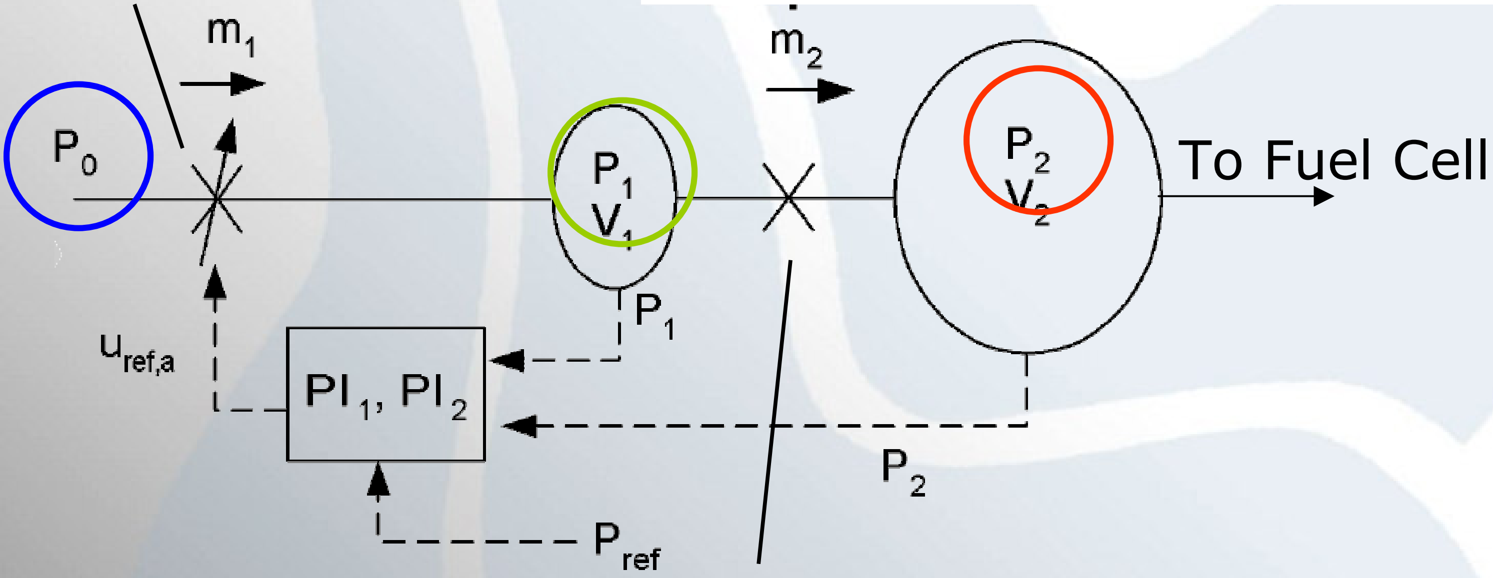
Control Strategies

- Step from 1 to 2.3 bar ref. pressure

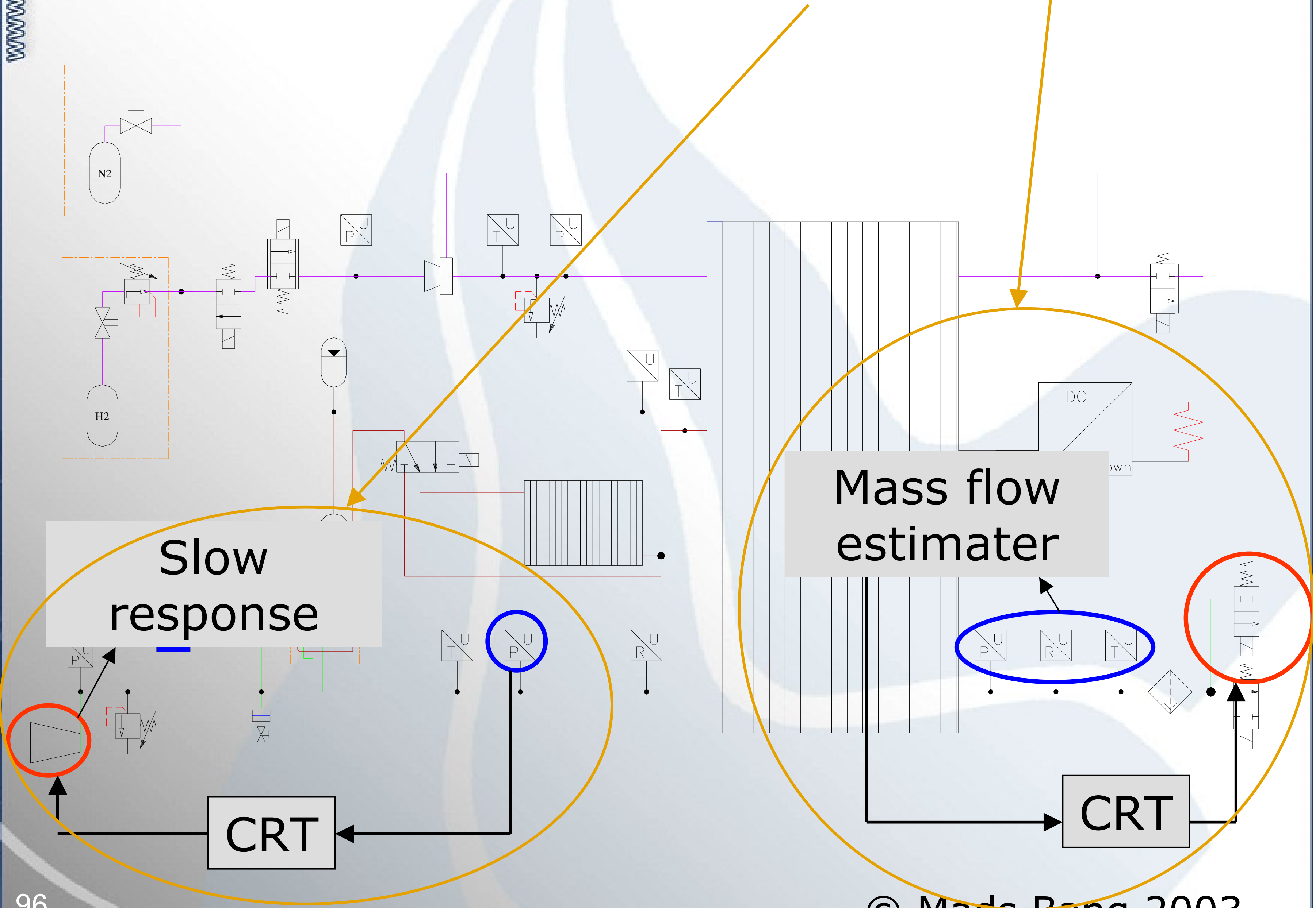


Control Valve



Ejector pump

Control Strategies – Cathode Pressure & Flow



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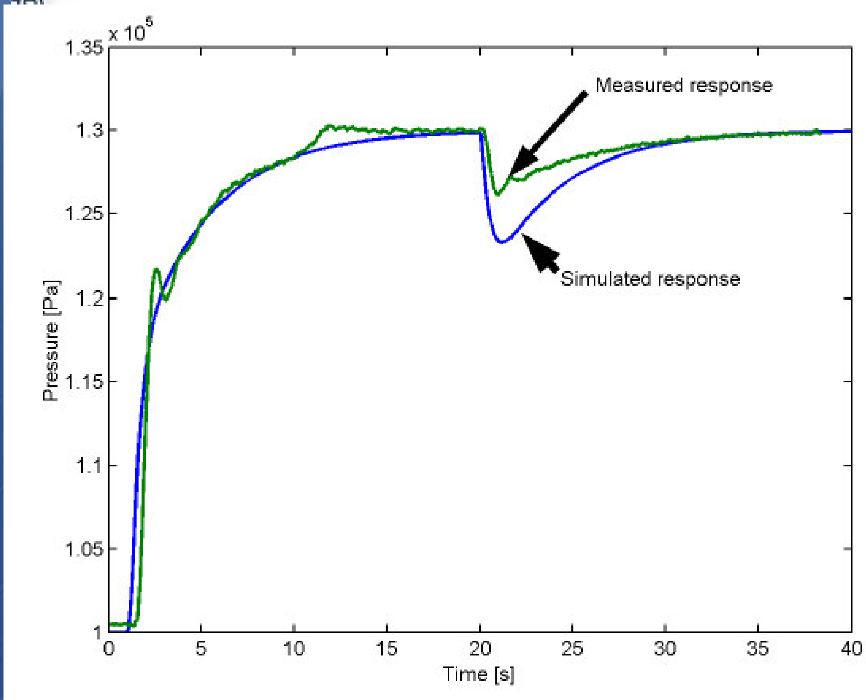
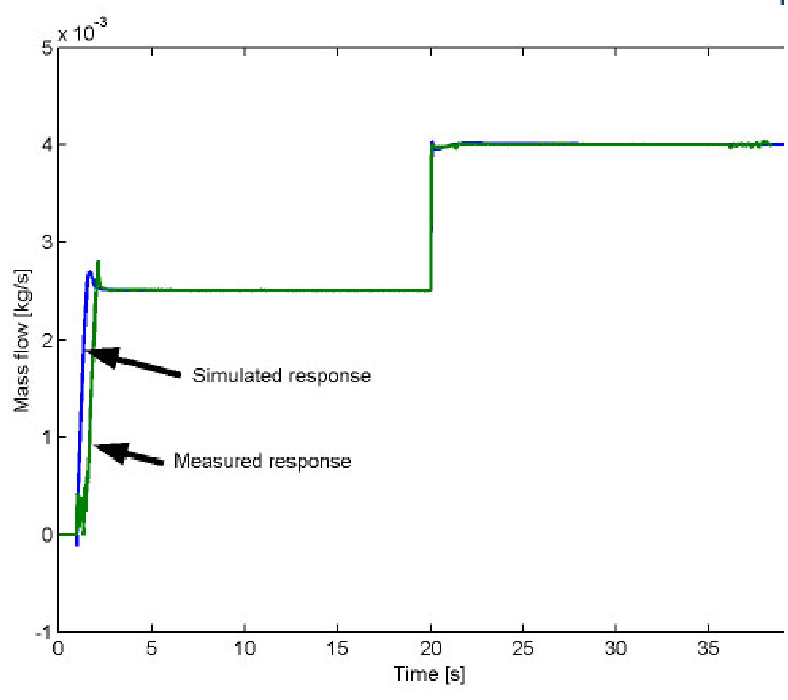
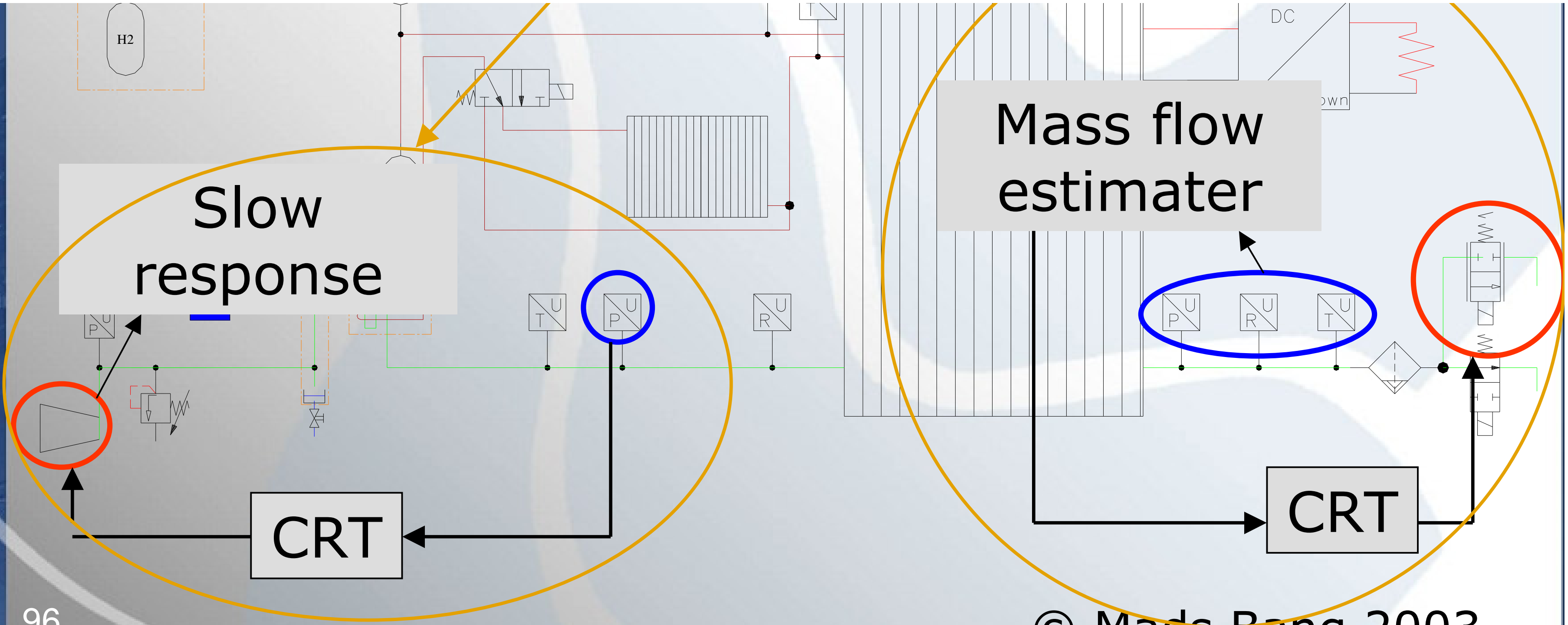






Slow response

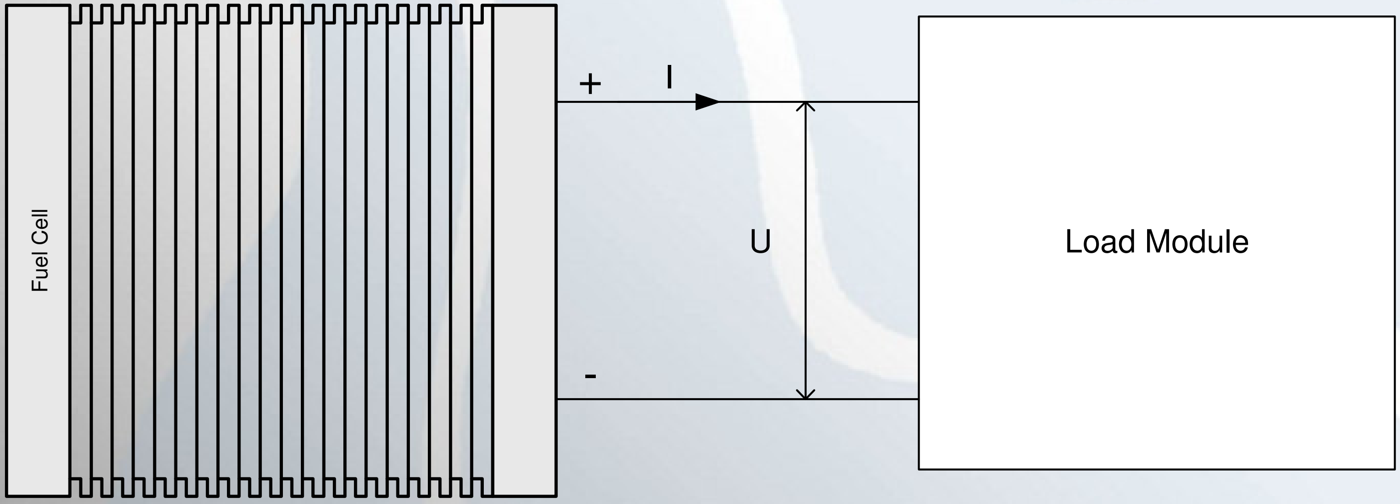
CRT

Mass flow estimater

CRT

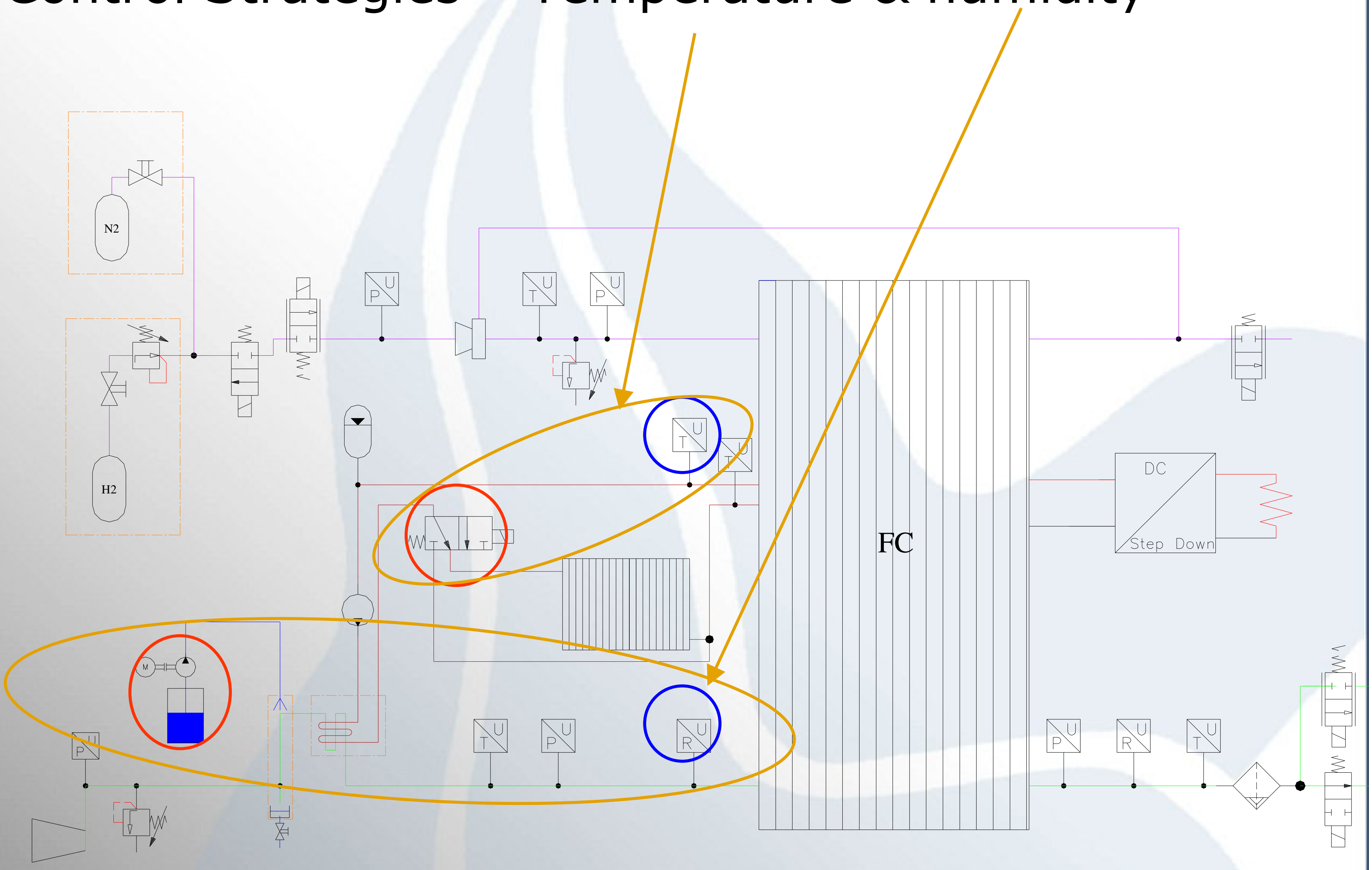
Control Strategies – Load Control

- Current (I-control)
- Voltage Control (U-control)
- Power Control (P-control)

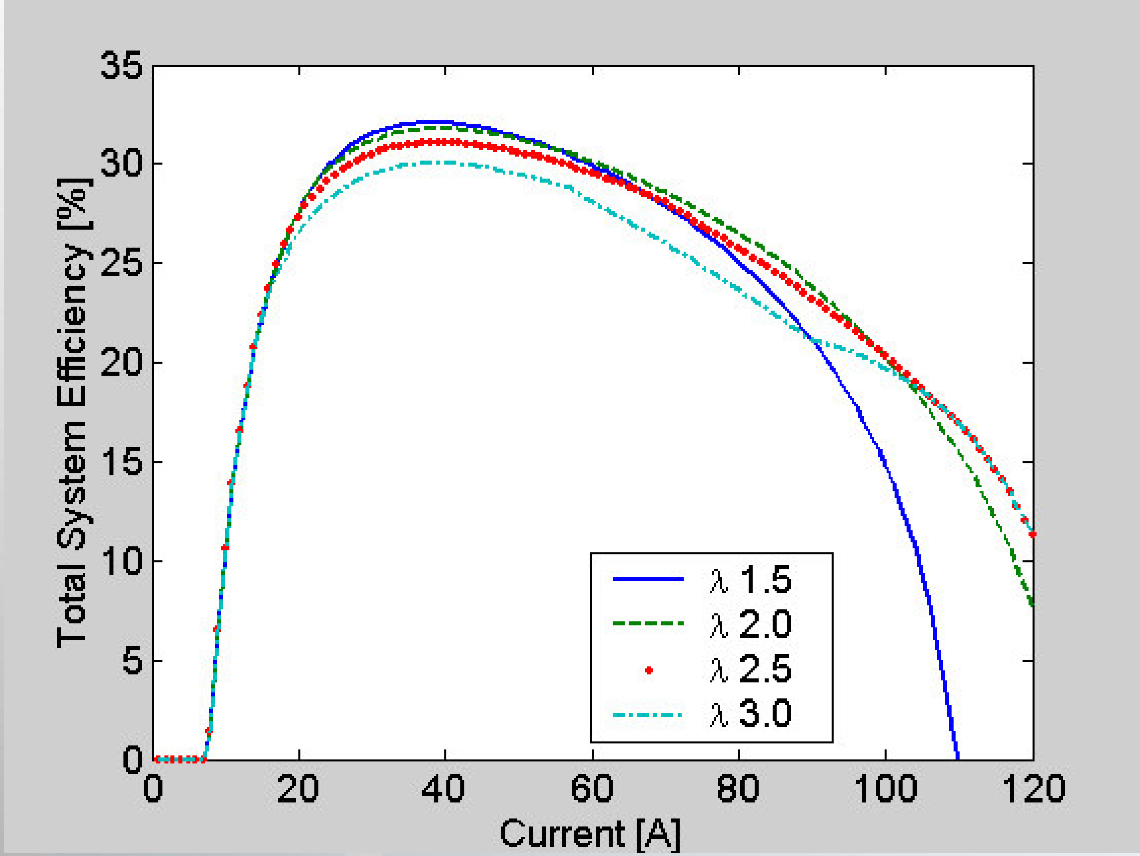


P=U I

Control Strategies – Temperature & humidity



FC-system efficiency (HHV)



Means to improve efficiency

- Higher efficiency of compressor (larger systems)
- Lower pressure on air side
  - Air Valves larger
  - Fuel Cell redesign.
- Higher pressure on hydrogen side (increase of cell voltage)

Future Laboratory facillities – Rerformate FC System

- Fuel cell facillity with Synthesis gas
  - Purpose: Investigate the influence of
    - Water content in membrane
    - CO-poisioning
    - CO2
- Combined Heat & Power (CHP) test facillity
  - Purpose: To investigate the performance of fuel cells in local households for heat and power production.

Current research activities within the control area

- Optimization of the Fuel Cell System response times.
- Dynamic simulation of fuel cell & reformer systems.
- Development of model based control to increase system stability and minimize the amount of sensors needed.
- Developent of diagnosis tools for determining fuel cell operating conditions.

Current FC Research at AAU IET:

- FACE9 project: “Experimental and Numerical study of discrete droplet transport in manifolds” (Study of two-phase flow distribution in fuel cell stacks)

- Modeling of inverters and DC/DC converters for fuel cell systems (Søren Bækhøj Kjær & Stig Munk-Nielsen)

- CFD-modeling of PEM-fuel cell stacks (Mads Bang)

- Modeling of Thermodynamic Fuel Cell Systems, (Mads Pagh Nielsen)

- Design and Control of Fuel Cell System for Transport Application (Anders Korsgaard, Claus A. Andersen and Morten Olesen Christensen).

- Development of stationary fuel cell system for household CHP generation. Involves building up a complete lab-scale plant with reforming system (Anders Korsgaard)

- Substituting Lead-Acid Batteries with DMFC fuel cells and controlling reforming systems (Looking for a candidate!)

- Industrial Ph.D. project concerning diagnosis of fuel cell stacks (Looking for a candidate!)

- Developing a test facility for a PEM-fuel cell stack reforming system using a Pt-Ru catalyst PEM stack (Mads Pagh Nielsen & Anders Korsgaard).

Industrial and Research Partners:

APC (American Power Conversion), UPS-plants

Sauer-Danfoss, Electric Drives, Nordborg

IRD Fuel Cell A/S, PEM and DMFC fuel cells, Svendborg

Danfoss A/S, Nordborg (Burner Division)

UVic (University of Victoria), BC, Canada

ECN (Energie onderzoek Centrum Nederland), Holland

Chemical Institute, Odense University

DTU, Lyngby

TI (Technological Institute), Århus

Risø, Roskilde and Haldor Topsøe, CPH. (Projects pending)

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For relevant links, downloads etc. please visit:

http://www.iet.auc.dk/