Electrochemistry for Materials Technology

ENERGY APPLICATIONS

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Electrochemistry – Energy Applications

Converting fuels *continuously* to electricity & useful heat:

- FUEL CELLS →

Converting fuels to electricity and vice-versa (*size-limited*):

- BATTERIES e.g. storage ⇄

Converting electricity to fuels and chemicals

- ELECTROLYSIS e.g. H_2 production ←
  e.g. Al production

FUEL CELLS – General aspects

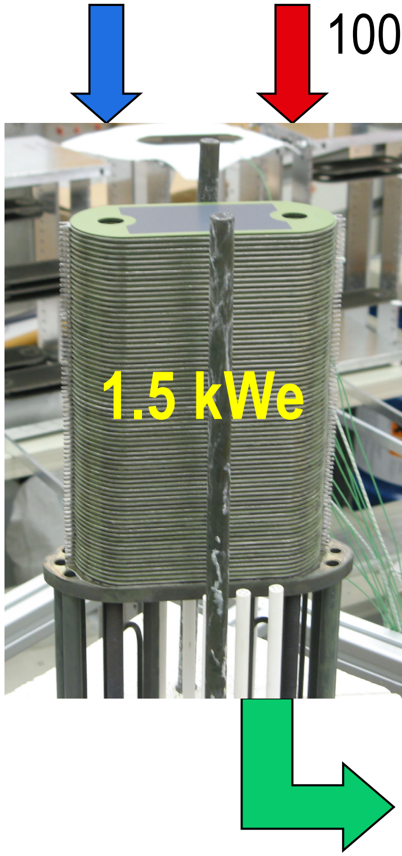
Principles, types, applications, strengths, efficiency

A Fuel Cell in a nutshell:

- works like a **battery**, fed with **gas**
- fuel is **directly** converted into electricity and useful heat
- typical sizes:
  - 1-20 W_e / H_2, MeOH / portable electronics
  - 1 kW_e / natural gas / a house
  - 20 kW_e / H_2 / an electric car
  - 1 MW_e / biogas / CHP
- status: pilot & demonstration, R&D, pre-commercial

Air

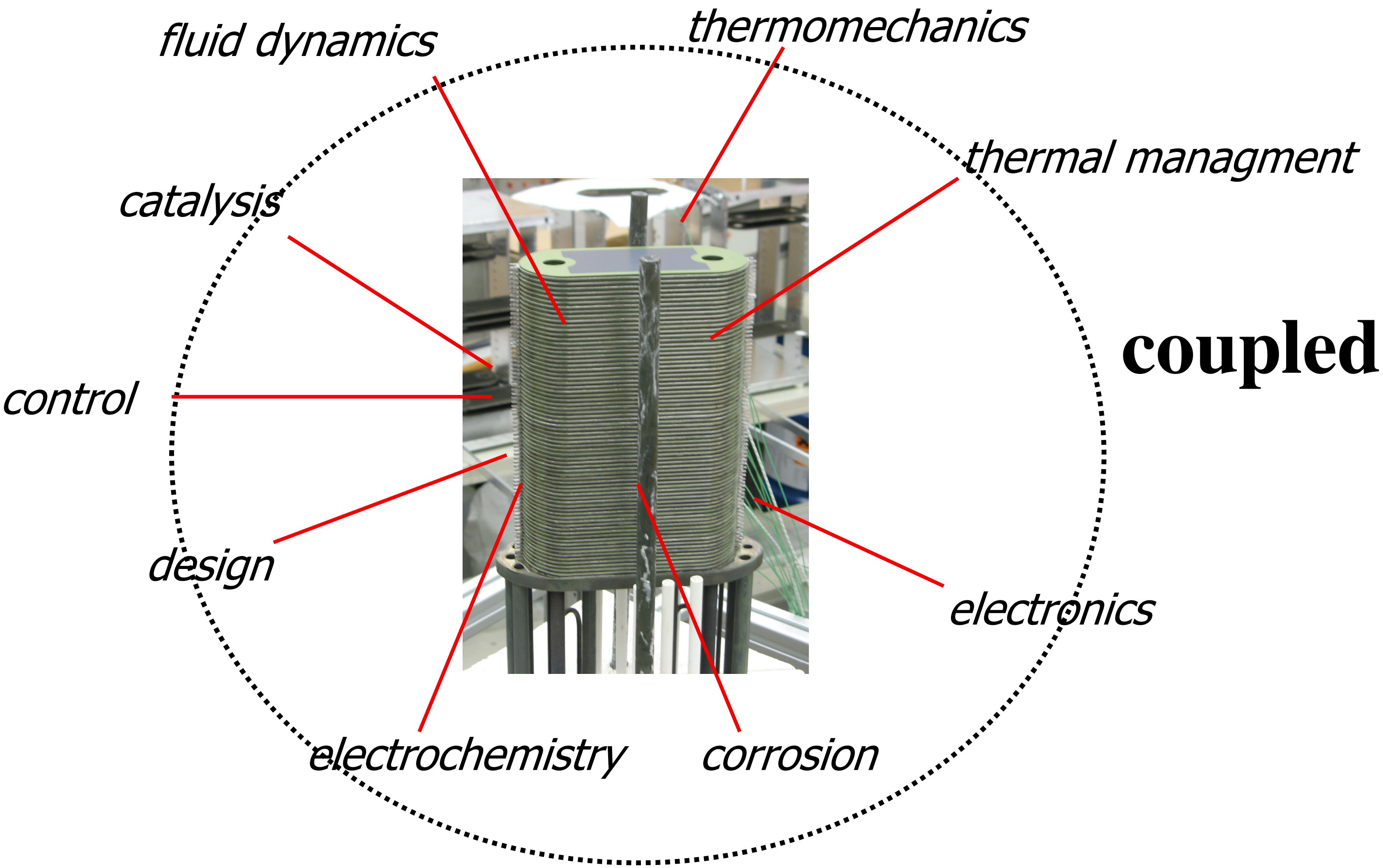
Fuel (natural gas, biogas,…)
100%



Stack of
66 cells
in series
(50 V)
of 80 cm^2
(30 A)

Electricity 60%
Heat 30%

Highly pluridisciplinary topic



coupled

*At the crossroads of mechanics, chemistry, **materials science** and electrical engineering*

Learning objectives on “Fuel Cells”

- understand the underlying **principles** in order to assimilate more specialised literature
- distinguish the different fuel cell types and know their specific **applications** and power sizes
- differentiate fuel cells from other conversion technologies (batteries, engines, microturbines,…), know and argue their strengths and limitations
- explain why electrical **efficiency** is high, including and especially for **small scale** conversion (kW-MW-scale)

Components of a fuel cell (=a *'gas battery'*)

- 2 solid electrodes (+,-) of **electronic** conduction

- **ionic** conductor (*solid* or *liquid*), electronically insulating, that separates the 2 electrodes

- at both **interfaces** between electronic and ionic conductors, there is
  - charge transfer (electrons)
  - mass transfer (molecules)

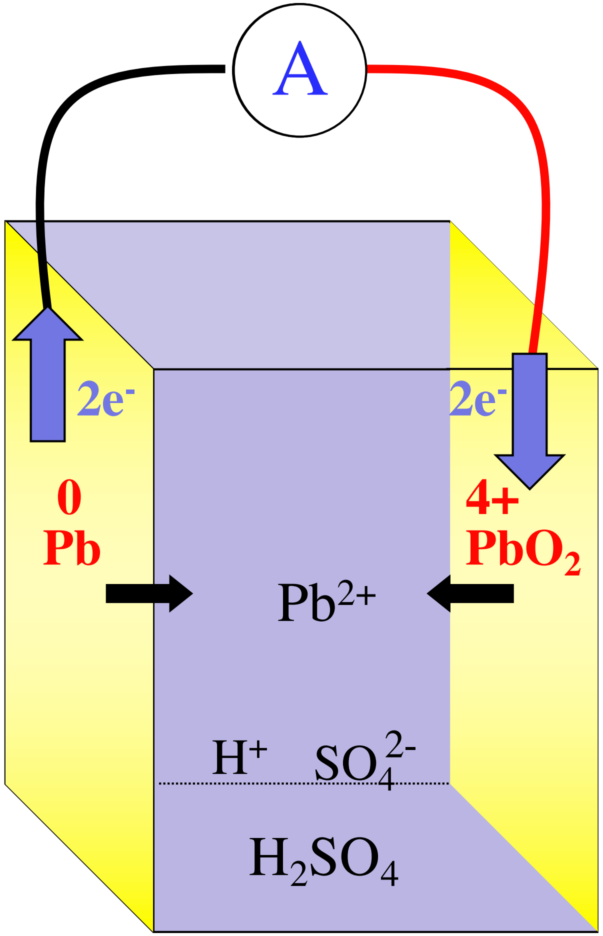
  to complete the circuit and sustain current flow (& mass flow), so as to deliver electricity

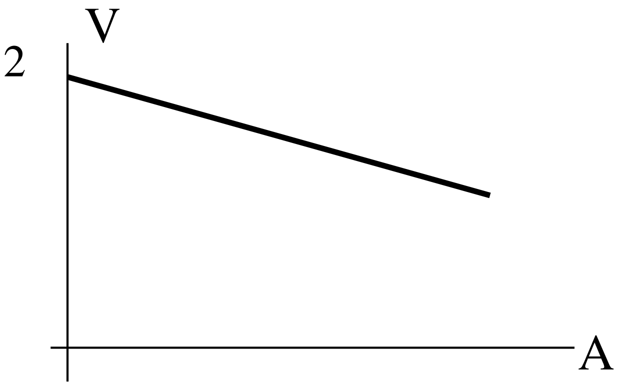
Operating principle

- we first describe the operating principle of a classical battery (lead - sulfuric acid)
- and then explain the similarities and differences with a fuel cell ('gas battery)'
- we consequently introduce different fuel cell types, one by one (5 in total), depending on the **materials** used
  - the fuel cell type (name) is designated by its **electrolyte** material,
  - which can be solid or liquid,
  - and conduct charge depending on the **operating temperature (RT to 1000C!)**

Lead acid battery

< 2 V





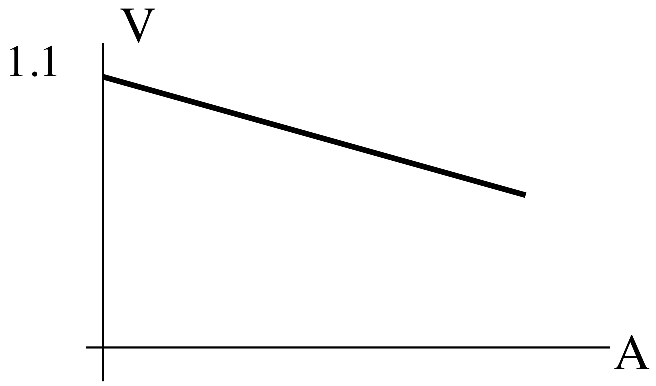
$$Pb \Leftrightarrow Pb^{2+} + 2e^-$$

$$PbO_2 + 2e^- + 4H^+ \Leftrightarrow Pb^{2+} + 2H_2O$$

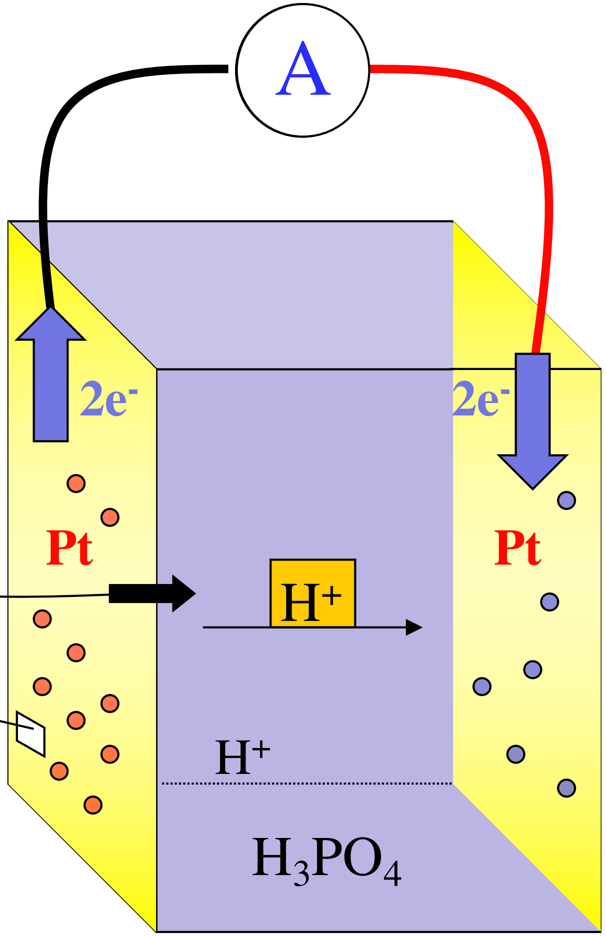
$$Pb + PbO_2 + 2H_2SO_4 \Leftrightarrow 2PbSO_4 + 2H_2O$$

Electrode consumption (« active masses »)

1. Phosphoric acid fuel cell (PAFC)



< 1 V



$H_2 \Leftrightarrow 2H^+ + 2e^-$

$300 \frac{mA}{cm^2}$

$\frac{1}{2}O_2 + 2e^- + 2H^+ \Leftrightarrow H_2O$

electricity

+

heat

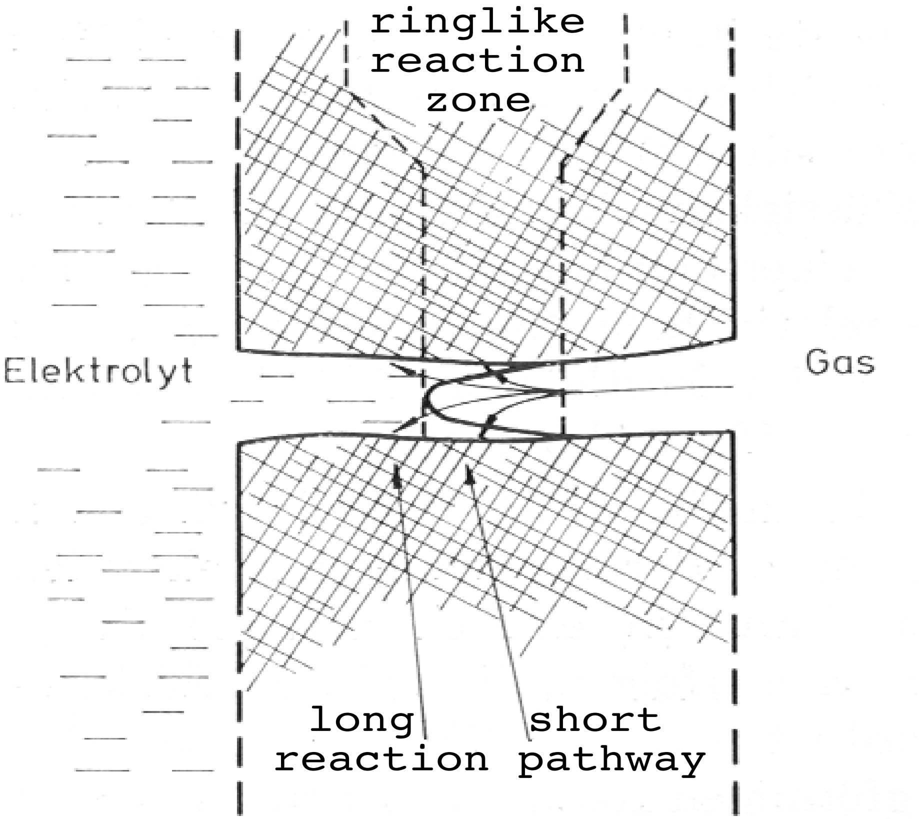
200C

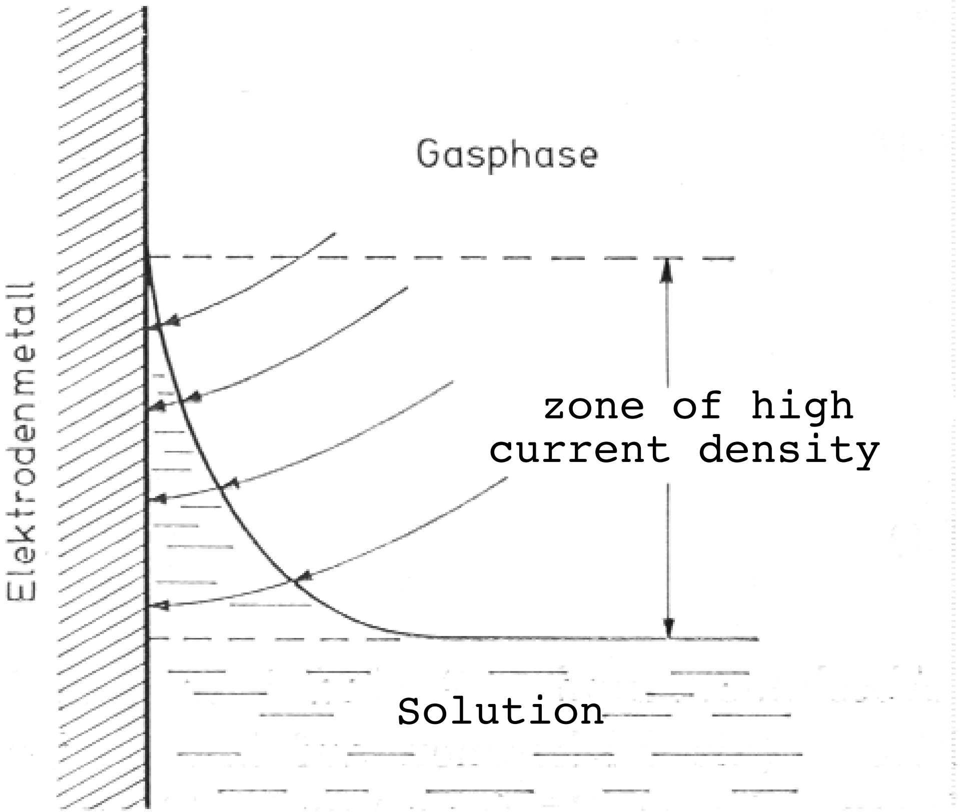
$$H_2 + \frac{1}{2}O_2 \Leftrightarrow H_2O$$

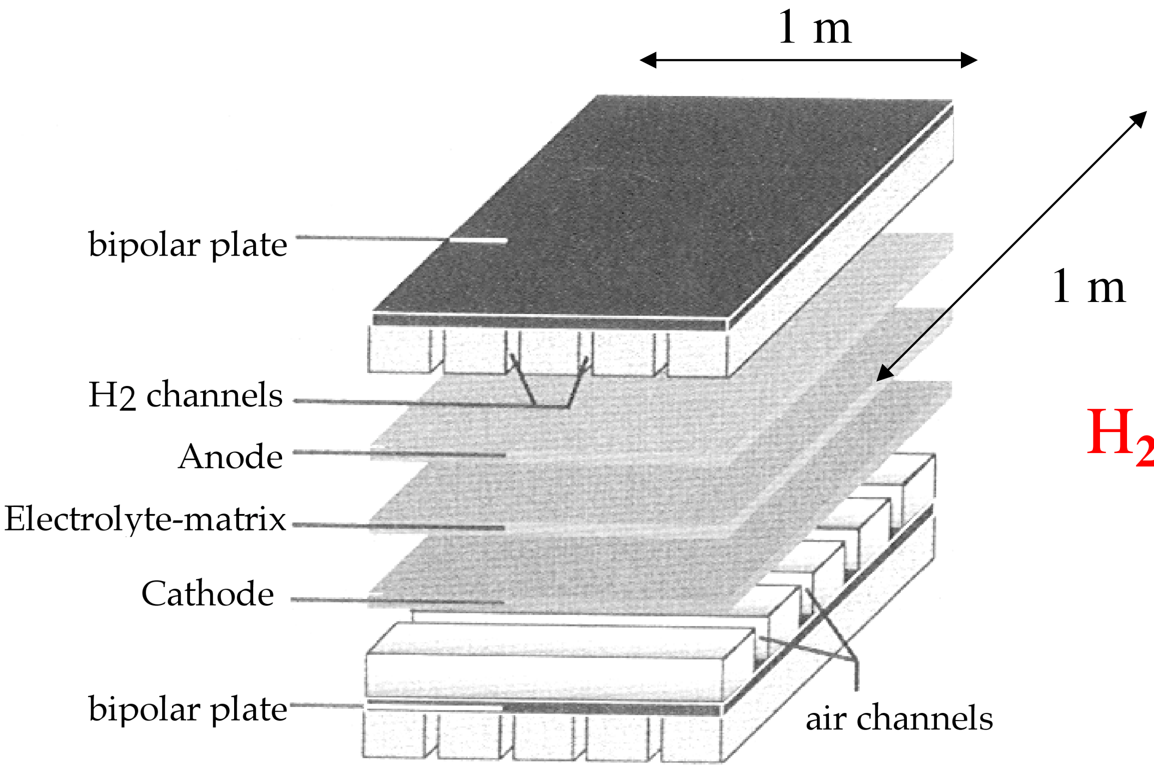
- consumption of gases
- electrodes are invariant (catalysts)

Gas diffusion electrodes

- allow to inject (extract) a gas into (from) a liquid
- reaction zone = “triple phase boundary” (gas/liquid/solid)

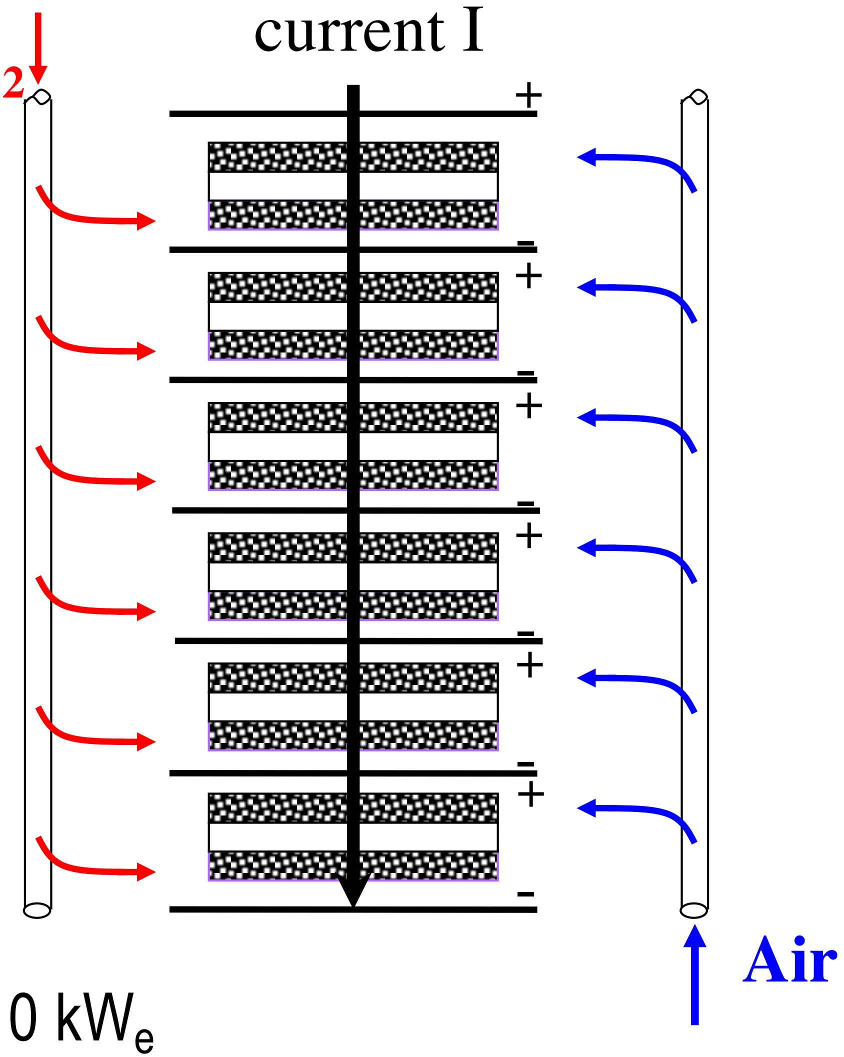






(Source: Ledjeff, 'Brennstoffzellen')

Increase electrode surface :
→ high **current** I (A)



Series connection :
add up the **voltages** (V)

Electric **power** P = **V** * **I**
f.ex. 100 cells of 1 m^2 surface

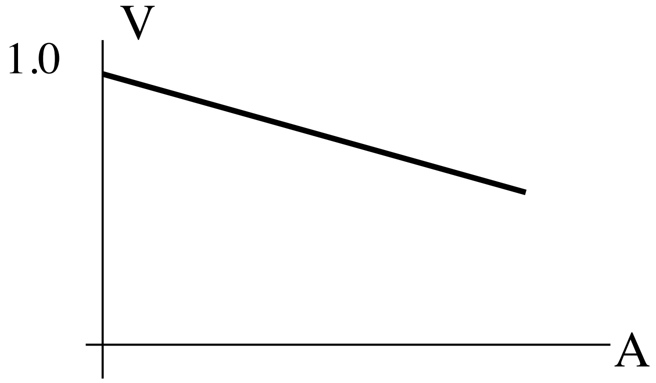
70 V * **3000 A** = 210 kW_e

Units exist from 50 kW_e to several MW_e

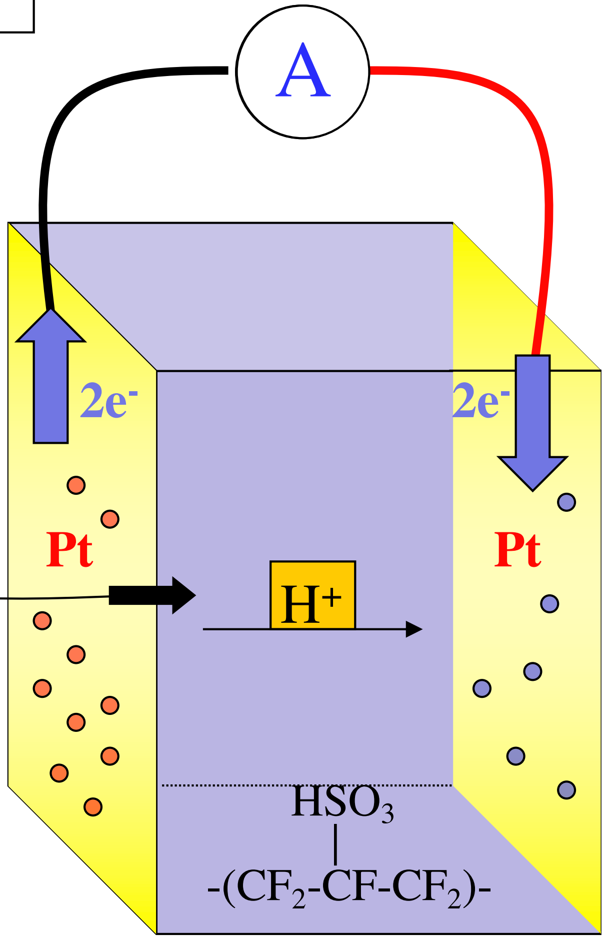
Typical size is 200 kW_e or 400 kW_e, operated on natural gas (NG)

(source : Thoma & Renz AG, Basel, CH)

2. Polymer Membrane FC Polymer Electrolyte FC (PEM or PEFC)



< 1 V



$H_2 \Leftrightarrow \boxed{2\,H^+} + 2e^-$

$\frac{1}{2}O_2 + 2e^- + \boxed{2H^+} \Leftrightarrow H_2O$

$$H_2 + \tfrac{1}{2}O_2 \Leftrightarrow H_2O$$

mobile application

↑

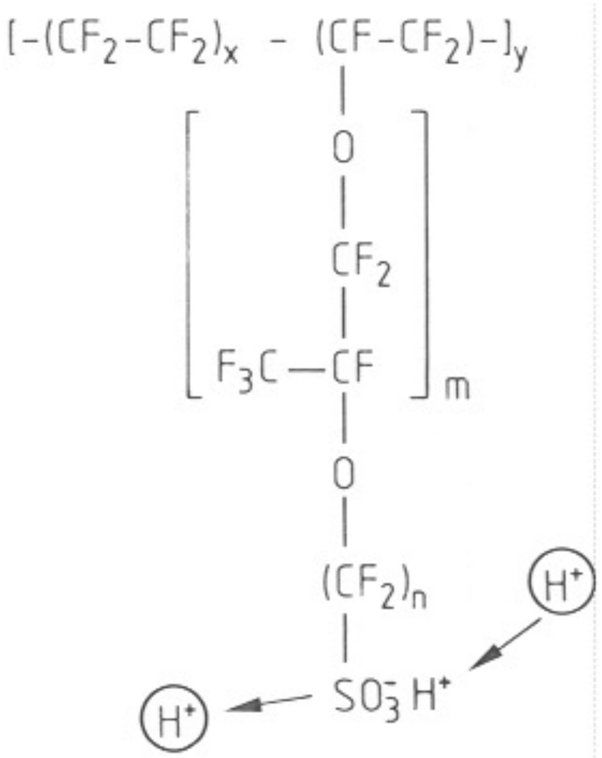
cold start

↑

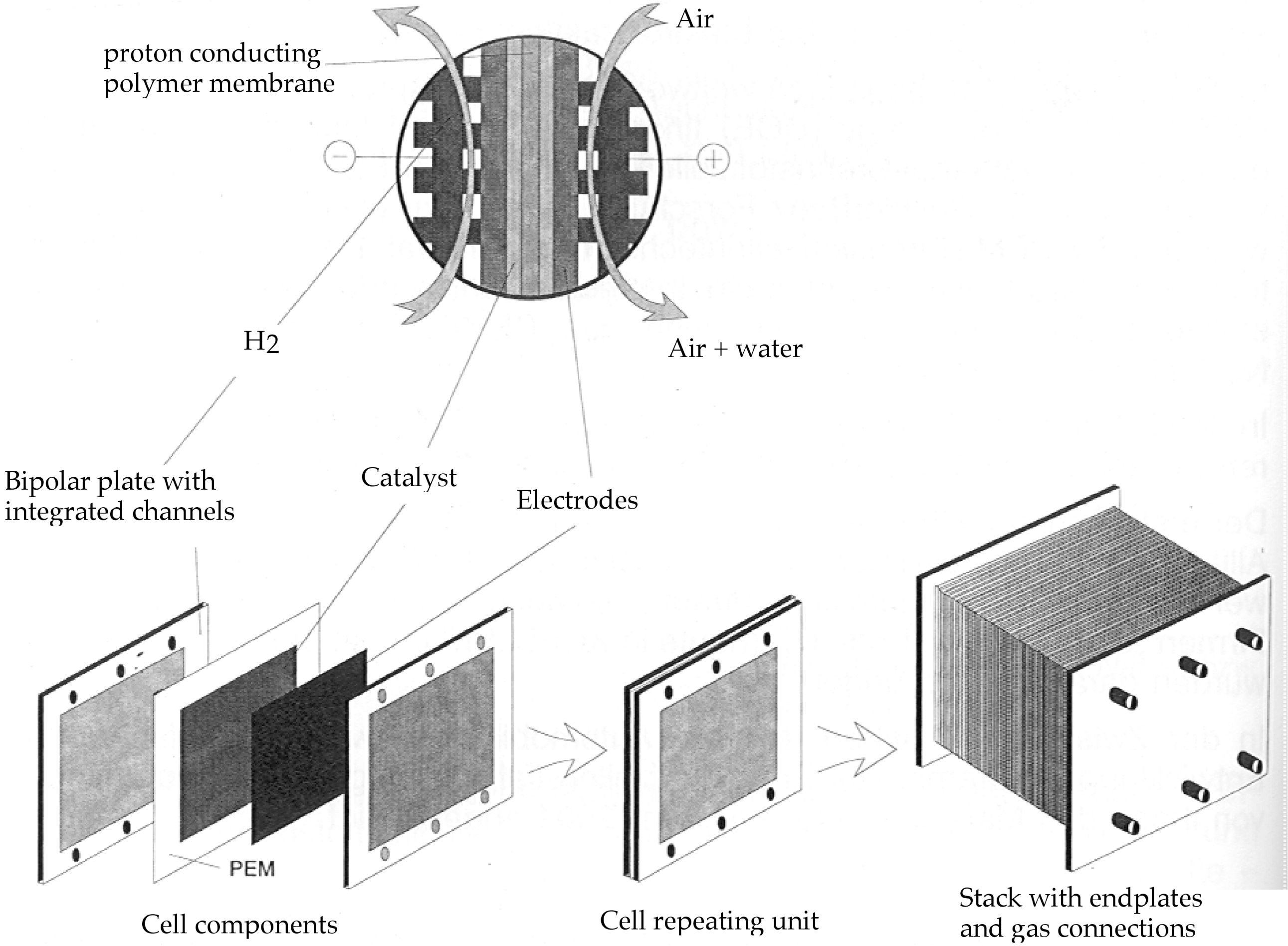
<u>0-80C</u>

<u>Rem.</u> : also capable to oxidise directly methanol as fuel

polymer membrane (50 µm thin)



series connection (« stack »)

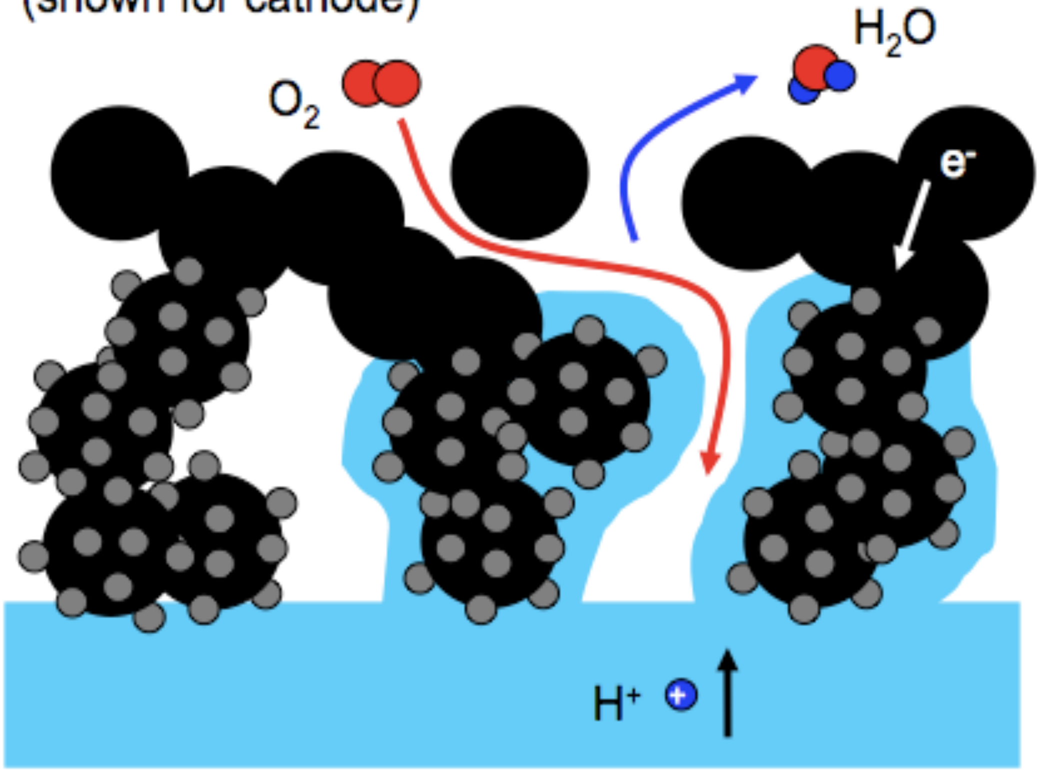


http://www.youtube.com/watch?v=yowRvfFtMgQ

‘Triple phase boundary’ concept

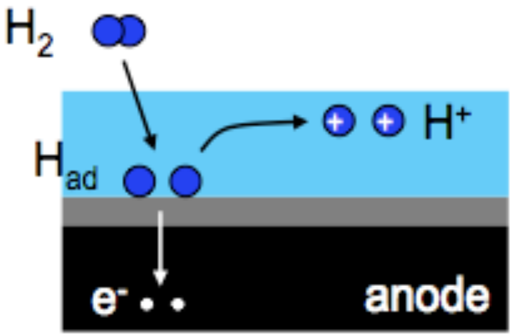
Copied from G.G. Scherer, PSI, European Fuel Cell Forum, Lucerne, Tutorial Course

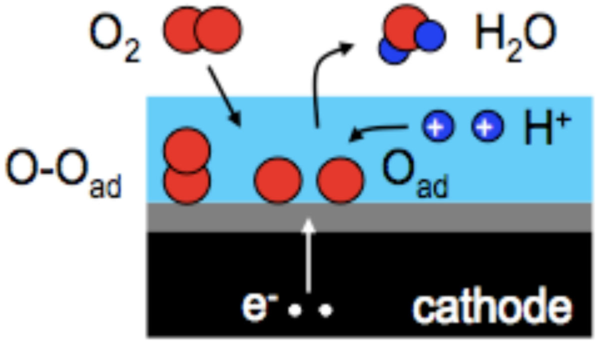
(shown for cathode)



access of:

1. electrons
2. protons
3. reactants / products





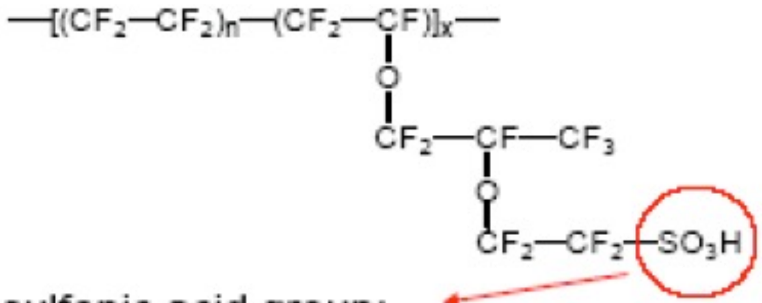
3 phases **must** meet: gas (pores), catalyst (electrons) and electrolyte membrane (ions)

Polymer membrane morphology

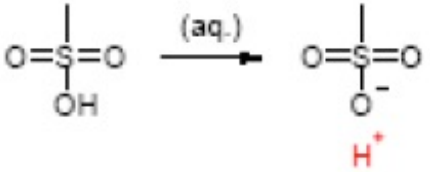
bi-continuous nano-phase separated microstructure

- hydrophobic backbone provides mechanical integrity
- proton transport occurs via water filled channels

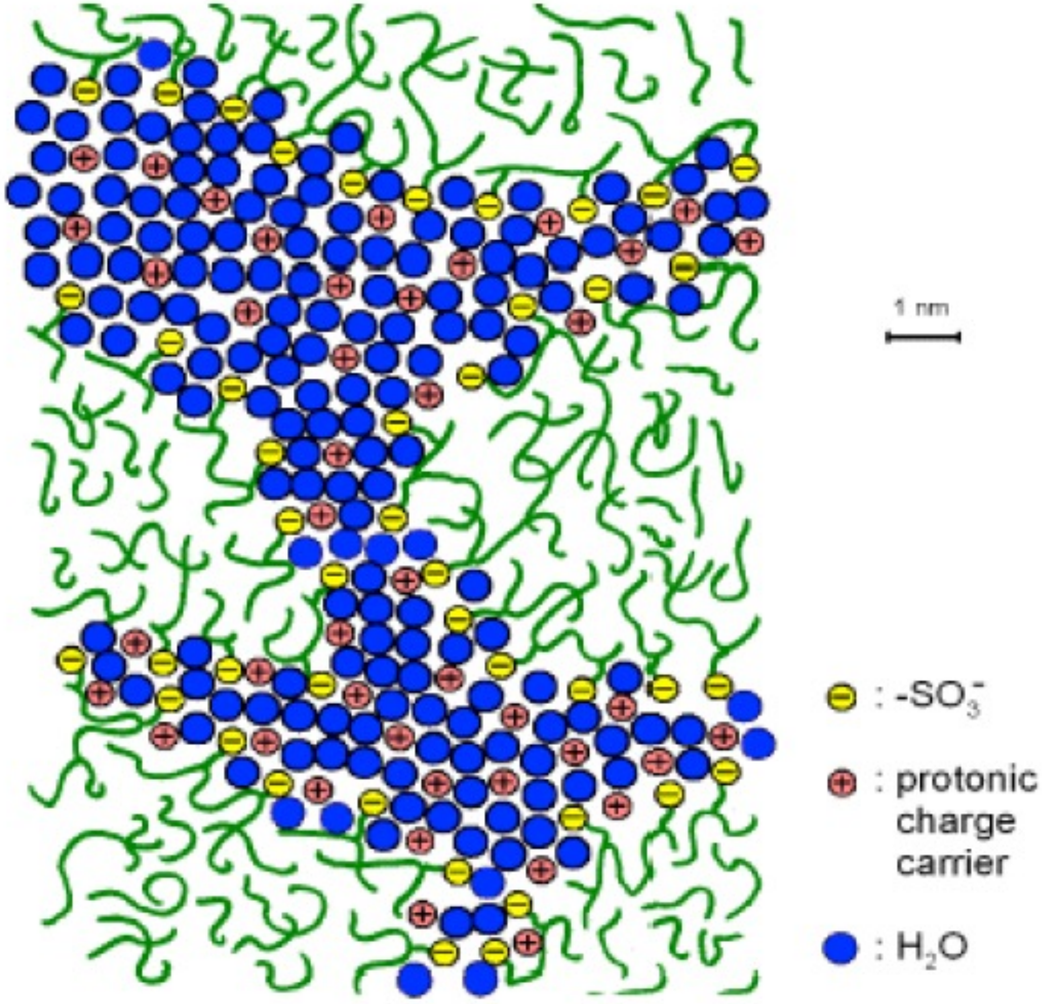
e.g. Nafion®:



sulfonic acid group:

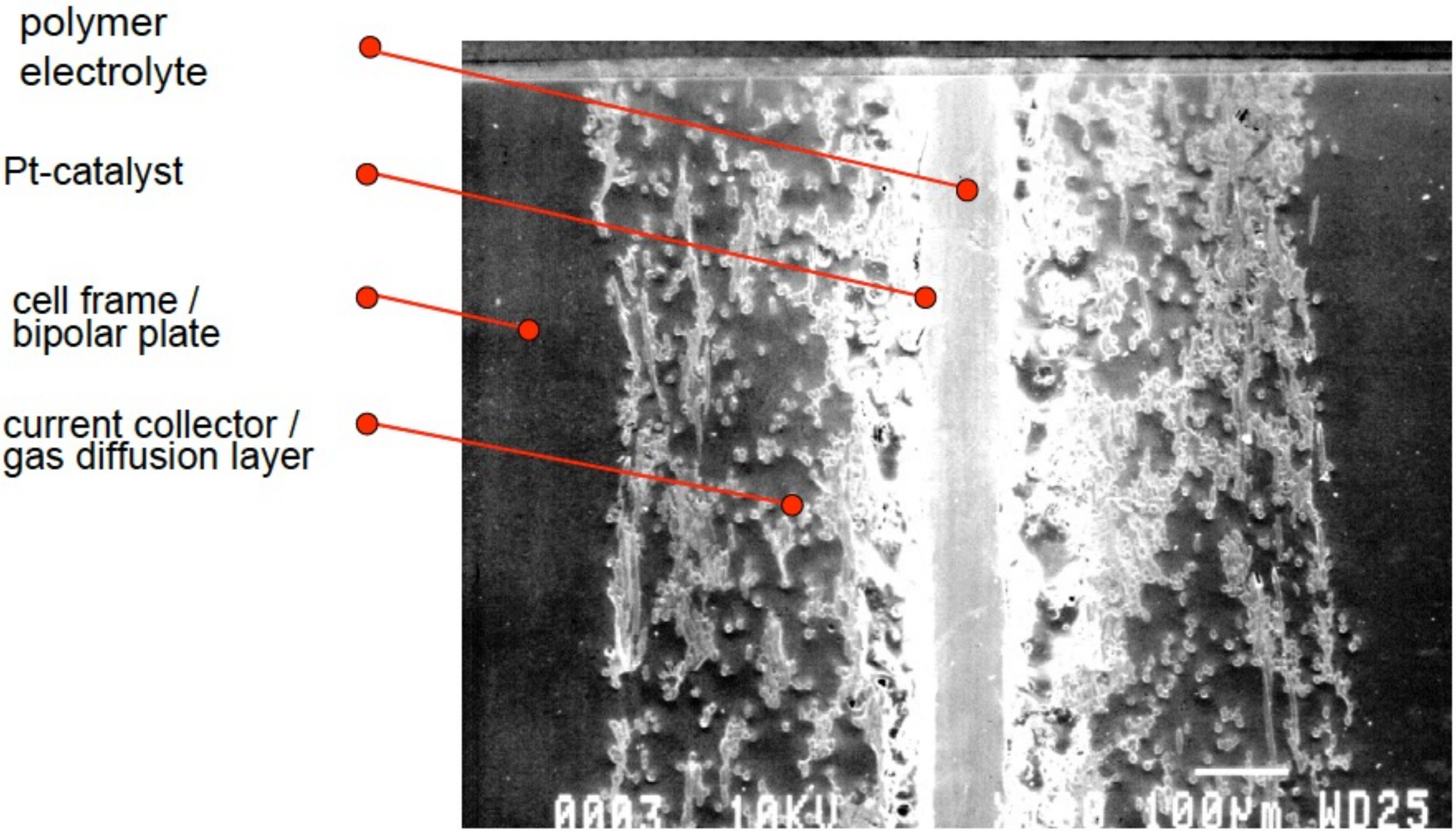


$pK_a \approx -6$



Copied from G.G. Scherer, PSI, Fuel Cell Tutorial, European Fuel Cell Forum, Lucerne

Membrane electrode assembly (MEA)


polymer electrolyte

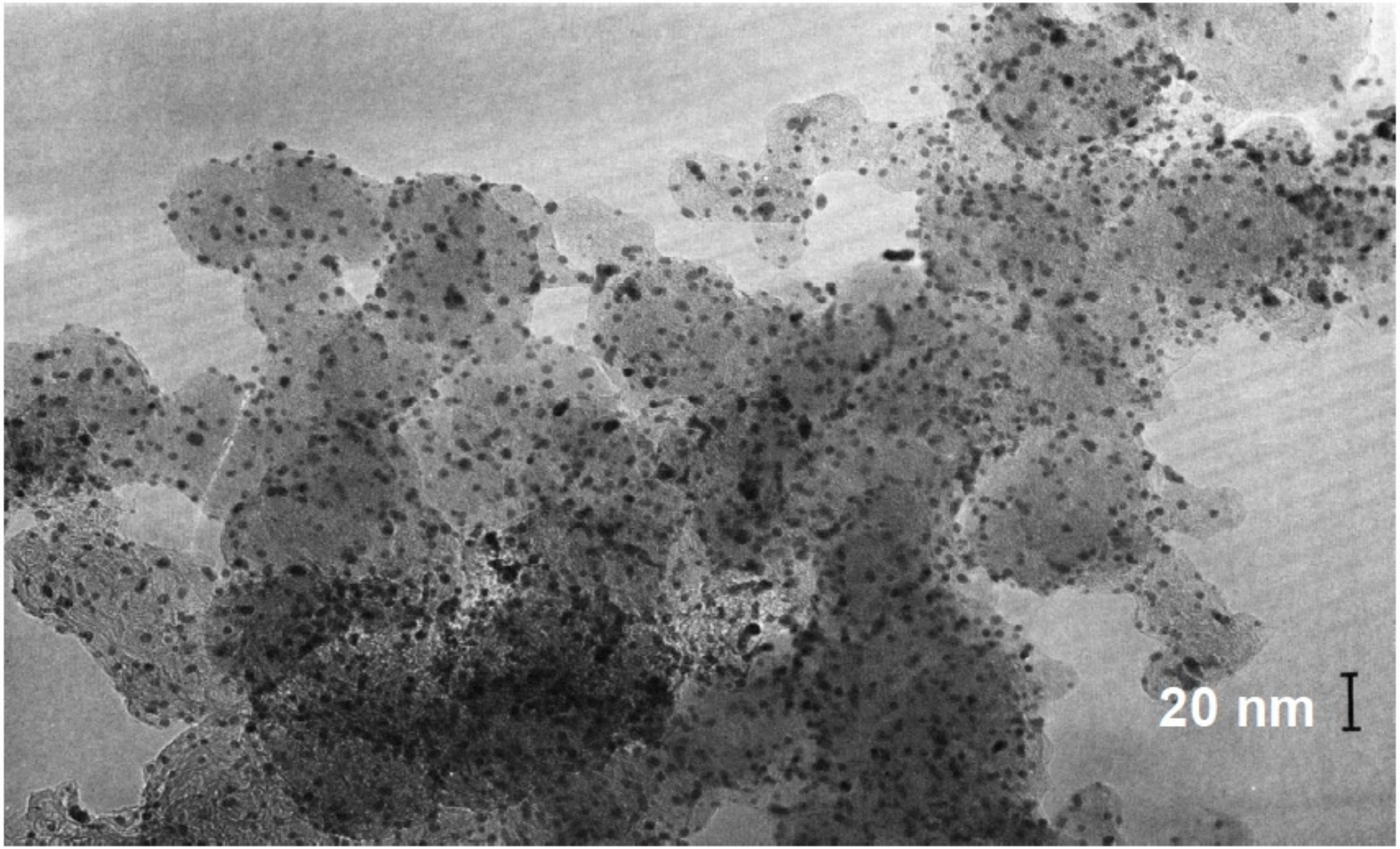
Pt-catalyst

cell frame / bipolar plate

current collector / gas diffusion layer

Copied from G.G. Scherer, PSI, Fuel Cell Tutorial, European Fuel Cell Forum, Lucerne

Platinum nano particles supported on carbon particles



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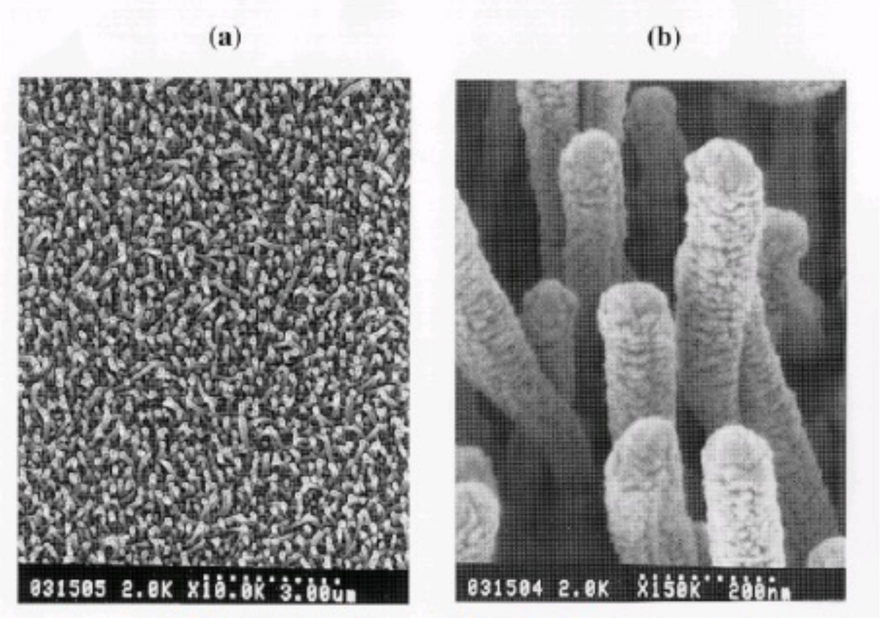
Example of commercial catalyst (3M)



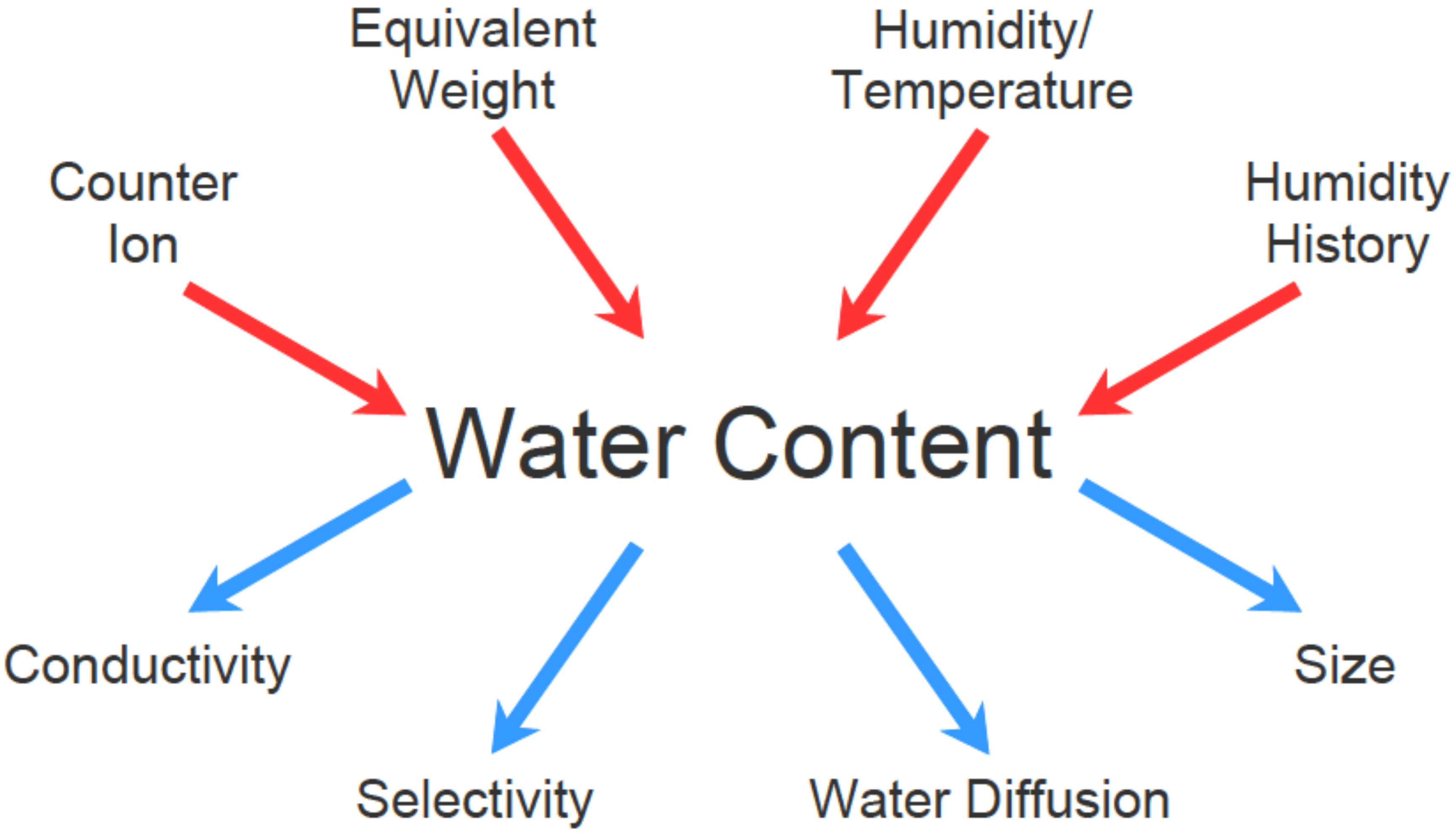
Pt coated nanostructured whisker supports (0.25 mg/cm^2), at 10,000 X plan view (left) and 150,000 X ,45° view (right).

Low platinum loading

No ionomer impregnation

Copied from G.G. Scherer, PSI, Fuel Cell Tutorial, European Fuel Cell Forum, Lucerne

PEFC : critical water management



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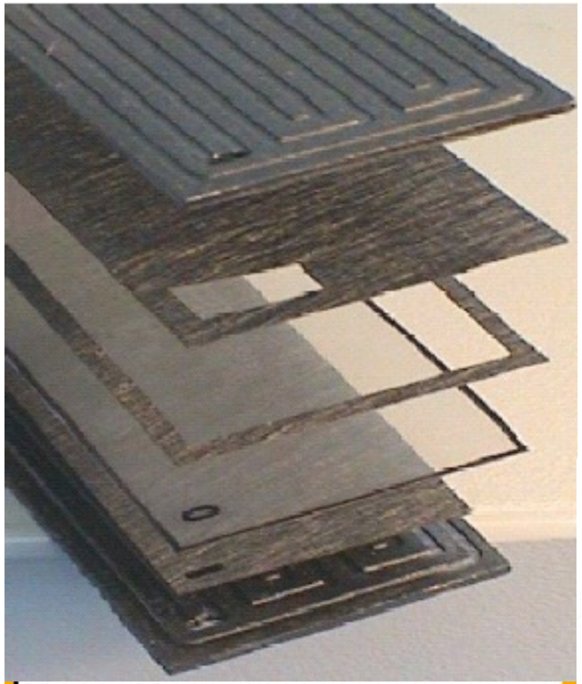
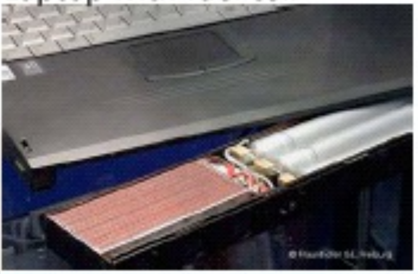



70 kW_e


2 kW_e

5 - 50 W_e

Laptop with fuel cell

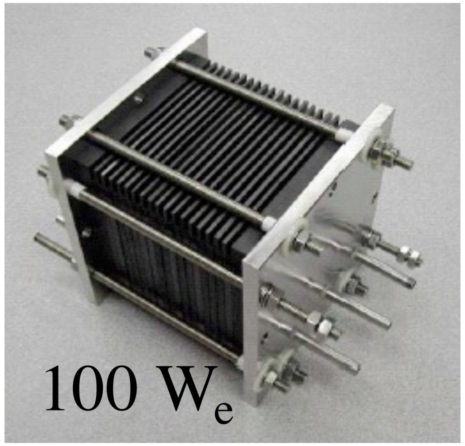


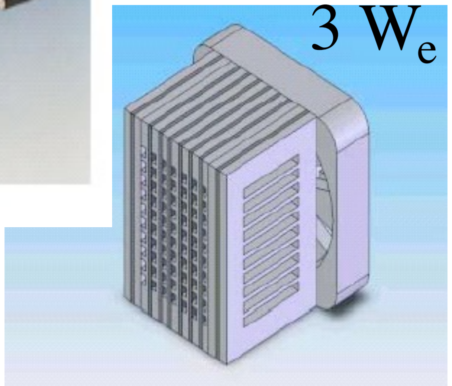
Fuel cell camcorder


5 kW_e


Fuel cell power box


Professional camera with fuel cell


100 W_e


3 W_e

PEFC applications

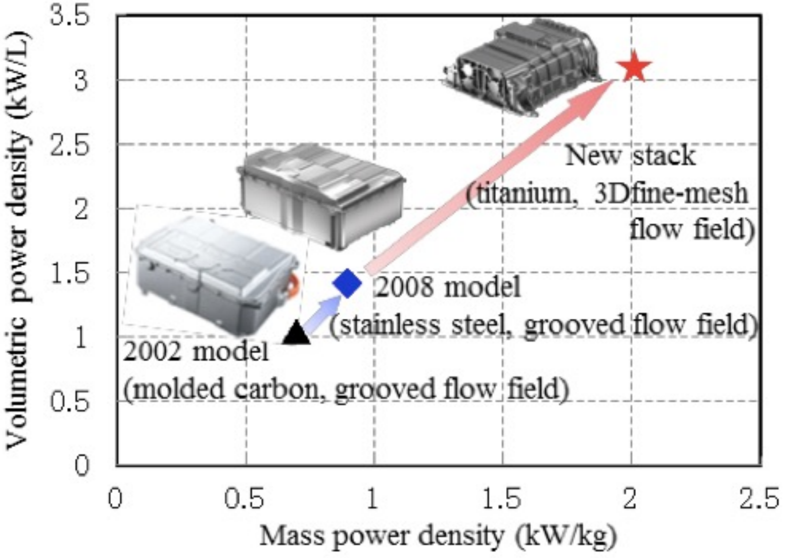
Daimler fuel cell car (PEFC)

- B-class F-CELL
- 30’000 km test
- 700 bar H_2 floor tank
- 400 km range
- 100 kW, 290 Nm

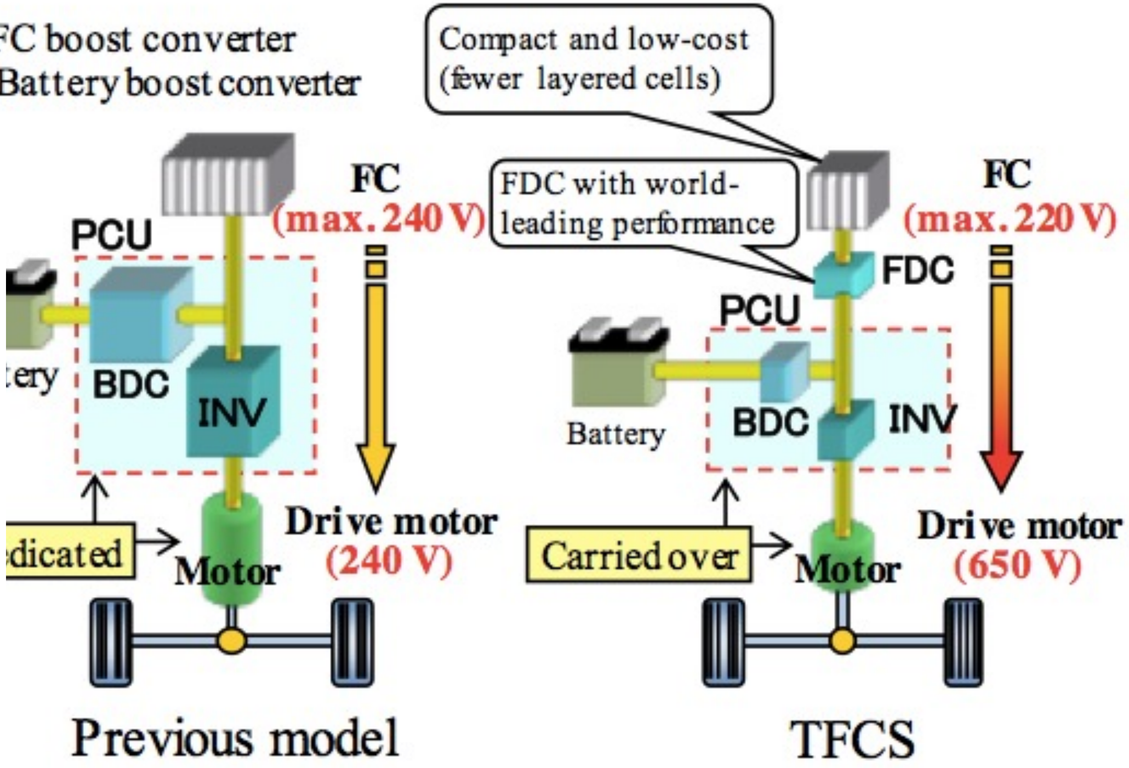
Toyoto Mirai

On the market since January 2015
Many 1000 vehicles sold.

https://www.youtube.com/watch?v=vmk15ZjgFXg



FDC: FC boost converter
BDC: Battery boost converter



Some facts

- Toyota invested 15 billion Fr in developing the Mirai car
- Hyundai employs 4000 fuel cell system engineers
- A fuel cell car consumes 1 kg H_2 per 100 km
  - 1 kg H_2 = 33 kWh
  - 1 L gasoline = 9 kWh
  - hence this is equivalent to <4L gasoline /100 km
- Cost:
  - H_2 price = 10€/kg
  - Gasoline price = 1.7 Fr/L
  - hence H_2 cost is (already) the same as for a 7L/100km gasoline car

Portable electronics: direct methanol PEFC 0.1 W

(Copied from G.G. Scherer, Tutorial, European Fuel Cell Forum, Lucerne)

Comment: (1) H^+ conduction

- The 2 former fuel cell types use **proton** (H^+) **conduction**, in a liquid (acid) or a wet membrane (polymer)
- They operate at 200C (acid) or below 100C (polymer)
- At such **low temperature**, the **only fuel** reactive enough to be (electrochemically) oxidized is **hydrogen** (H_2)
  - …and methanol (MeOH), but with much reduced power output
- Moreover, the **only electrodes** capable to catalyze this reaction ($H_2 + ½O_2 \rightarrow H_2O$) at such low temperature are the **noble metals** (Pt-group) – cf. activation overpotential (charge transfer at cathode) and exchange current density j_0

=> limited to H_2 and Pt

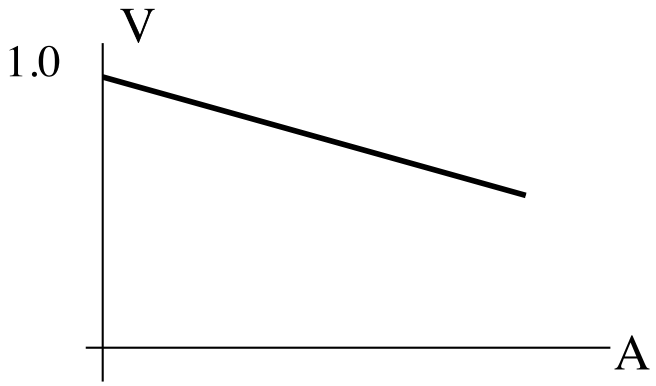
Comment: (2) oxygen conduction

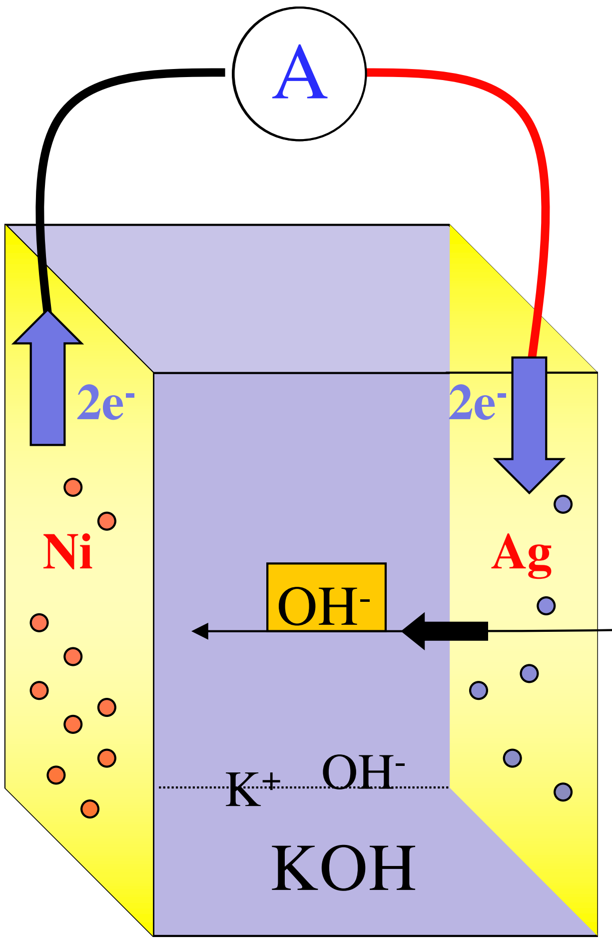
- The following 3 fuel cell types use a form of **oxygen** ion **conduction**
- Two use a ceramic resp. molten salt conductor, which operate at high temperature (>600C)
- At such **high temperature**, **other fuels than H_2** become reactive enough for (electrochemical oxidation) (CO, CH_4,..)
- Moreover, high temperature is favorable for fast electrode kinetics, making **cheaper catalysts** than noble metals possible (Ni, oxides,..)

=> possible with hydrocarbons, on Ni catalyst

3. Alcaline Fuel Cell (AFC)

< 1 V





$$H_2 + \boxed{2OH^-} \Leftrightarrow 2H_2O + 2e^-$$

$$\tfrac{1}{2}O_2 + 2e^- + H_2O \Leftrightarrow \boxed{2OH^-}$$

$$H_2 + \tfrac{1}{2}O_2 \Leftrightarrow H_2O$$

on-board 12 kW_e

application:
transport, or
low cost stationary

80C

Alcaline FC

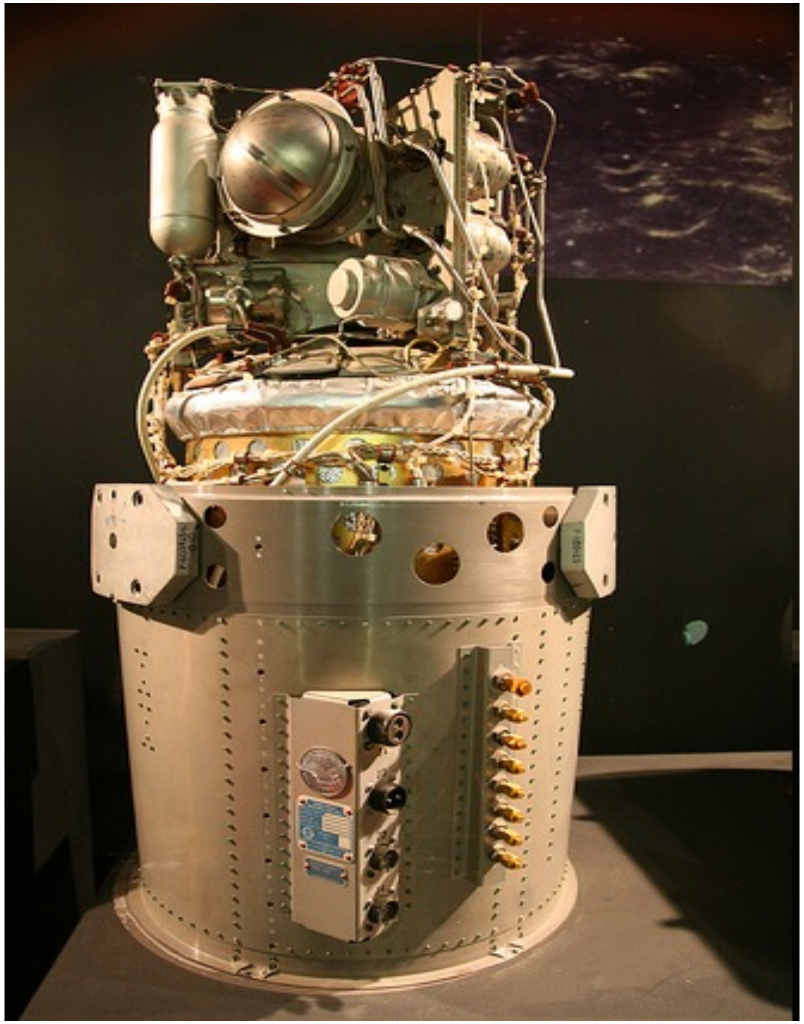
- requires pure H_2, air without CO_2 (carbonatisation of KOH electrolyte)
- …but CO_2 is easily scrubbed out
- cheaper catalysts possible, as alternative to Pt (Ni anode, Ag cathode)
- robust
- can be mass-manufactured
- 60% efficiency based on H_2

  - Varta batteries (D)
  - Siemens (transport)
  - Univ. Graz (AUT, Prof. Kordesh)
  - **AFC Energy (UK) => 0.5-1 MWe systems**

    (market: H_2 byproduct from NaCl salt electrolysis)

AFC example from Apollo Spacecraft (1970'ies)

Manufacturer: Pratt & Whitney Aircraft Division of United Aircraft Corporation



3 fuel cells stacks on board

pure liq H_2 and O_2

operating T 206 ° C

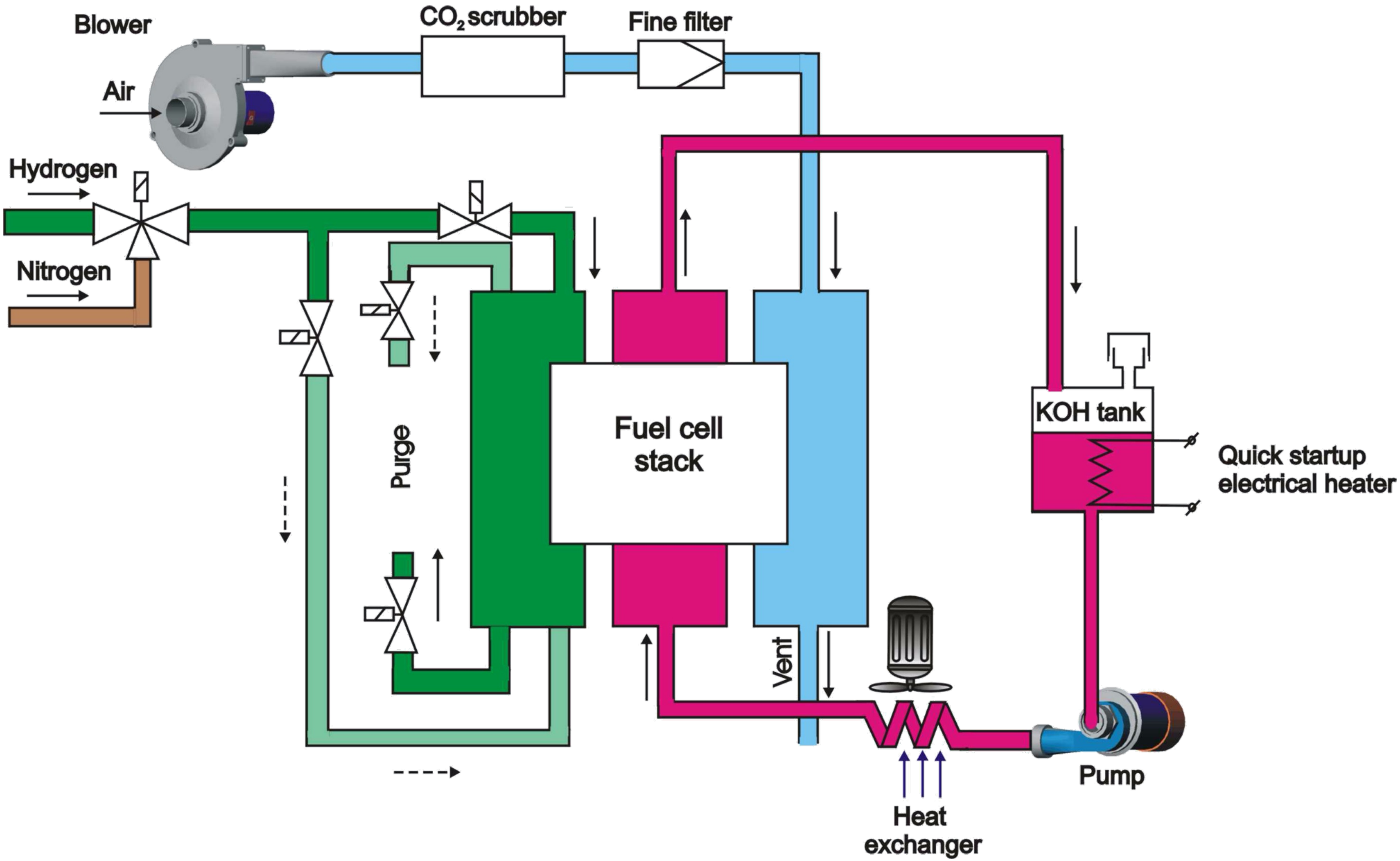
efficiency 70% !

31 cells in series operating at 27-31 V for a
power output of 0.56-1.42 kW,
and a max of 2.3 kW (each stack)

Construction materials: Ti, stainless steel, Ni
Electrodes: Ni with Pt catalyst
(no limit on noble metal use for space application!!)

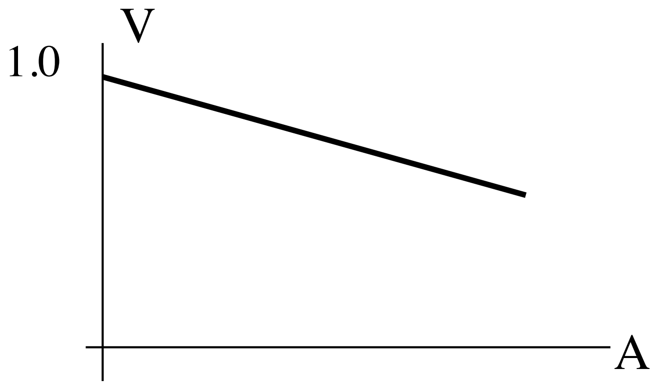
AFC system

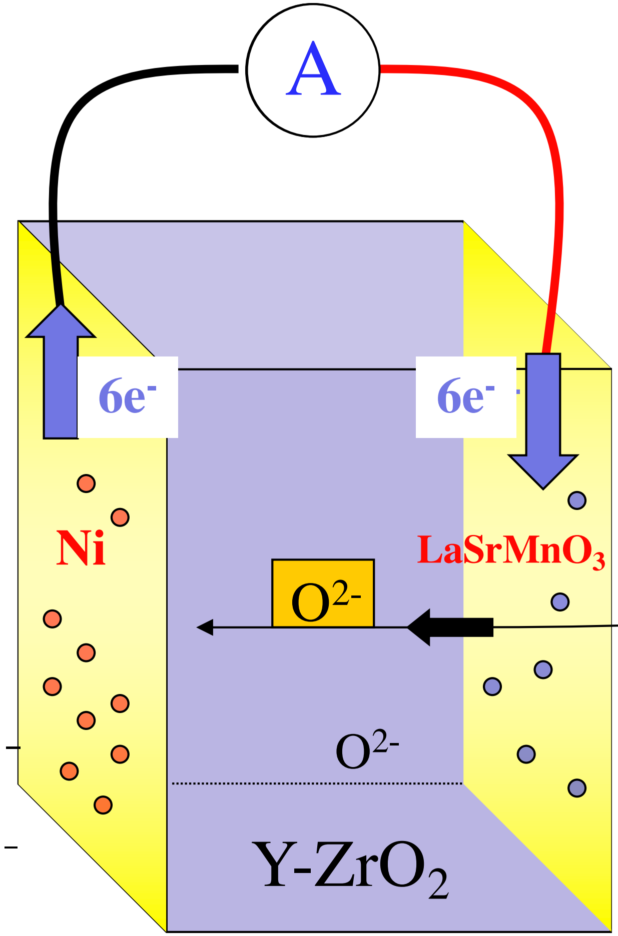
characterised by a ***circulating electrolyte***



4. Solid Oxide Fuel Cell (SOFC)

< 1 V





$$H_2 + \boxed{O^{2-}} \Leftrightarrow H_2O + 2e^-$$

$$CO + O^{2-} \Leftrightarrow CO_2 + 2e^-$$

$$CH_4 + 4O^{2-} \Leftrightarrow 2H_2O + CO_2 + 8e^-$$

$$CH_3OH + 3O^{2-} \Leftrightarrow 2H_2O + CO_2 + 6e^-$$

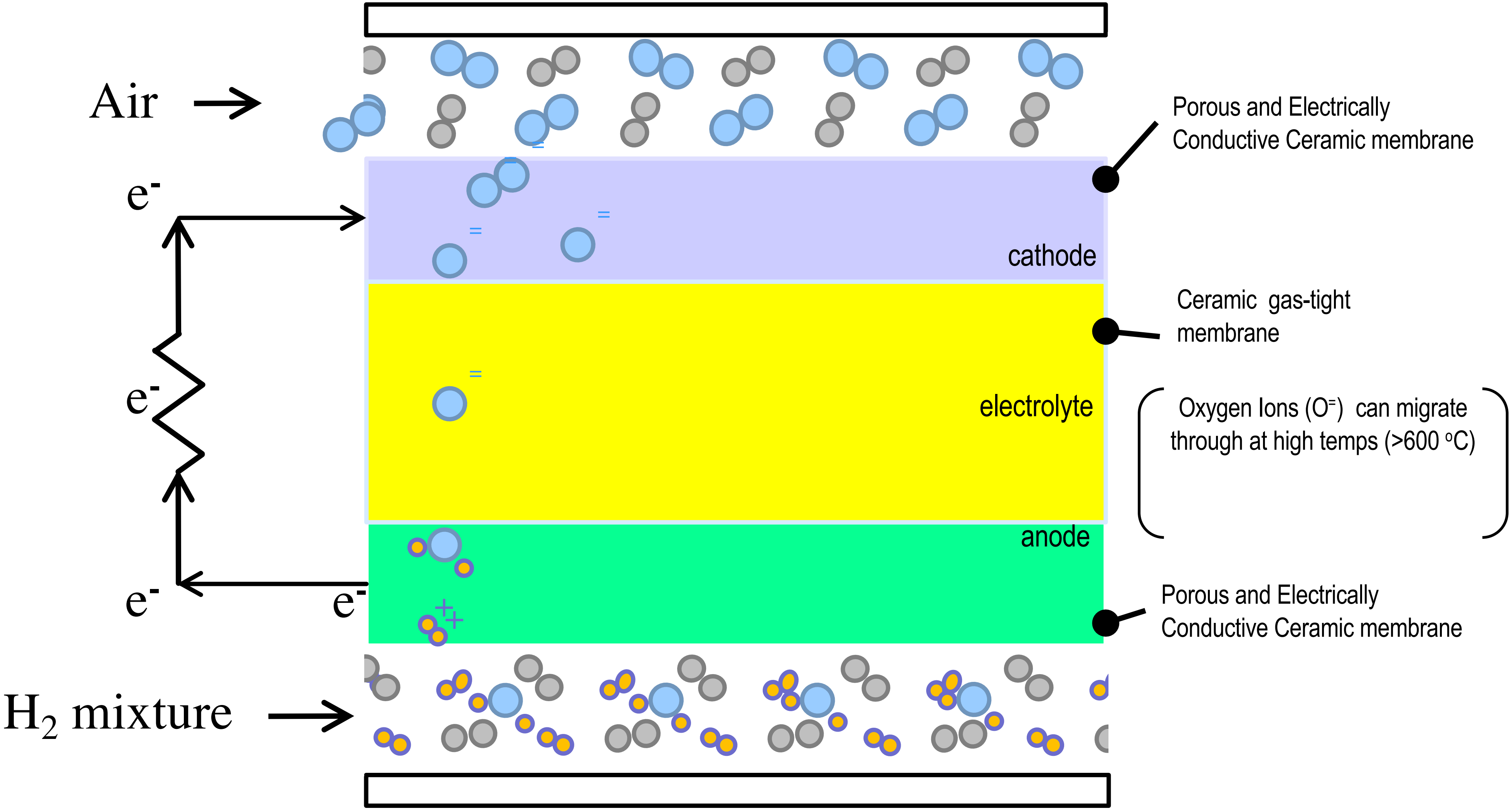
$$\tfrac{1}{2}O_2 + 2e^- \Leftrightarrow \boxed{O^{2-}}$$

$$H_2 + \tfrac{1}{2}O_2 \Leftrightarrow H_2O$$

cogeneration, stationary

600-1000C

Animated SOFC



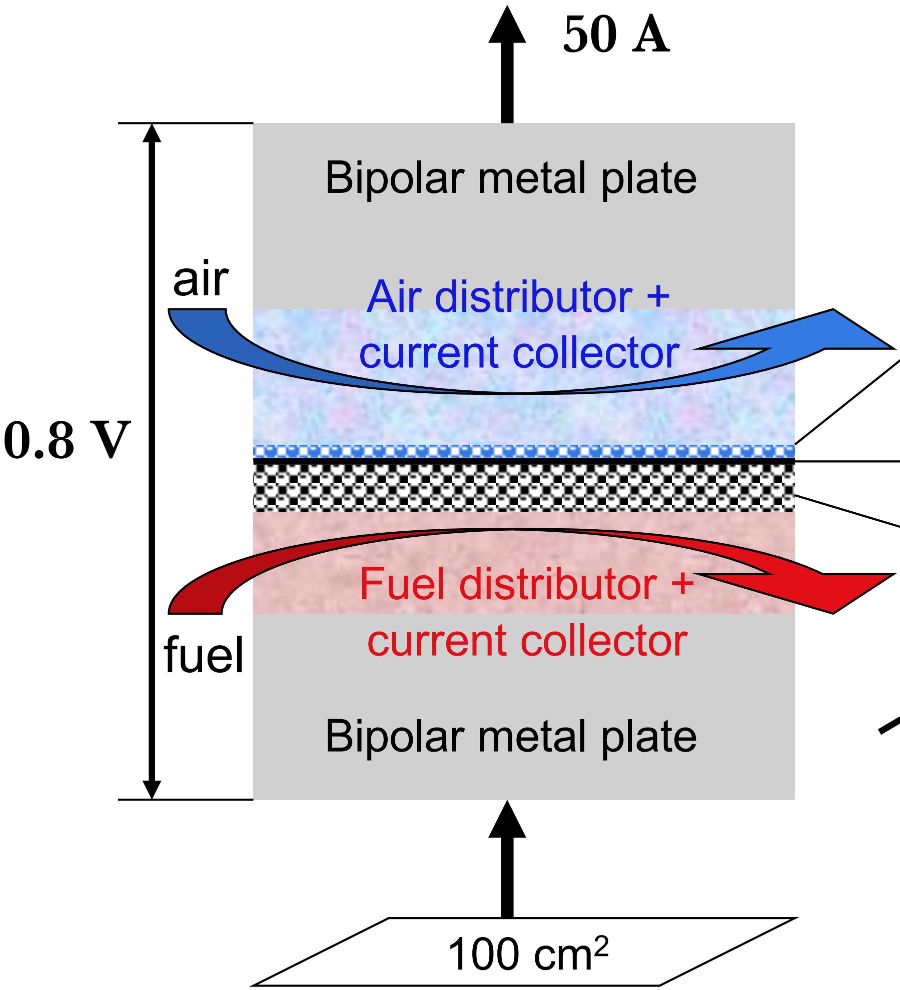
Porous and Electrically Conductive Ceramic membrane

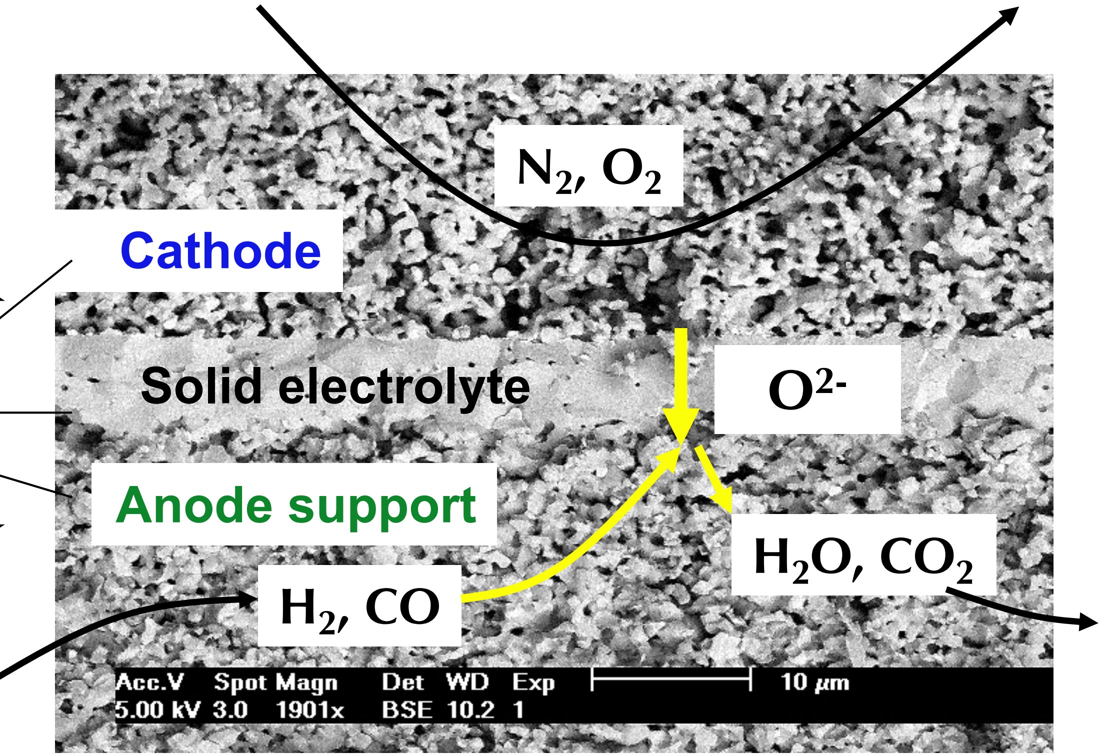
Ceramic gas-tight membrane

Oxygen Ions ($O^=$) can migrate through at high temps (>600 °C)

Porous and Electrically Conductive Ceramic membrane

SOFC interfaces detail

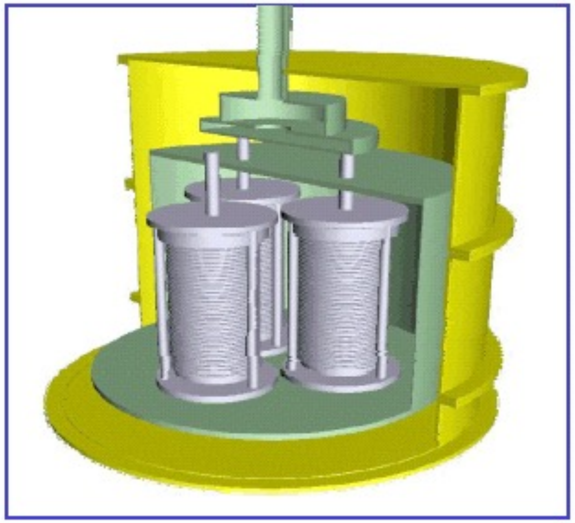




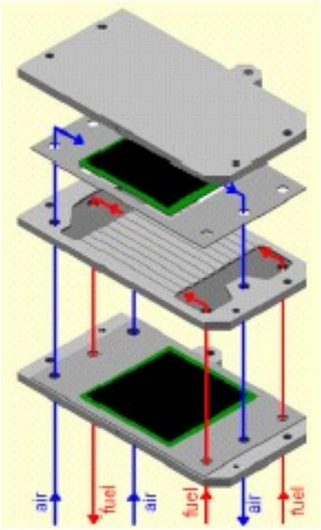
Operating regime :
700-800C
1 bar (to 5 bar)

TOHO GAS
1 kW_e

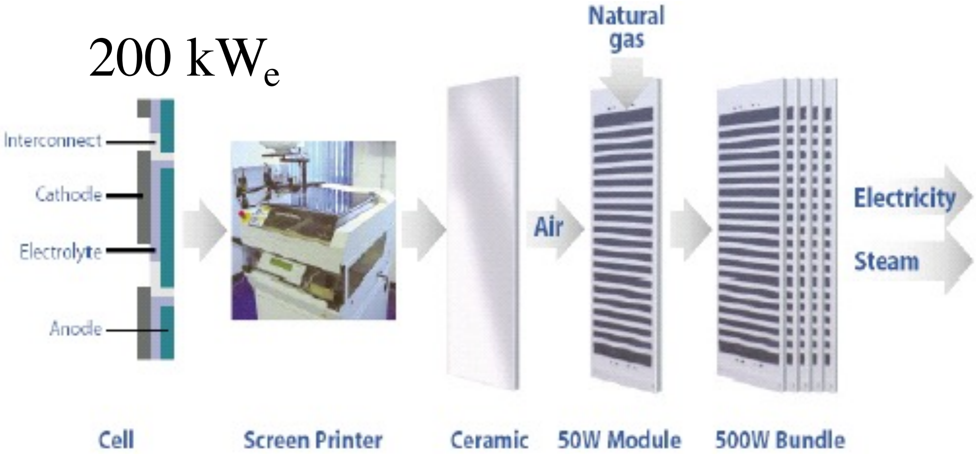
Kansai Electric
3 kW_e



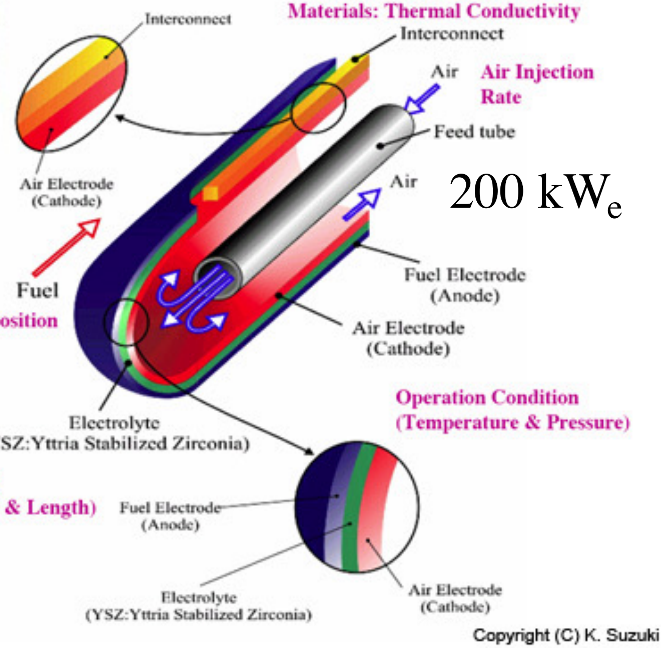
FZJülich (D)



200 kW_e



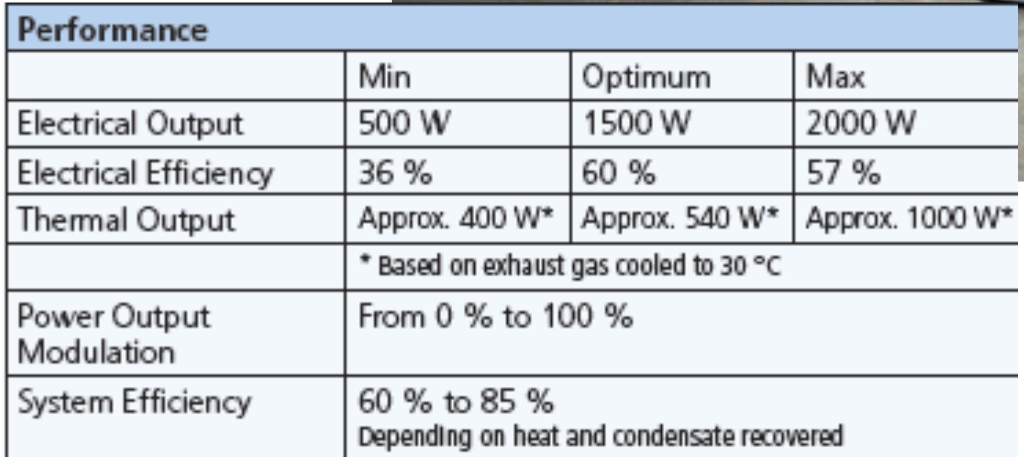
RollsRoyce Power (UK)



200 kW_e

Siemens-Westinghouse

2 kWe net 63% ac efficient SOFC system



Performance			
	Min	Optimum	Max
Electrical Output	500 W	1500 W	2000 W
Electrical Efficiency	36 %	60 %	57 %
Thermal Output	Approx. 400 W*	Approx. 540 W*	Approx. 1000 W*
	* Based on exhaust gas cooled to 30 °C		
Power Output Modulation	From 0 % to 100 %		
System Efficiency	60 % to 85 % Depending on heat and condensate recovered		

https://www.dailymotion.com/video/x2p2rmd

Multi-100 kWe SOFC

Inputs	
Fuels	Natural Gas, Directed Biogas
Input fuel pressure	15 psig
Fuel required @ rated power	0.661 MMBtu/hr of natural gas
Water required (for startup only)	120 gallons municipal water
Outputs	
Rated power output (AC)	100 kW
Electrical efficiency (LHV net AC)	> 50%
Electrical connection	480V @ 60 Hz, 4-wire 3 phase
Physical	
Weight	10 tons
Size	224" x 84" x 81"
Emissions	
NOx	< 0.07 lbs/MW-hr
SOx	negligible
CO	< 0.10 lbs/MW-hr
VOCs	< 0.02 lbs/MW-hr
CO_2 @ specified efficiency	773 lbs/MW-hr on natural gas, carbon neutral on Directed Biogas

www.bloomenergy.com/products

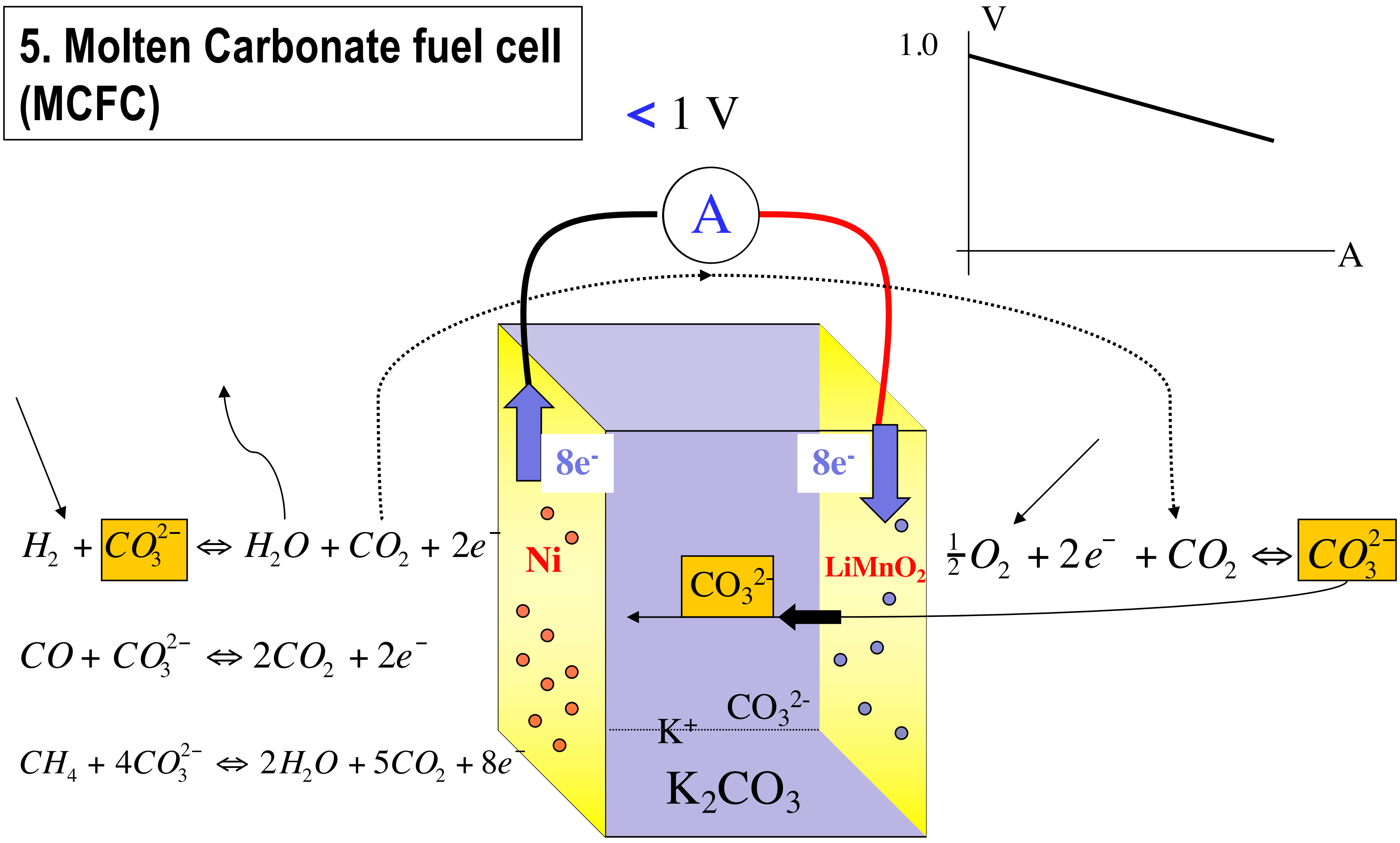
SOFC characteristics

- tubular : robust (>12 yr proven lifetime), but expensive

  goal = few MWe in a hybrid cycle with a micro-gasturbine
- planar : proven lifetime 70’000 h, with **mass-manufacturing** potential; typically 1-10 kW_e modular units, demonstrated up to MWe
- **60% η_{el}** achieved for both designs
- fuel : NG, LPG, diesel, biogas, NH_3, alcohols, wood gas,…
- **Materials challenges** :
  - FeCr steel interconnect corrosion
  - electrode poisoning from CrO_x steel vapors
  - anode (Ni) reoxidation (=> NiO : expansion) during operation
  - differential thermal expansion, layer delaminations
  - imperfect sealing (leaks)
  - electrode microstructure coarsening, e.g. Ni particle growth
  - …..

5. Molten Carbonate fuel cell (MCFC)

< 1 V



$H_2 + \boxed{CO_3^{2-}} \Leftrightarrow H_2O + CO_2 + 2e^-$

$CO + CO_3^{2-} \Leftrightarrow 2CO_2 + 2e^-$

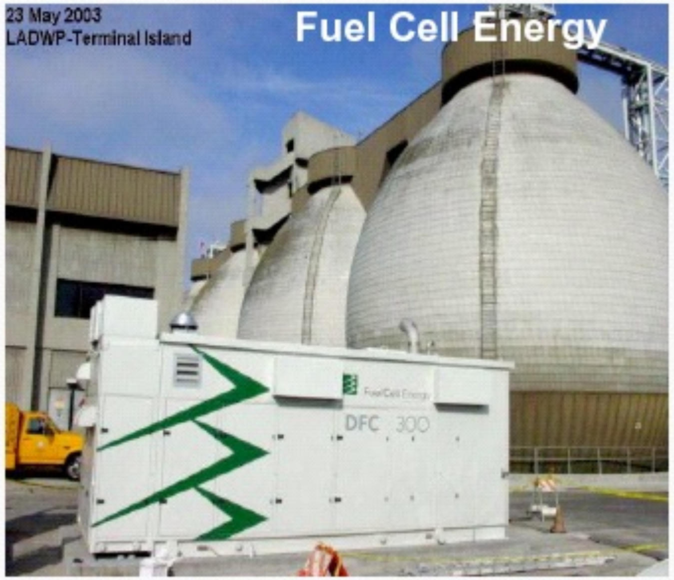
$CH_4 + 4CO_3^{2-} \Leftrightarrow 2H_2O + 5CO_2 + 8e^-$

$\tfrac{1}{2}O_2 + 2e^- + CO_2 \Leftrightarrow \boxed{CO_3^{2-}}$

$$H_2 + \tfrac{1}{2}O_2 \Leftrightarrow H_2O$$

650° C

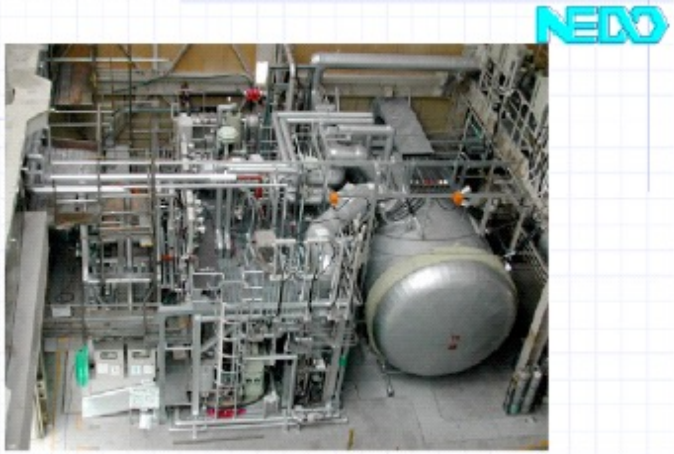
Photos courtesy of: FCE, AFC, MTU,NEDO, KEPRI


23 May 2003
LADWP-Terminal Island

Fuel Cell Energy


Rhon-Klinikum Hospital (MTU)
Bad Neustadt & Bad Berka,
Germany


Ansaldo Fuel Cells S.p.A.



Full View of 300kW-class Compact System
in KAWAGOE Test Station


KEPRI

MCFC cogeneration units of 250 kW_e - 1 MW_e

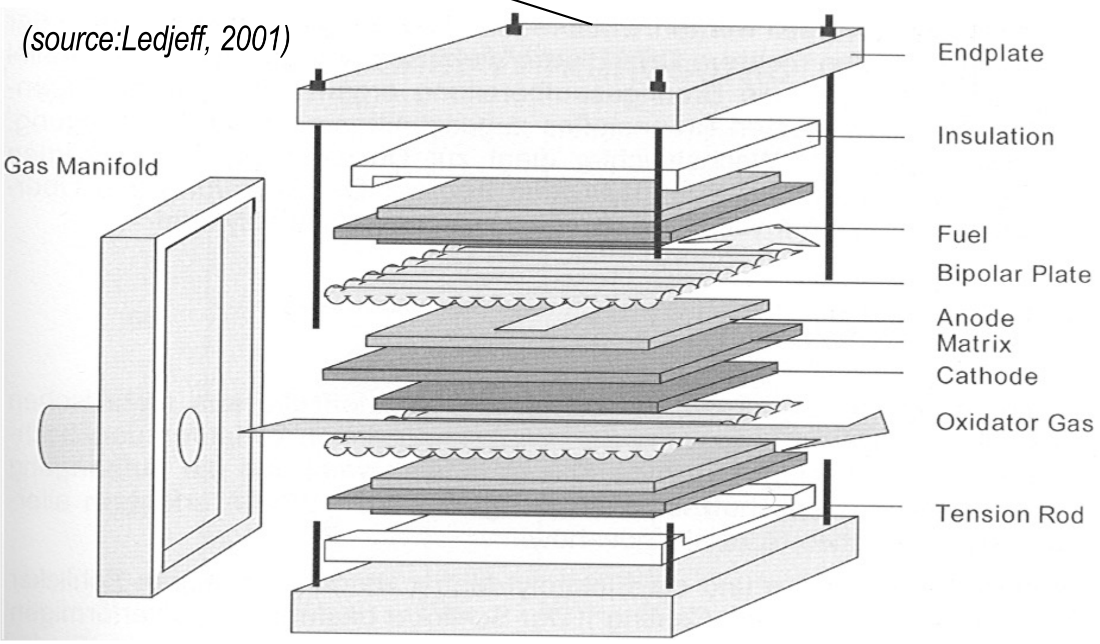
MCFC design & materials

World leading : FUEL CELL ENERGY company :

https://www.youtube.com/watch?v=lYmOHfmfSsU

650C

1 m^2



(source:Ledjeff, 2001)

- electrolyte = Li_2CO_3 or Na_2CO_3 mixed with K_2CO_3, molten at 600-700° C, in a porous ceramic matrix of $LiAlO_2$
- anode : NiCr or NiAl
- cathode : Li-doped NiO
- interconnection : stainless steel

- CO_2 recirculation imposes a minimal size on the system (250 kW_e)
- 4 modules are combined to one 1 MWe unit etc.

MCFC characteristics

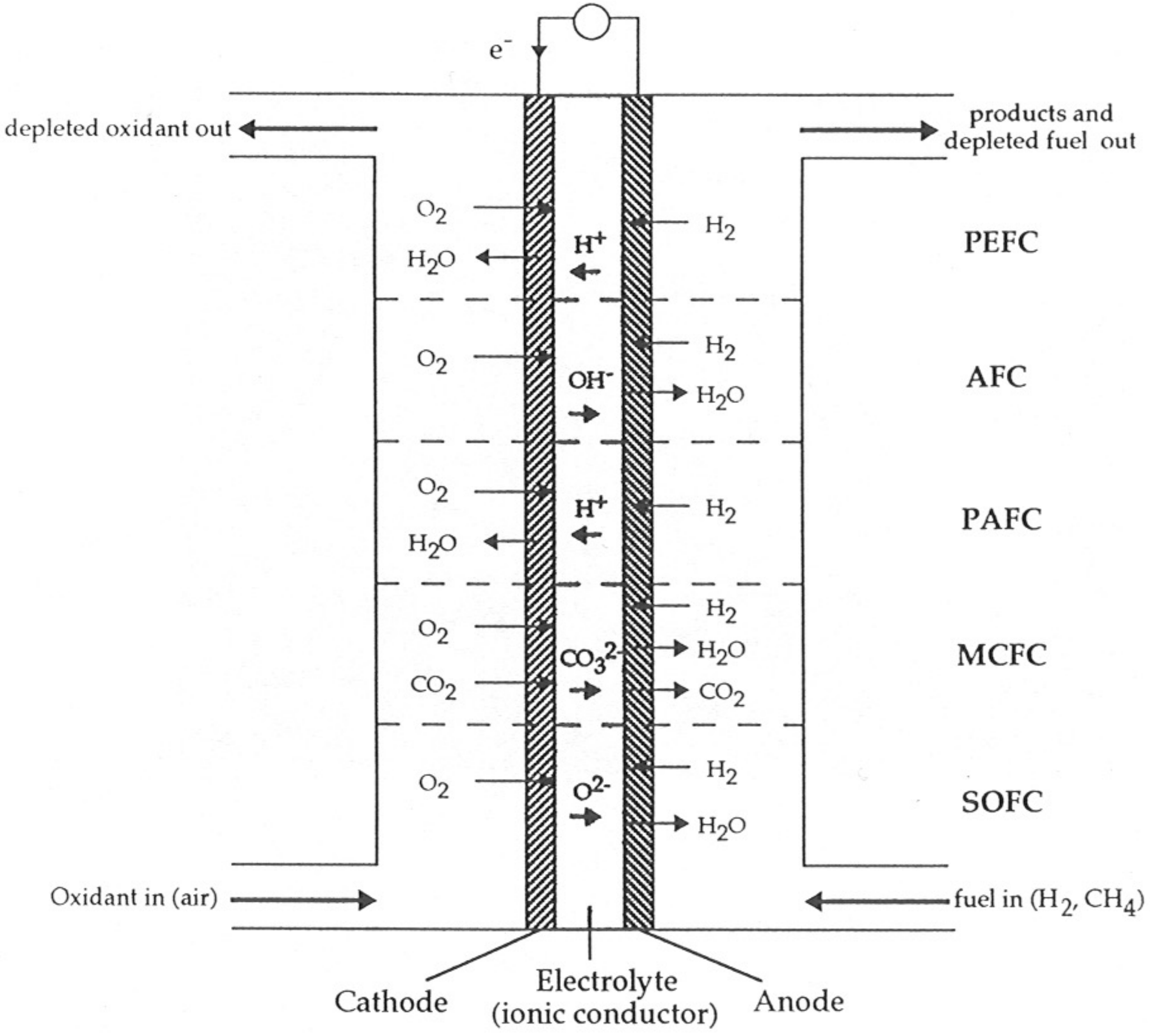
- high $T_{operation}$ allows thermal integration of fuel processing
- η_{el} 47% at 100 kWe
- goal: 55% at 1 MWe
- CC with μ-turbine : 56% @ 300 kWe
- market = 0.5-3 MWe cogeneration
- NG, coal gas, esp. **biogases**

Limitations :

- **steel corrosion** by molten salt
- gradual NiO **cathode dissolution** in the electrolyte (causing short-circuit); this explains why the electrolyte is thick (1 mm) => short-circuiting is “delayed” until several years …
- anode **creep** **(stack weight!)**
- cost :$4000/kW

The 5 FC types (summarised)

(according to $T_{operation}$ and the ionic conductor)



$T_{operation}$

50-100° C

50-100° C

200° C

650° C

650-1000° C

Fuels: distinction low vs. high T (H_2 vs C_xH_y)

Type	Electrolyte	Temperature	Fuel
AFC	Alcaline solution	20-100° C	**H_2**
PEFC DMFC	Polymere membrane	20-100° C	**H_2** **methanol**
PAFC	liquid acide	20° C	**H_2 (nat. gas)**
MCFC	Molten salt	650° C	**C_xH_y**
SOFC	Solid ceramic	600-1000° C	**C_xH_y**

"direct" methanol ← DMFC

Materials in fuel cells: low vs high T (Pt vs Ni)

Type	Electrolyte	Cathode	Anode	Interconnect	Dimensions
AFC	KOH	Ag	Ni	conducting composite	flat,50-500cm^2
PEFC	« Nafion » («sulfonated teflon »)	**Pt** on C	**Pt**(-Ru)	graphite	flat, 5-500 cm^2
PAFC	H_3PO_4	**Pt** on C	**Pt** on C	graphite	flat, 1 m^2
MCFC	$(Na,K,Li)_2$-CO_3	NiO or $LiCoO_2$	**Ni**	inox	flat, 1 m^2
SOFC	90% ZrO_2 + 10% Y_2O_3	$LaSrMnO_3$ $LaSrFeO_3$ $LaSrCoO_3$	**Ni**	Ferritic Cr or high Cr steel	flat,10-400 cm^2 tubes / (2 m long * 2 cm diam.)

Performance figures

Type	Cell size	Life (h)	W/cm^2	kW/L
PEFC	500 cm^2	80’000	1	3
AFC	500 cm^2	20’000	0.3	1
PAFC	1 m^2	100’000	0.3	0.2
MCFC	1 m^2	60’000	0.2	0.2
SOFC	400 cm^2	100’000	0.5	0.5

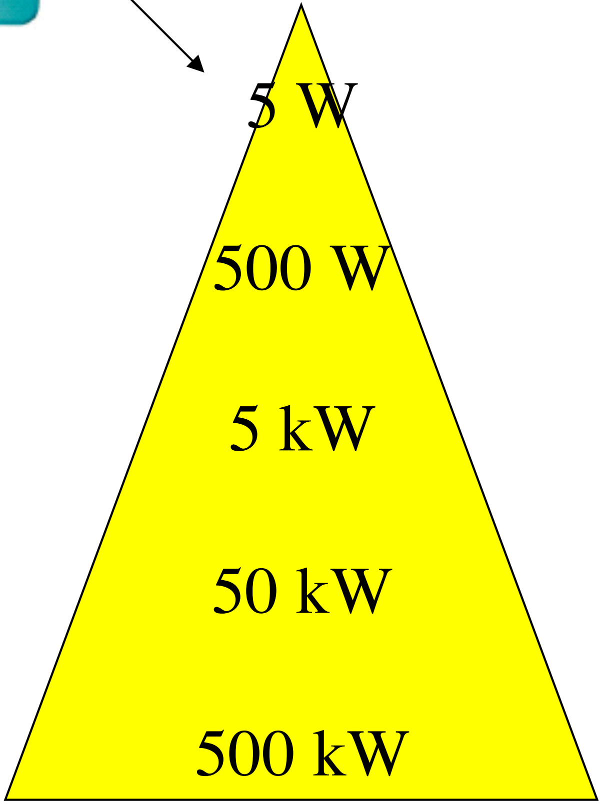
SOFC stack assembly (movie)

APPLICATIONS OVERVIEW

Portable	0.1-100 W	electronics (competing with batteries)	**DMFC, PEFC**
Small cogen.	1 kW - 100 kW	«best» range (lower competition from μT or diesel engines)	**SOFC, PEFC**
Transport	10 kW - 200 kW > 1 MW	vehicles, buses ships	**PEFC, DMFC, AFC** **MCFC, SOFC**
Medium cogen.	0.2 MW - 3 MW	offices, schools, hotels, hospitals, supermarkets; industry (chem./ steel/ foods)	**PAFC, AFC** **MCFC** **SOFC**

Power size

Application examples

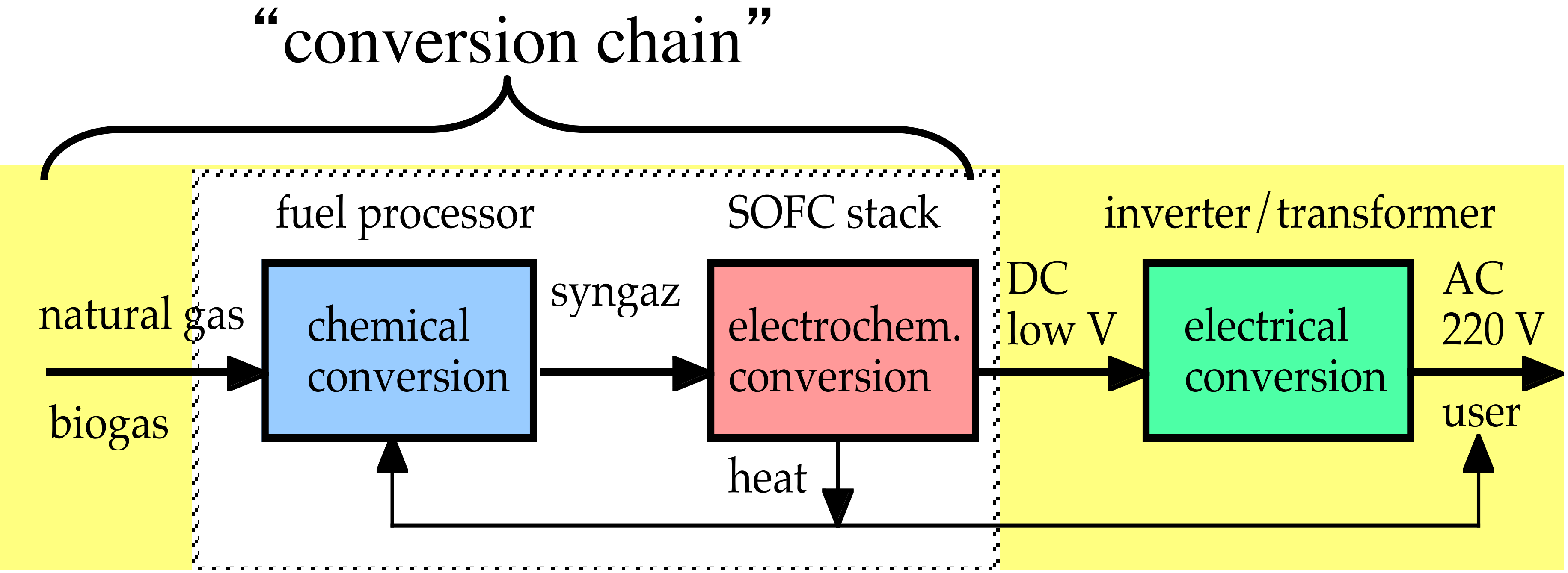


- Portable electronics
- Aggregates
- Houses
- Transport
- Urban cogeneration

(from F. Büchi, PSI)

PEFC
800 kW_e

FUEL CELL **SYSTEM**



A system of 3 series converters :

1. FUEL PROCESSOR (fuel treatment)
2. FUEL CELL STACK
3. Electrical conditioning (DC/AC, DC/DC)

ADVANTAGES of Fuel Cells

I. High **electrical efficiency**
    a) for small power size (1 We - 1 MWe)
    b) especially at *partial* load

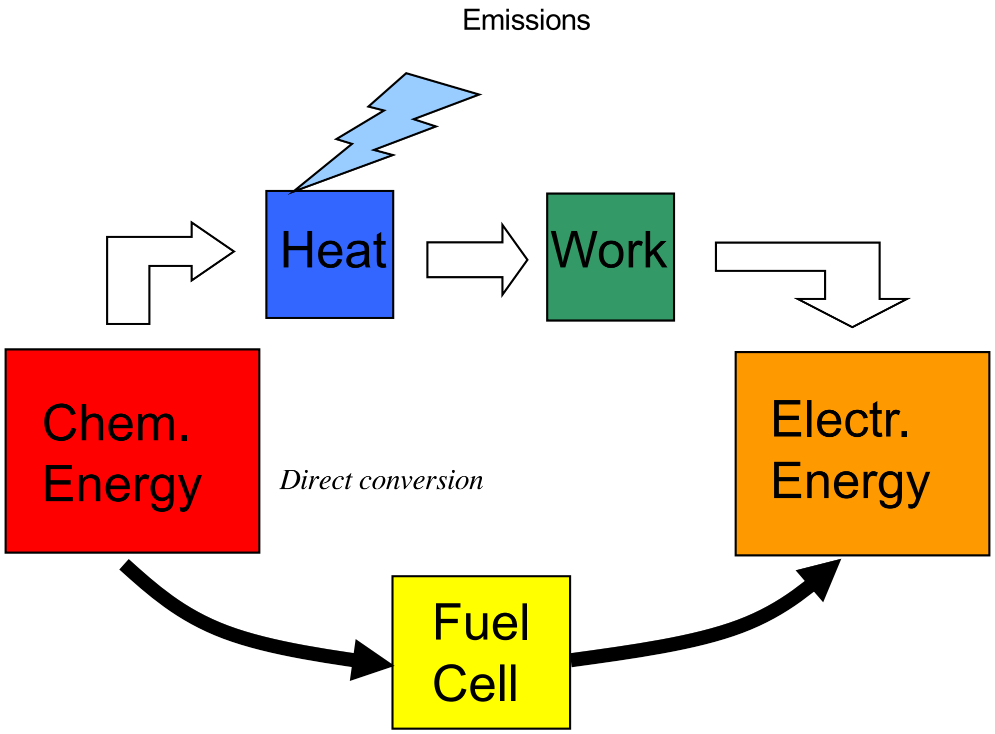
II. Low chemical and acoustical emissions

III. Cogeneration of electricity & heat

IV. Modularity

V. Fuel flexibility
    a) **fossils** (natural gas, diesel, coal gas,…)
    b) **renewables** (biogas, biodiesel, woodgas, ethanol,…)

A fuel cell bypasses a mechanical cycle



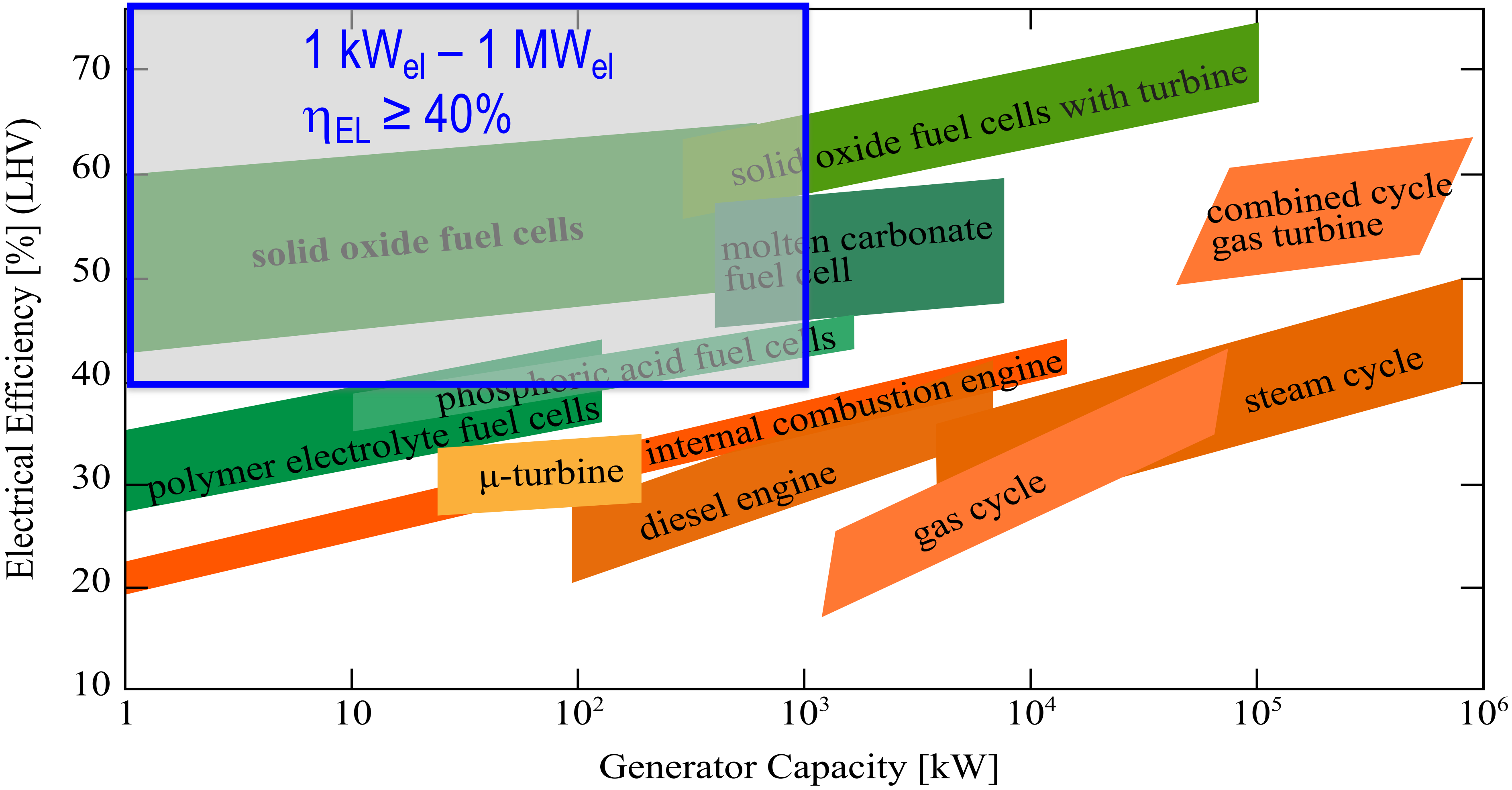
- rational use of (fossil) energy (**efficiency**)
- lowering **emissions** (integrated plants)
- electrical valorisation of **renewable fuels** (biogases, H_2, woodgas,..)

=> Motivation for fuel cell development

High electrical conversion at small power range

(based on natural gas, LHV)

(compiled by Quentin Jeangros, EPFL-CIME/Fuelmat)



electrical efficiency as fct(power size)

Electrical efficiency: combustion vs electrochemistry

CH_4 + air => $H_2O + CO_2$ + heat

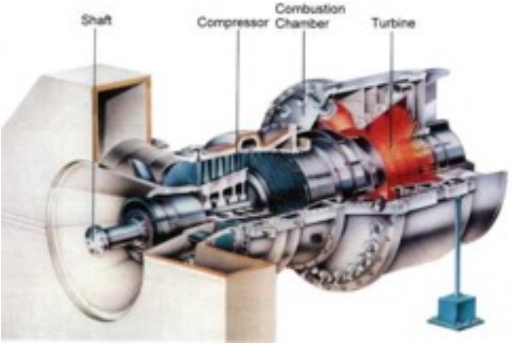
combustion → polluting emissions

ENGINES

http://www.sdeciepower.com/8.3L_Natural_Gas_Engine.htm

0.1 – 5 MW_{el}
η_{EL} 33-45%

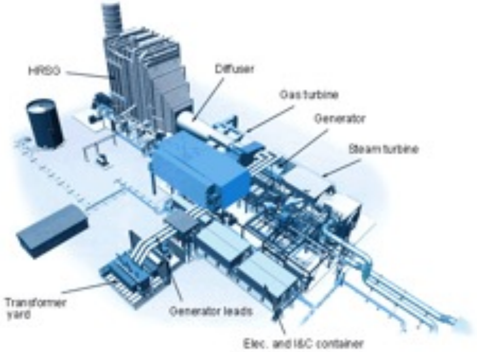
TURBINES



http://www.wartsila.com/sv/kraftverk/learning-center/gas-turbine-for-power-generation

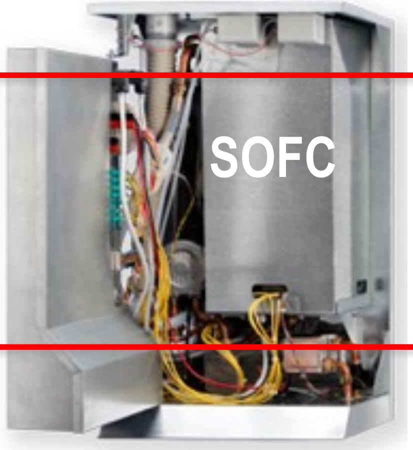
5-100 MW_{el}
η_{EL} 27-40%

COMBINED CYCLES



http://www.zeroco2.no/capture/sources-of-co2/combined-cycle-power-plant

50-500 MW_{el}
η_{EL} 50-60%



$CH_4 + 4\,O^{2-}$ ← $4\,O^{2-}$

↓ ↑

$H_2O + CO_2 + 8e^-$ → $8e^-$ + air (O_2, N_2)

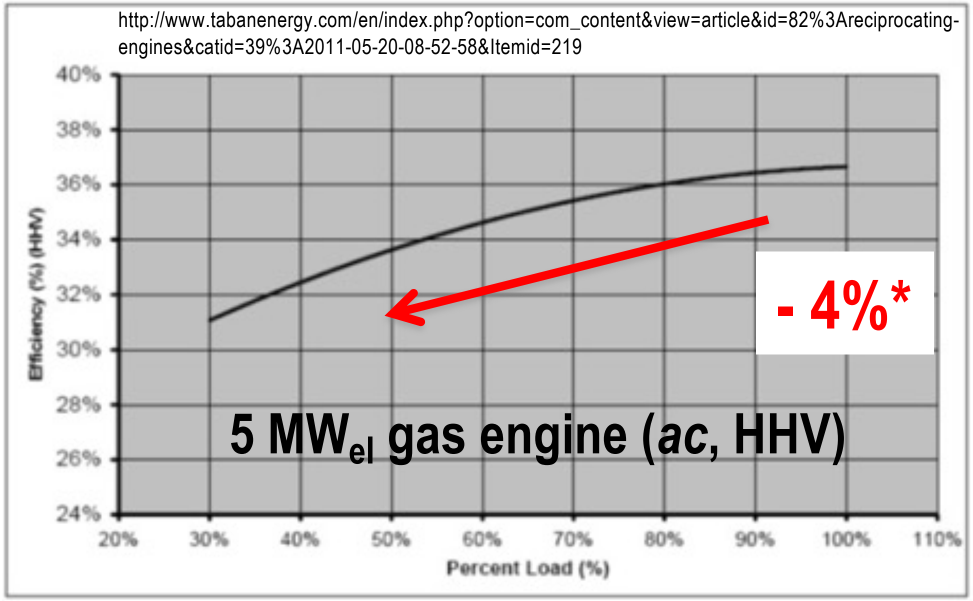
electrochemical
"combustion"

1 – 100 kW_{el}
η_{EL} 50-60%

no pollution

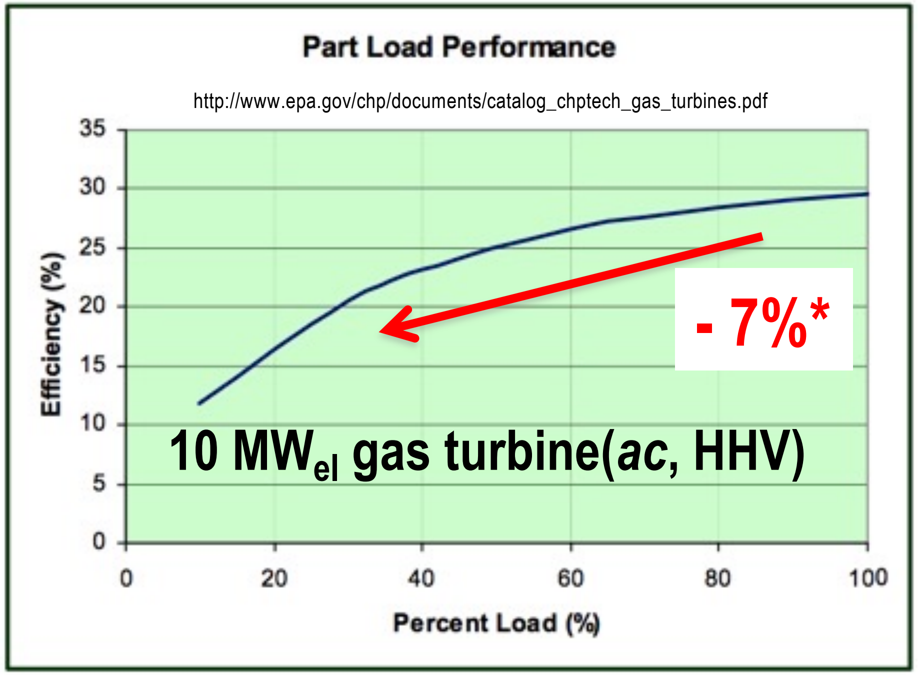
CH_4 + air => $H_2O + CO_2$ + ***dc* current** + cogenerated useful heat

Part load: technology comparison


http://www.tabanenergy.com/en/index.php?option=com_content&view=article&id=82%3Areciprocating-engines&catid=39%3A2011-05-20-08-52-58&Itemid=219

- 4%*

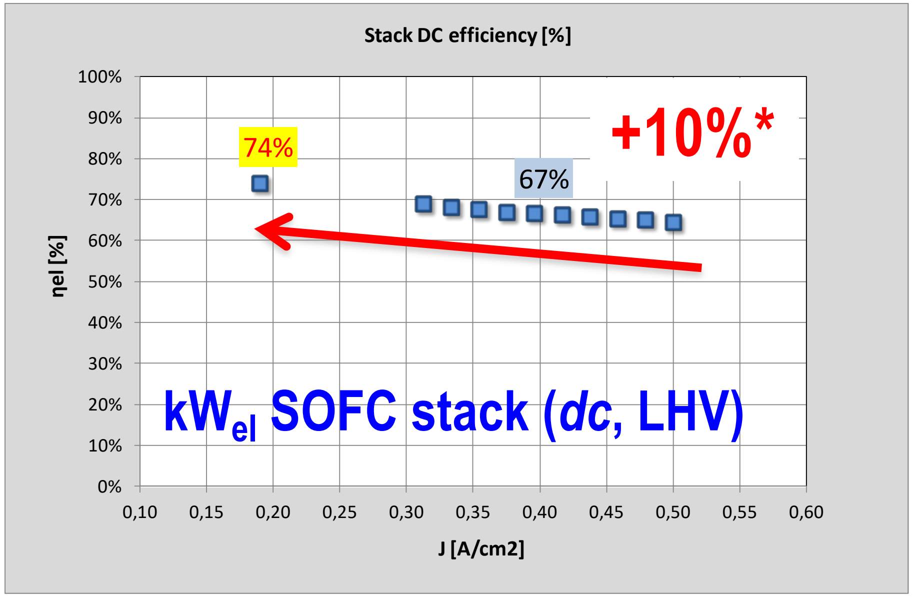
5 MW$_{el}$ gas engine (*ac*, HHV)


Part Load Performance

http://www.epa.gov/chp/documents/catalog_chptech_gas_turbines.pdf

- 7%*

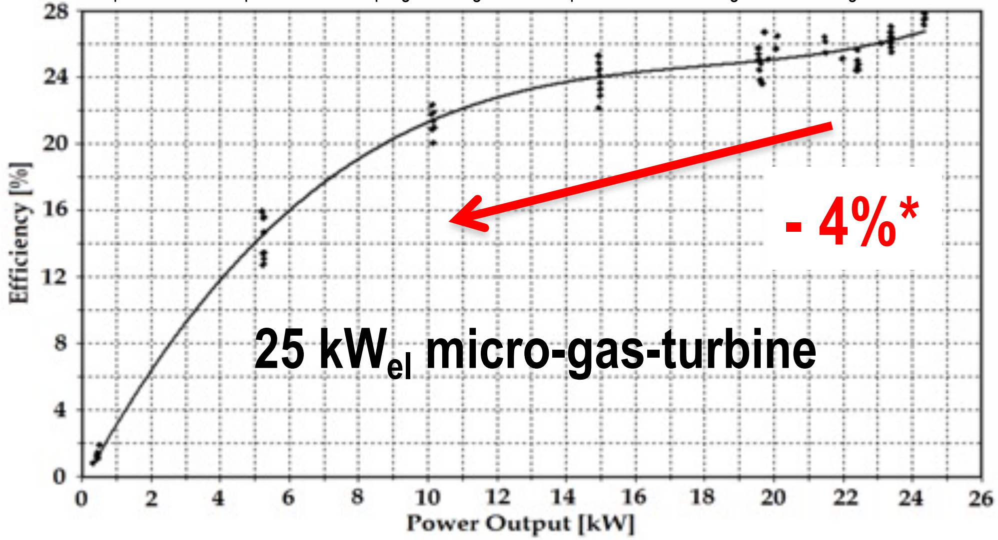
10 MW$_{el}$ gas turbine(*ac*, HHV)



+10%*

kW$_{el}$ SOFC stack (*dc*, LHV)

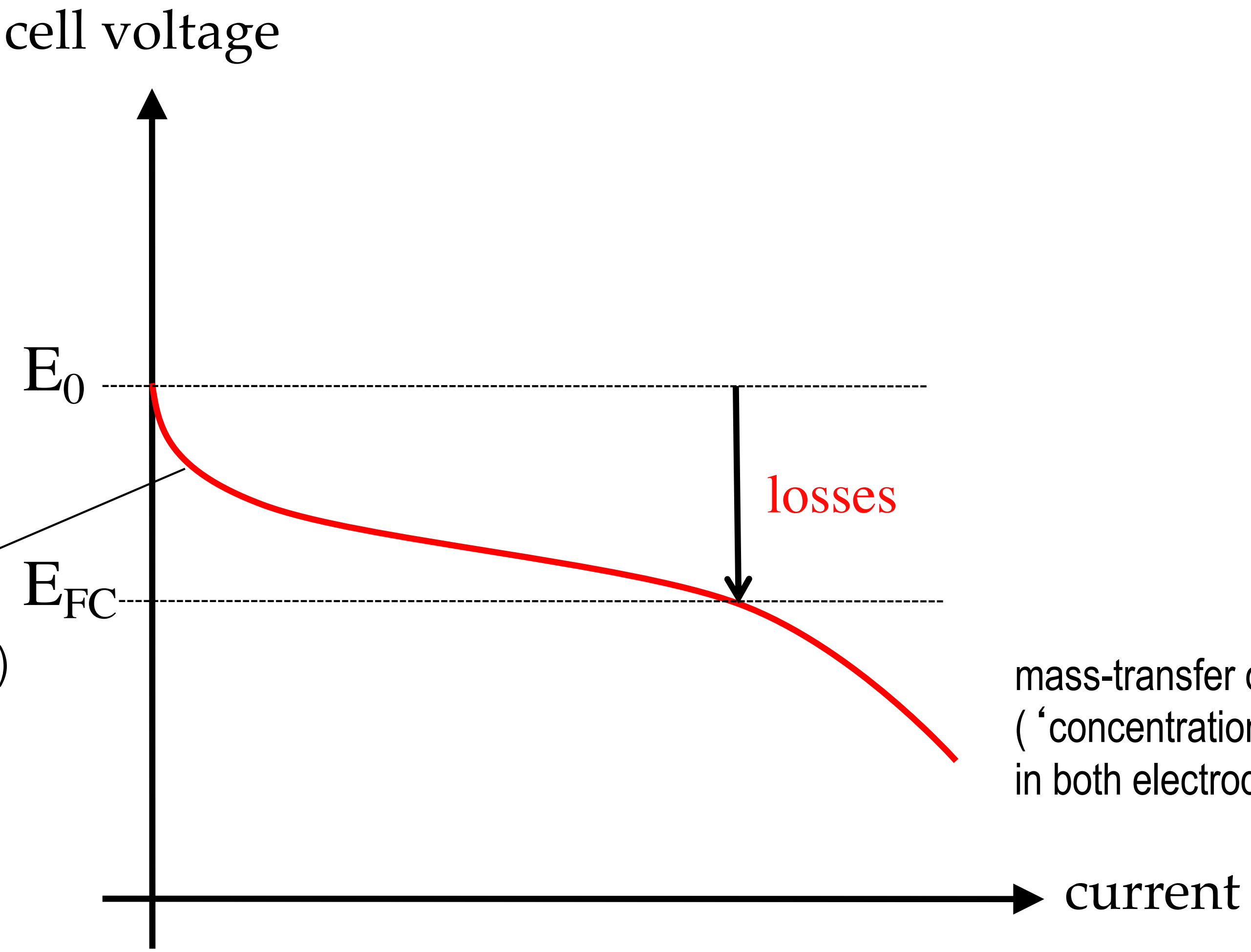
http://www.intechopen.com/books/progress-in-gas-turbine-performance/micro-gas-turbine-engine-a-review


- 4%*

25 kW$_{el}$ micro-gas-turbine

*from 100% to 40% power modulation

Characteristic i-V (current-voltage curve) of a fuel cell



Nernst voltage

charge-transfer
overpotentials
(‘activation’ losses)
at both electrodes

mass-transfer overpotentials
(‘concentration’ loss)
in both electrodes

Nernst equilibrium voltage and thermodynamics

- in a fuel cell at equilibrium (start-up, no net external current), fed with H_2/O_2 (air), one observes the **creation of a voltage**, characteristic for the reaction H_2/O_2 : **1.229 V** (at 298K and 1 atm)
- the useful **work** (here: **electricity**) exploitable from this reaction H_2/O_2 is given by the **Gibbs free enthalpy** of the corresponding chemical reaction $\Delta G_r = \Delta H_r - T\,\Delta S_r$:

  for $H_2 + 0.5\ O_2 \ \text{->} \qquad H_2O$

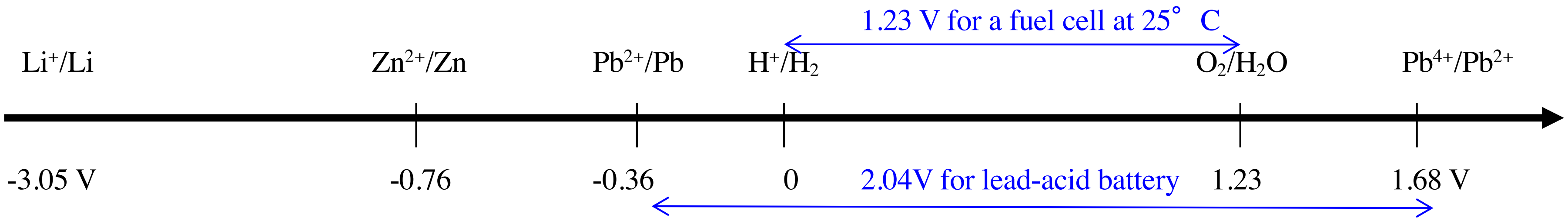
  where $\Delta G^0_r(298K,\ 1\ atm) = \mathbf{-237'150\ J/mole}$

- the link between ΔG_r (J/mole) and the created voltage, E (or V, or U) is given by the amount of charge (in Coulomb, C) that can be exchanged across this voltage :

  $\Delta G_r = -\ nF.E$

  (with n = 2 exchanged electrons for H_2, F = Faraday constant = 96484 C / mol e^-),

  which leads to the value $E^0 = \mathbf{1.229\ V}$ (for H_2/O_2 at 1 atm, 298 K)



Energy balance in a fuel cell :

from fuel heating value INPUT (ΔH^0) to electrical power OUTPUT (η_{el})

ΔH_{fuel}^{o} total thermal energy at inlet (often at 298K and 1 atm)

(LHV/ HHV of fuel = total heat)

loss $T\Delta S_r$ ↓

ΔG_{fuel} useful mechanical energy (total theoretical work)

↓ transformation Joule->Volt : relation ΔG - E : $\Delta G = -nFE$

(n = number of electrons exchanged per molecule of fuel)

(F = Faraday constant, 96484 C/mol)

E_{Nernst} equilibrium voltage (theoretical maximum, zero current))

voltage loss ↓

U_{cell} voltage losses (U_{cell} always < E_{Nernst})

- ohmic loss in each layer (R.i)
- transfer loss at each interface (polarisation η_{anode}, $\eta_{cathode}$)

=> useful cell power

$$E_{pile} \quad = \quad E_{Nernst}(p,T) - (\, i\,.R_{ohmique} + \left|\eta_{cathode}\right| + \eta_{anode})$$

$$P_{él} \quad = \quad E_{pile} \times i$$

Typical current density: 0.4 A/cm^2
Typical useful voltage E$_{pile}$: 0.75 V
Series connection of cells ("stack") to increase E$_{tot}$

Example of PAFC :
- 240 cells in series (170 V)
- electrodes of 0.66 m x 0.66 m (1300 A)
- the stack module (1 m^3) delivers 200 kW$_{él}$ (and 200 kW heat)

with electrical efficiency : 40%
and global efficiency (cogeneration) >80%

Fuel cell electrical efficiency

$$\eta_{cell} = \frac{P[W]}{\dot{f}[mol/s] \bullet \Delta H_{293K}[J/mol]} \rightarrow \eta_{cell} = \frac{I \bullet E_{cell}}{\dot{f}[mol/s] \bullet \Delta H_{293K}[J/mol]} \frac{\Delta G(p,T)}{\Delta G(p,T)}$$

$$\eta_{cell} = \frac{I[A]}{\dot{f}[mol/s] \bullet nF[C/mol]} \frac{E_{cell}\ [V]}{E_{Nernst}[V]} \frac{\Delta G(p,T)[J/mol]}{\Delta H_{293K}[J/mol]}$$

$$\downarrow$$

$$\boxed{\eta_{cell} = \eta_I \bullet \eta_V \bullet \eta_{THDYN}}$$

current efficiency, “fuel utilisation”

voltage efficiency

thermodynamic efficiency

Efficiency H_2 vs. CH_4, with air

	H_2, 80C (PEFC)	H_2, 800C (SOFC)	CH_4, 800C (SOFC)
Fuel utilisation	1	0.85	0.8
* Voltage efficiency	0.65	0.8	0.8
* Thermodynamic efficiency (LHV)	0.93	0.78	**1**
= Electrical efficiency (LHV)	0.6	0.53	0.64

- these values have been achieved in real systems.
- there is usually co-generation of useful heat, for total efficiencies of ≈ 90%.
- CH_4 has the intrinsic benefit of presenting **no entropy loss**.
- H_2 carries an additional intrinsic loss as it has to be synthesized first.

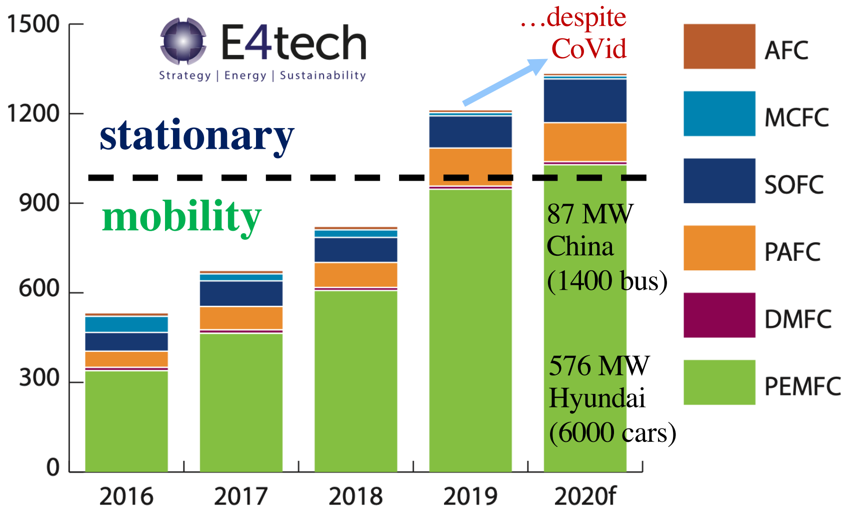
➔ **Methane-FC (natural gas, biogas) are (in principle) more efficient than H_2-FC.**

World fuel cell market growth: by type, MW's, and numbers

53'600 PEFC / 1030 MWe
25'000 SOFC / 150 MWe

Micro-CHP (53'000):
47'000 Japan, 5'000 Germany
Forklifts (10'000)
Portable FC (4'000)

Megawatts by fuel cell type 2016 - 2020



stationary

mobility

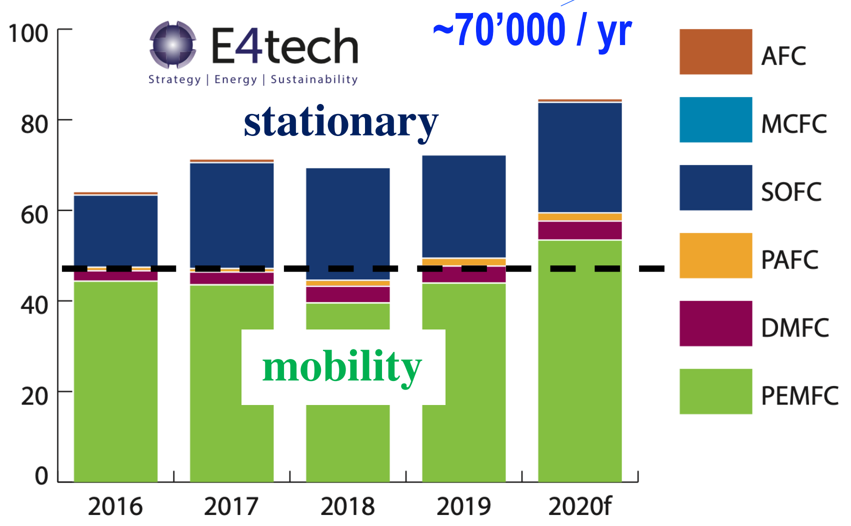
…despite CoVid

87 MW China (1400 bus)

576 MW Hyundai (6000 cars)

Total installed power now > 4.5 GWe

Shipments by fuel cell type 2016 - 2020 (1,000 units)



~70'000 / yr

stationary

mobility

Total cumulated now > 550'000 systems

360'000 Micro-CHP in Japan
self-sustaining market (no more subsidy)
12 yrs life

Facts & figures update 2020

https://www.e4tech.com/resources/246-e4tech-produced-its-annual-fuel-cell-industry-review-now-in-its-7th-year.php

- In 2020, 82500 FC units were shipped, up by 100 MW to a total of 1’300 MW
  - >50000 fuel cell micro-CHP units went to Japan and Germany
  - Hyundai shifted 8500 NEXO cars
  - Materials handling units (forklifts) was up too, with Plug Power shipments of 10’000 units

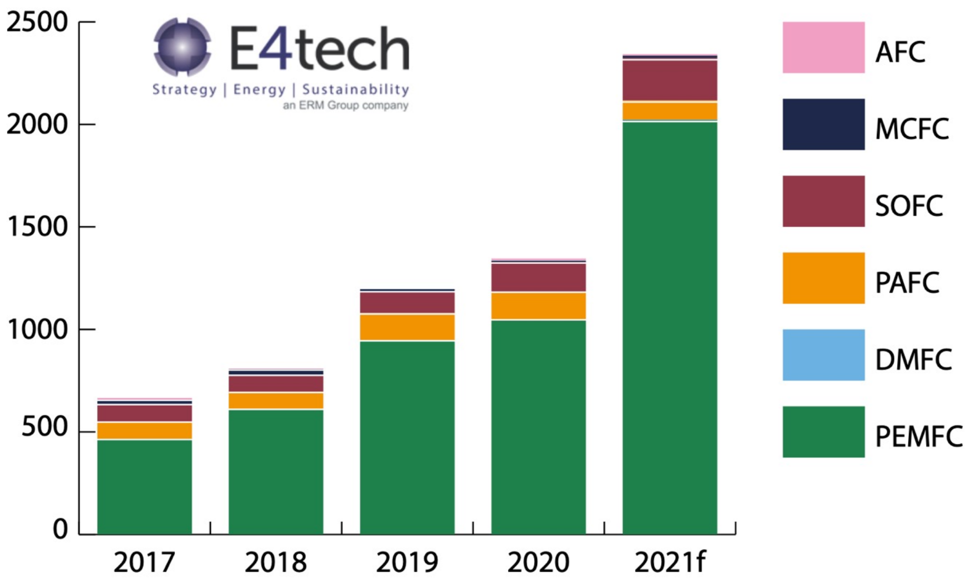
- Asia remains in the lead because of **policy**

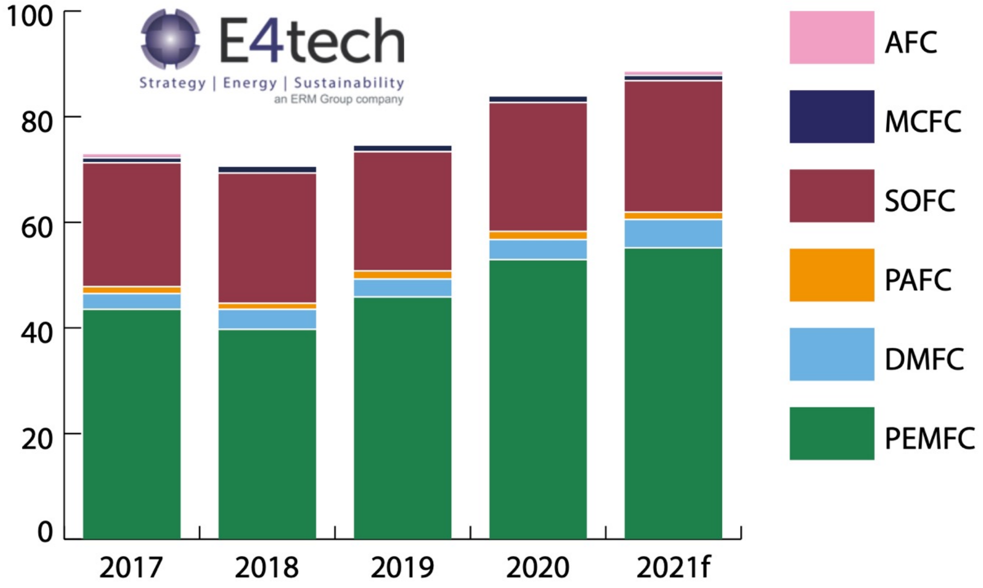
- Strong drive in **automotive** industry:
  - New Mirai (Toyota) in 2020: 20% smaller and 50% lighter FC stack for higher power (128 kW); 30% higher range
  - 2020 shows a record number in new hydrogen refuelling stations (HRS)
    - California adding 110 HRS until 2025 to 60 existing HRS
    - Japan has 133 (target 320 by 2025); Korea 43; 100 in D, 80 in F/UK/N/other; China 37
  - First 10 Xcient Hyundai buses are delivered to Switzerland; 190kWe, 400km range 1 charge; the EU targets 5000 trucks by 2025
  - Weichai China has 20’000 unit per annum PEM factory
  - 115 FC buses circulate in EU; hundreds are on order; China is clearly in the lead for buses (3600 now)
  - 50’000 vehicles are intended to be on Chinese roads by 2025
  - Hyundai targets 200’000 cars by 2025 in Korea, Toyota 200’000 cars by 2025 in Japan
  - Daimler and Volvo set up a fuel cell truck JV (on liq. H_2)
  - Marine activities: Ballard, Nedstack, Powercell and Proton Power have all taken maritime orders, Hyundai has its own ship company.
  - The first FC excavator has been developed

- Largest installed **stationary** powers:
  - 59MW MoltenCarbonateFC power in Korea
  - 50 MW PhosphoricAcidFC power in Korea, H_2-fueled (from by-product H_2)
  - 30MW SOFC (Bloom)
  - Korea plans a 400MW/yr FC power deployment

E4tech
an ERM Group company

Update with 2021 numbers





MW shipped :
2 GW **PEM**
207 MW **SOFC** (Enefarm, Bloom, prime power in USA + SK).
100 MW **PAFC** Doosan.

Units shipped :
55’000 **PEM**
25’000 **SOFC** (Enefarm).
200 **PAFC** Doosan units
5300 **DMFC** units (SFC Energy) for 500 kW total.
AFC very low (UK and Israel GenCell).

Facts & Figures 2021

- 86'000 units shipped in 2021:
  - 40’000 Enefarm (kWe) units
  - 16’000 units to USA (Toyoto Mirai and forklifts)
  - 14’000 units in Europe (630 mobile units, rest uCHP and forklifts and portable).
  - 16% of all units (14’000) are forklifts (+3’500 in Europe).
- 2.3 GW shipped in 2021:
  - Hyundai (38% of power => Korea, 8500 Nexos)
  - Toyota (33% of power => Japan + California, 2500 Mirai)
  - Mirai + Nexo account for 72% of MW. With buses/trucks : 83%. With forklifts : 85% (2GW).
- Uptake of <u>heavy duty</u> (trucks, buses; 1800 in China alone). PEM supply chain is put in place.
- EU: 300 HRS by 2025, 1000 HRS by 2030
- <u>Buses</u> : 1100 made in 2021
- <u>Trains</u>: 50 now exist
- <u>Ships</u> : Doosan (using Ceres SOFC), Prototech/Clara (Sunfire stacks), TECO 2030 (AVL fuel cells) and Topsøe.
- 3 bio$ in shares in 2021. Large breadth of investments in 2021 (almost every type of fuel cell and every end-use market)
- The action happens in Asia: 1.5 GW or 65% of power. USA 0.6 GW. Europe 0.2 GW.
- PEM mobility accounts for 86% of power
- Other : domestic uCHP (44000 units, Japan 40000, Europe 4000); remote power ; prime power (Bloom + Doosan) in SK. Portable units 6000.

Many H_2 roadmaps exist

- 20 countries have strategies, about 500 projects for a total of 700 bio$ until 2030.
- Japan 2030: 800k cars, 1.2k buses, 10k forklifts, 900 HRS and 5.3m Ene-Farm units.
- Korea 2040: 2.9m FC cars (plus 3.3m for export), 80k FC taxis, 40k FC buses, 30k FC trucks, 1.2k HRS, 8 GW of FC large-scale domestic power generation (plus 7 GW for export) and 2.1 GW of FC domestic power generation for homes and buildings by 2040.
- Europe 2040 : 3.7m FC cars, 500k FC light commercial vehicles, 45k FC trucks and buses, 570 FC trains and 3.7k HRS by 2030, as well as 2.5m FC CHP units.
- USA 2030: 1.2m FCEVs, 300k FC forklifts and 4.3k HRS
- China 2030 : 1m FCEVs
- F 2030: 20-50k light duty vehicles, 800-2000 heavy duty vehicles, and 400-1000 HRS
- NL 300k FCEV
- Electrolyser targets 2030: 6.5 GW in France, 5 GW in Germany and Italy, 4-6 GW in Denmark, 4 GW in Spain, 3-4 GW in the Netherlands and 2 GW in Portugal. Chile 25 GW.

- Plug Power becomes a general player, also in PEMEL, targeting 3 GW capacity by 2025.

Summary

- great progress in Fuel Cells since 2 decades
  - H_2-cars and buses (50 – 200 kW_e PEFC)
  - residential micro-CHP (1-2 kW_e SOFC, natural gas)
  - efficient clean cogeneration plants (MW_e-sized SOFC + MCFC, incl. biogas)
- big effort in R & D continues
- competition (engines, batteries,…) progresses a lot too!
- issue of the H_2-storage & distribution, H_2-society
- electrolysers (reverse fuel cells) are coming up strongly (combined with renewable electricity increase (PV, wind)