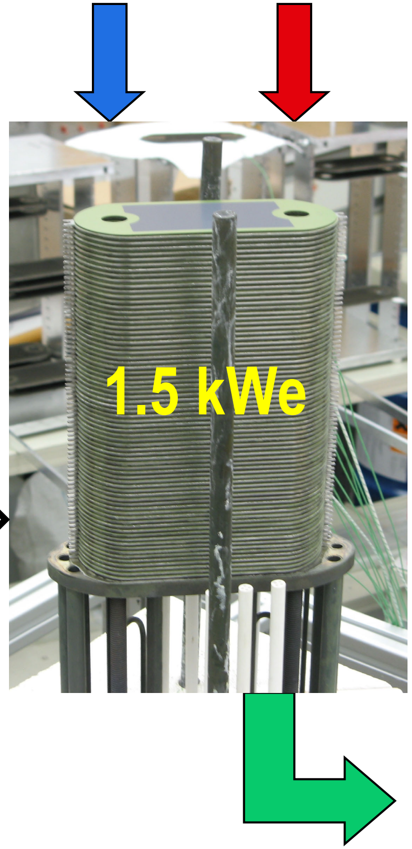
Conversion in Fuel Cells

Contents

A fuel cell at a glance

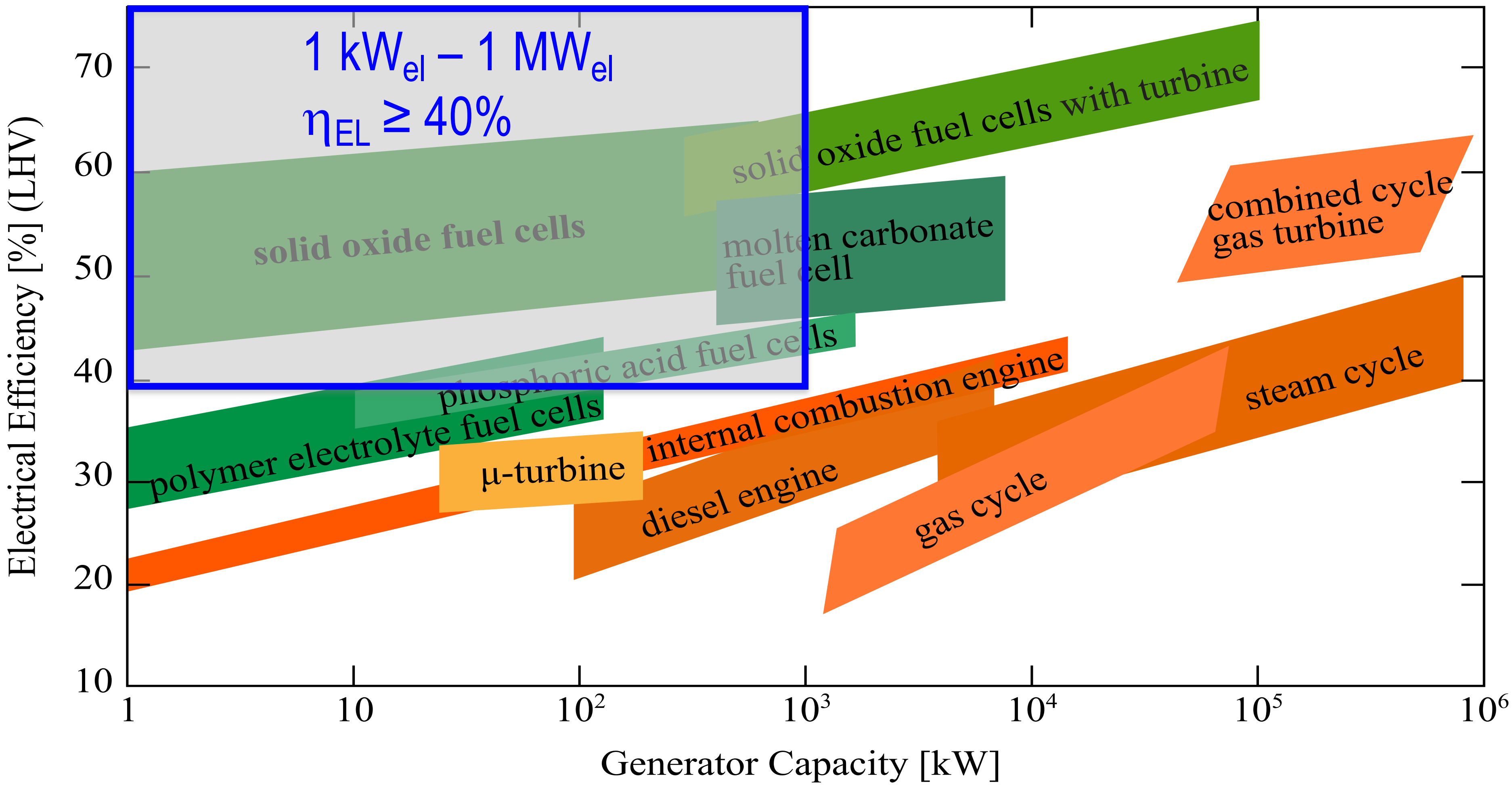
- works like a <u>gas battery</u>
- chemical fuel is <u>directly</u> converted into electricity and useful heat
- typical sizes and applications:
  - 1-20 W_e / H_2, MeOH / portable electronics
  - 1 kW_e / natural gas / a house
  - 50 kW_e / H_2 / an electric car
  - 1 MW_e / biogas / CHP
- status: R&D, P&D, pre-commercial



Electrical efficiency as fct(power size)

(based on natural gas, LHV)

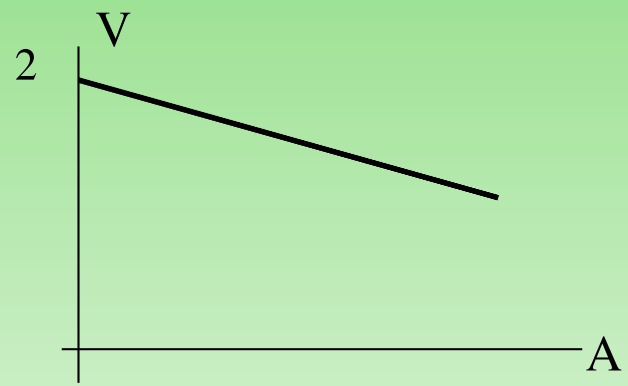
(compiled by Quentin Jeangros, EPFL-CIME/Fuelmat)



Part 1: operating principle; components

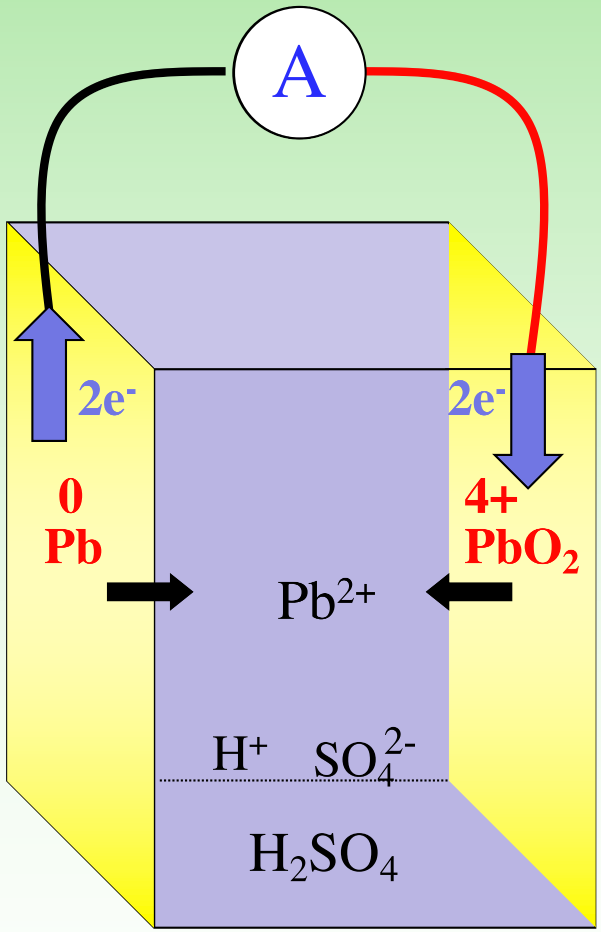
- Electrochemistry of a *battery*
- Electrochemistry of a *fuel cell*
- Components of fuel cells
- **Types (5)** of fuel cells

Classical car battery : 'lead (Pb) -acid'



< 2 V

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



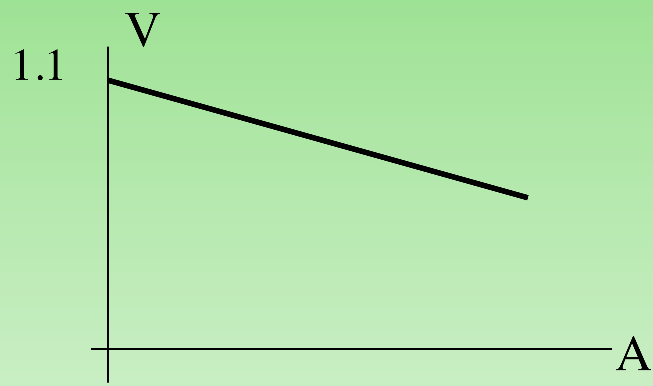
$$PbO_2 + 2e^- + 4H^+ \Leftrightarrow Pb^{2+} + 2H_2O$$

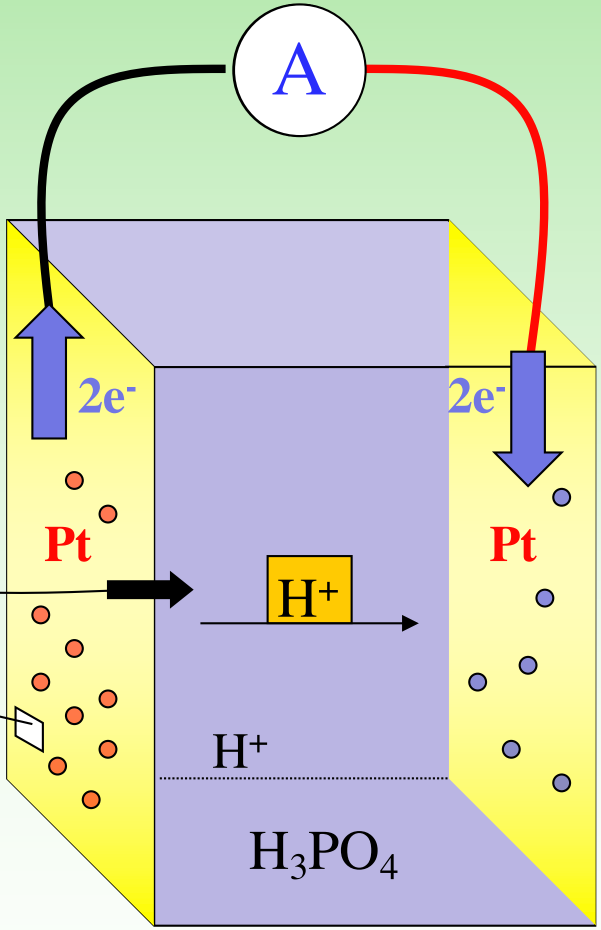
$$Pb + PbO_2 + 2H_2SO_4 \Leftrightarrow 2PbSO_4 + 2H_2O$$

electrodes are consumed (« active mass »)

Phosphoric Acid Fuel Cell (PAFC) – type 1

< 1.1 V





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

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

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

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

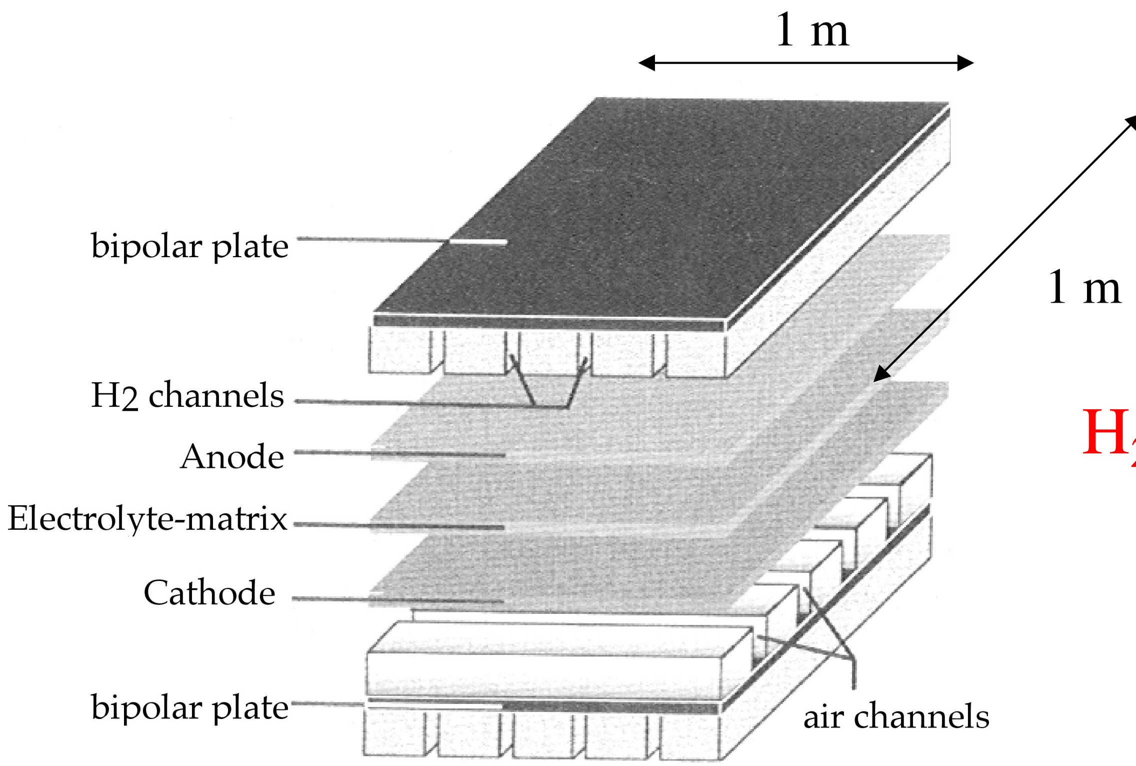
- gases are consumed
- electrodes are invariable (=catalysts)

electricity

+

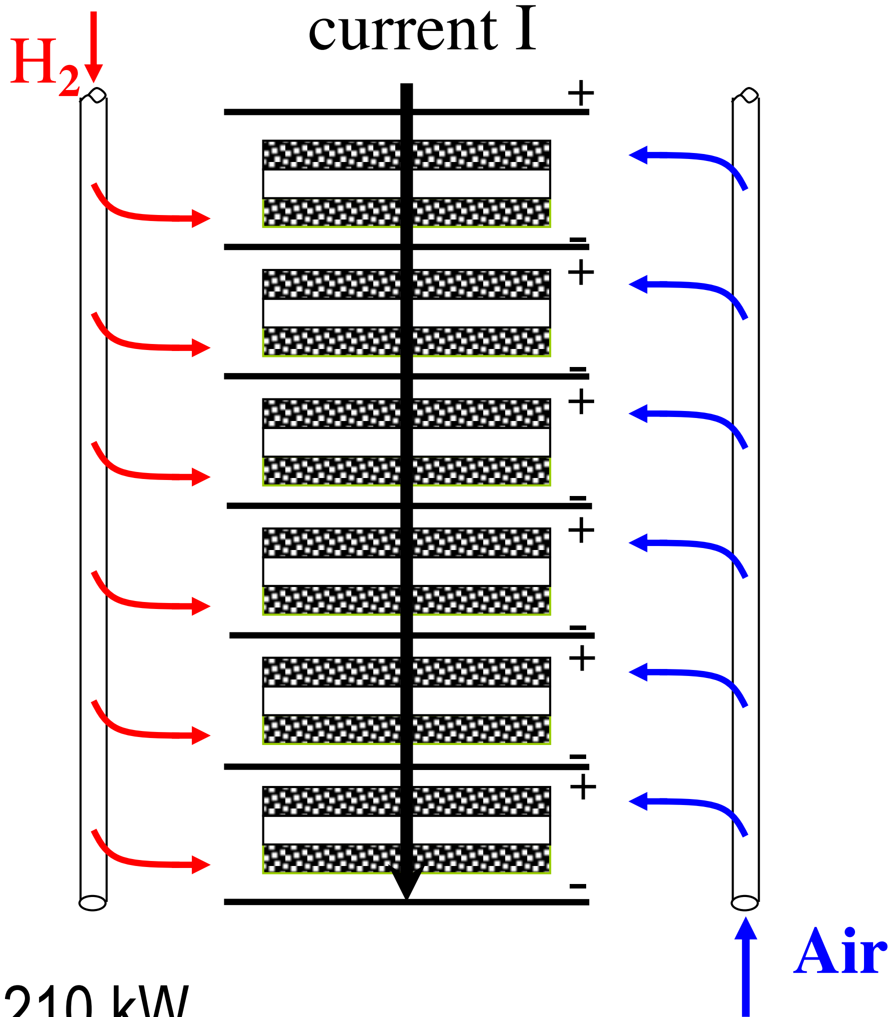
heat

200C



(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

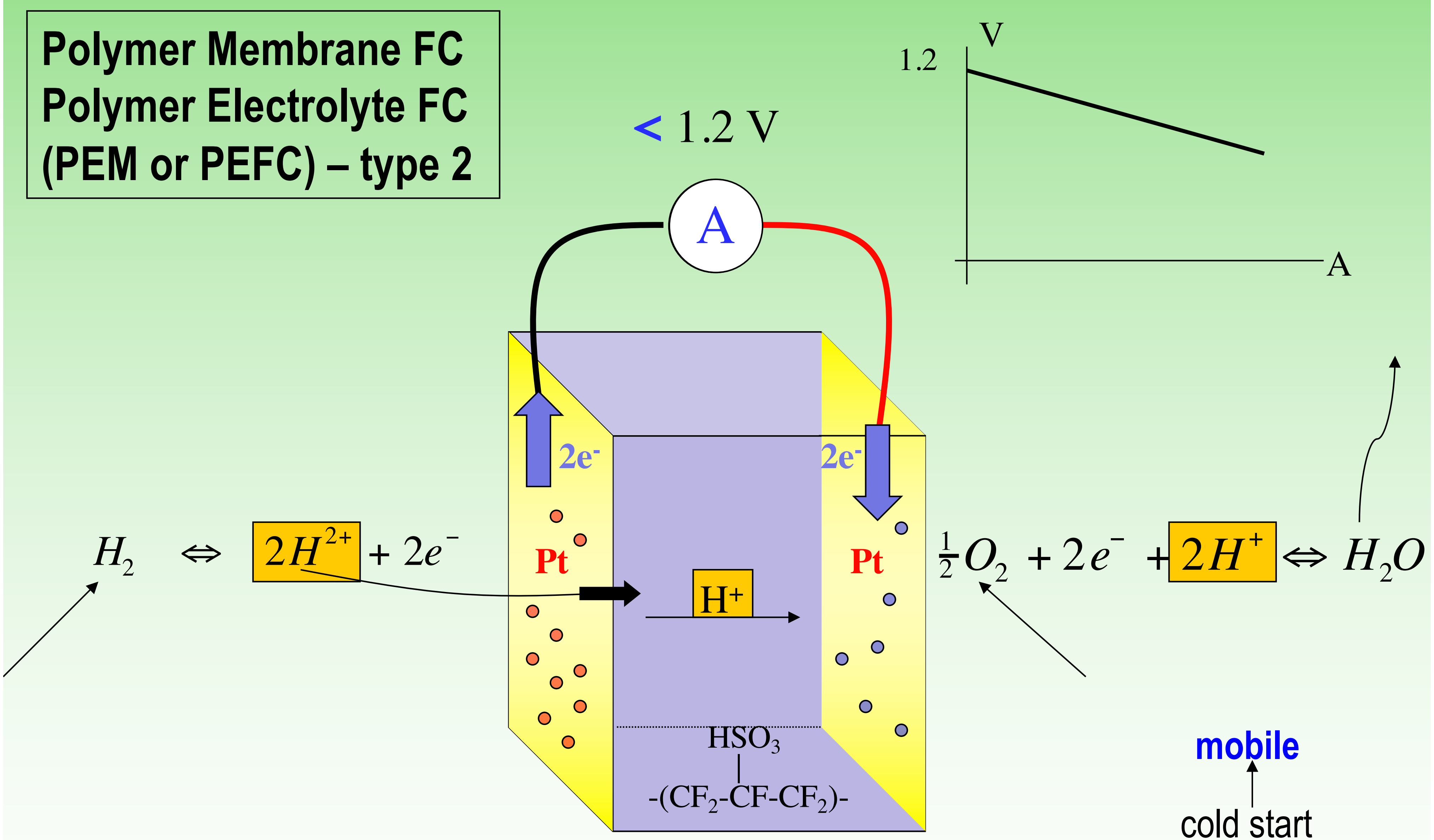
70 V * **3000 A** = 210 kW_e

Units exist from 50 kW_e to several MW_e

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

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

Polymer Membrane FC
Polymer Electrolyte FC
(PEM or PEFC) – type 2

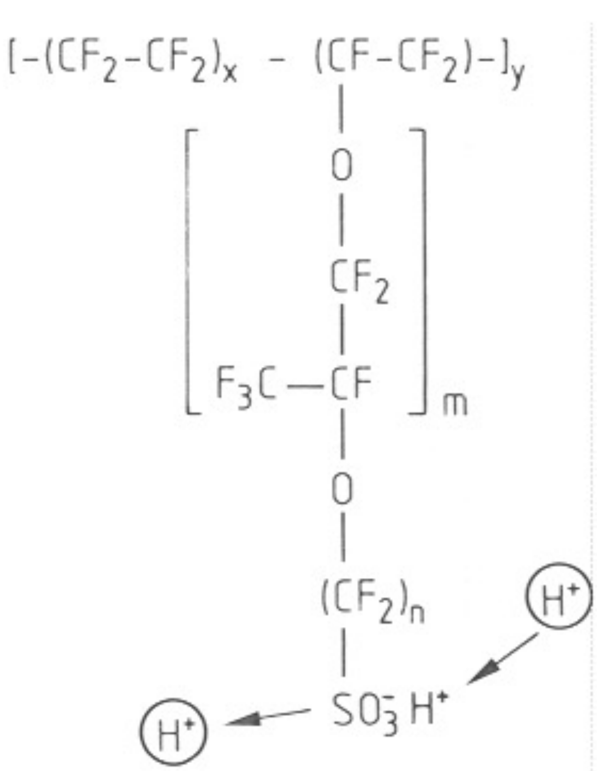


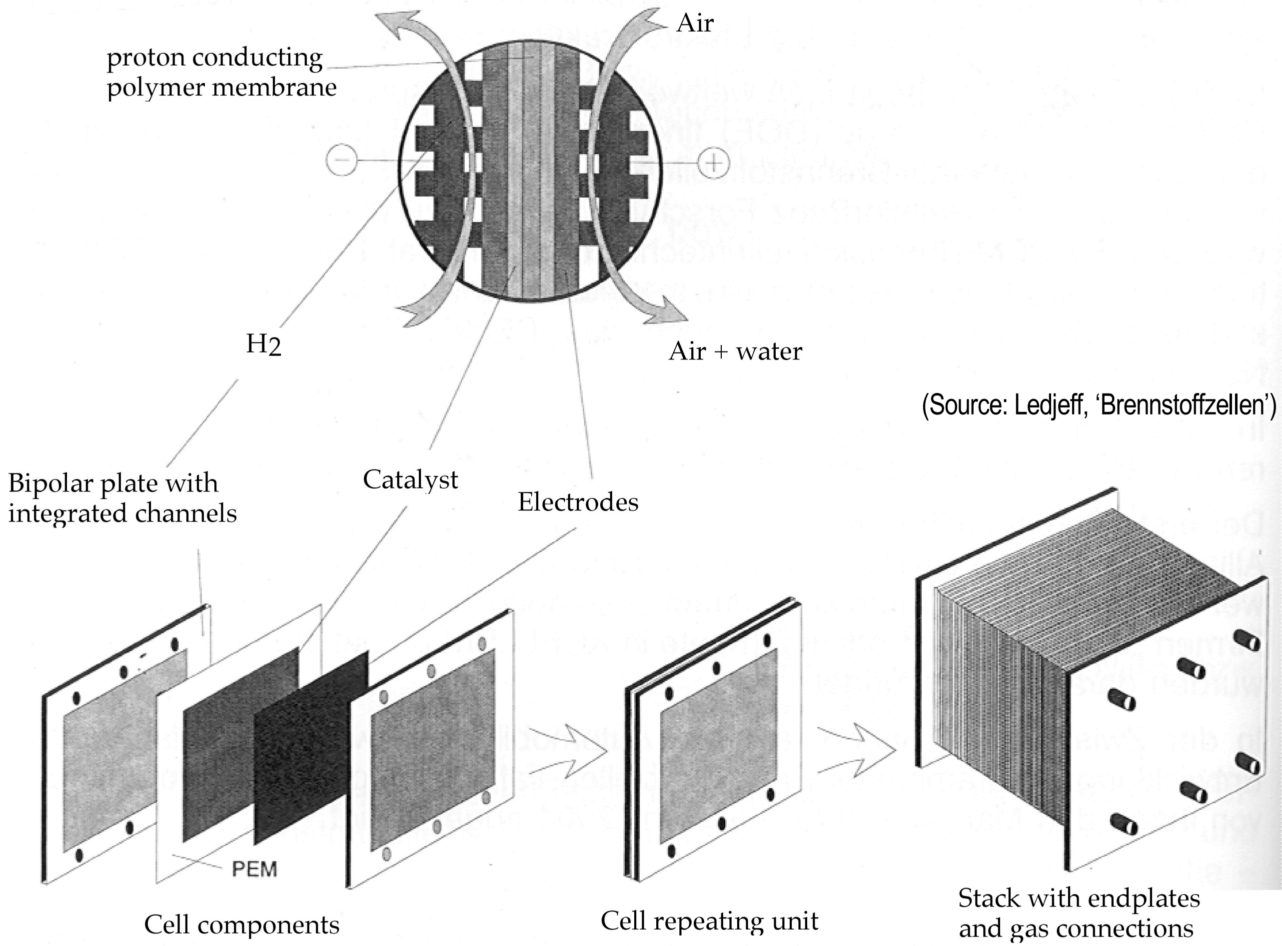
$$H_2 + \frac{1}{2}O_2 \Leftrightarrow H_2O$$

mobile
↑
cold start
↑
0-80C

polymer membrane (50 μm thin)

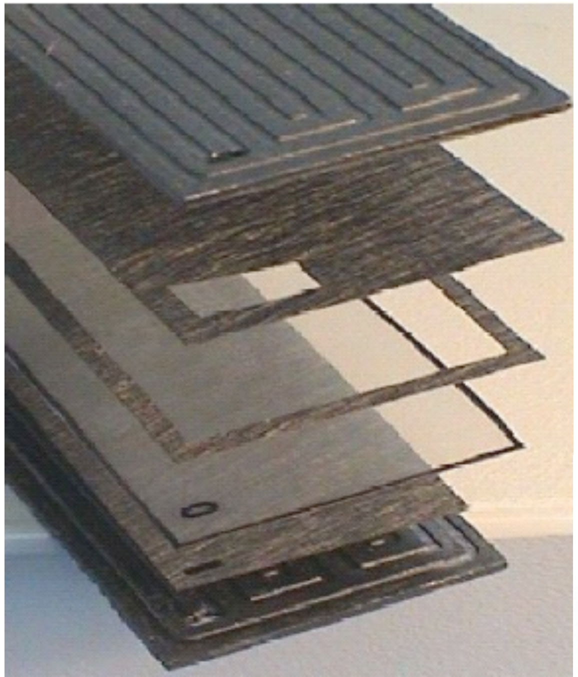
series connection (« stack »)





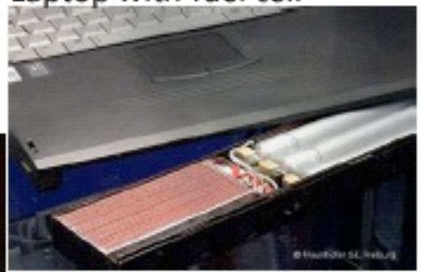
(Source: Ledjeff, 'Brennstoffzellen')

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



5 - 50 W$_e$

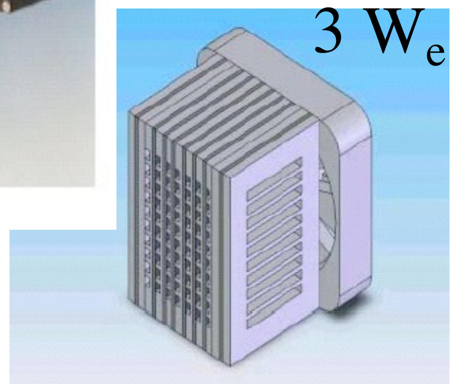
Laptop with fuel cell

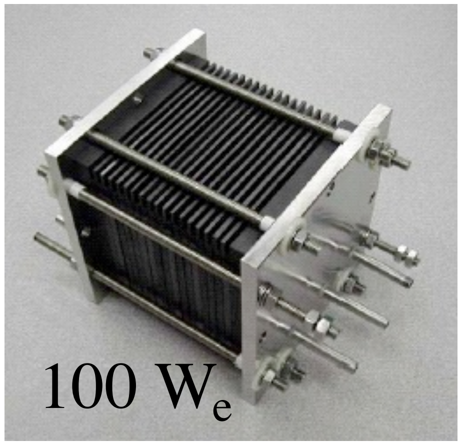


Fuel cell camcorder

Fuel cell power box

Professional camera with fuel cell





PEFC applications

Comment (1)

- The 2 fuel cell types seen so far 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 ($H_2 + ½O_2$ ➔ H_2O) at such low temperature are the **noble metals** (Pt-group)

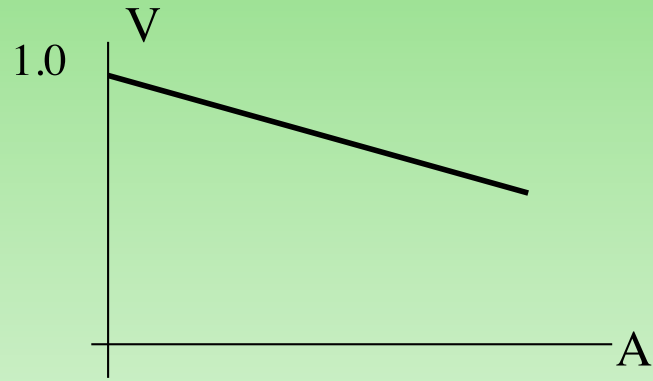
=> limited to H_2 and Pt

Comment (2)

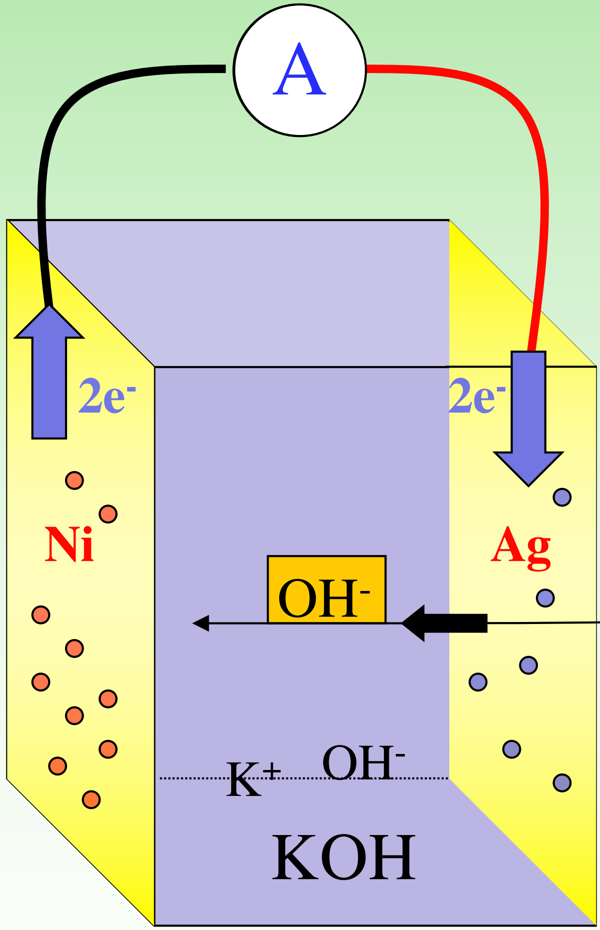
- The following 3 fuel cell types use a form of **oxygen ion conduction**
- Two of them use a ceramic resp. molten salt conductor, which operate at high temperature (>600C)
- At such **high temperature**, **other fuels than H_2** become reactive enough for (electrochemical oxidation) (CO, **CH_4**,..)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

=> possible with <u>hydrocarbons,</u> on Ni catalyst

Alcaline Fuel Cell (AFC) – type 3



< 1 V



$$H_2 + 2OH^- \Leftrightarrow 2H_2O + 2e^-$$

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

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

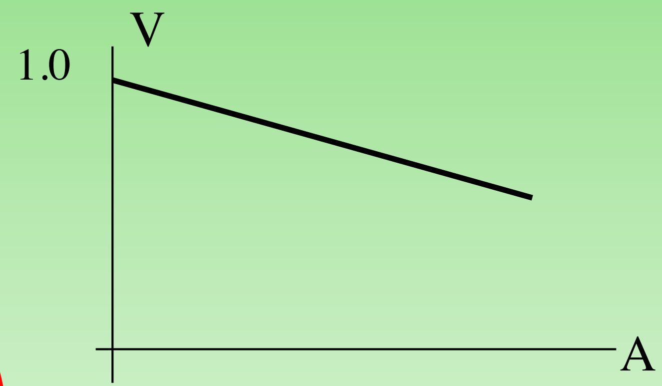
12 kW$_e$

application: transport

80C

Solid Oxide Fuel Cell (SOFC) – type 4

< 1 V

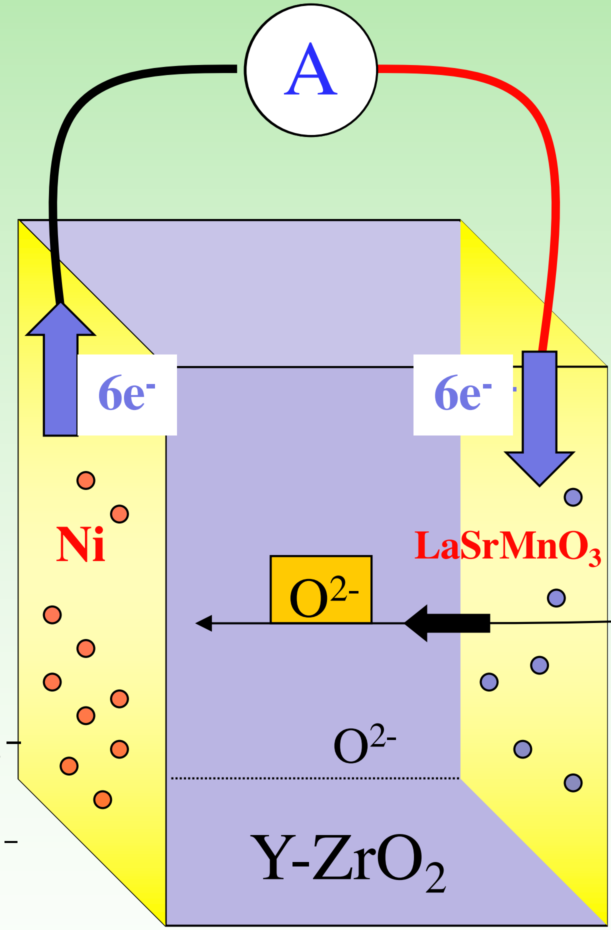


$$H_2 + O^{2-} \Leftrightarrow H_2O + 2e^-$$

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

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

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



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

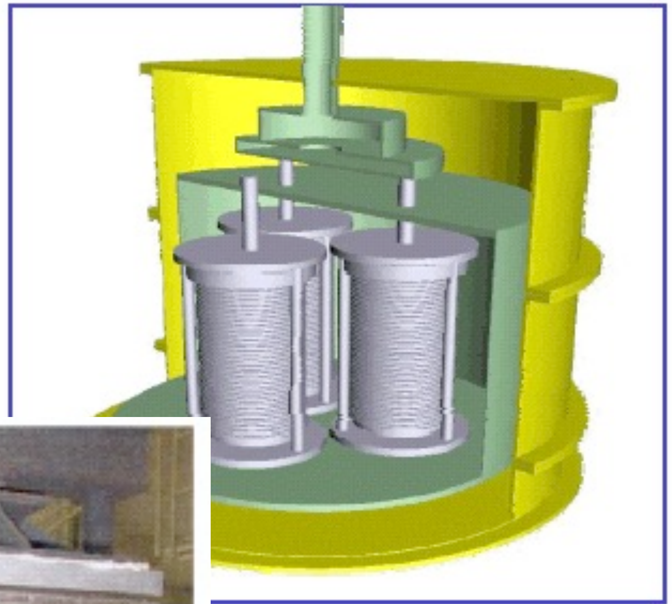
$$H_2 + \tfrac{1}{2}O_2 \Leftrightarrow H_2O$$

cogeneration

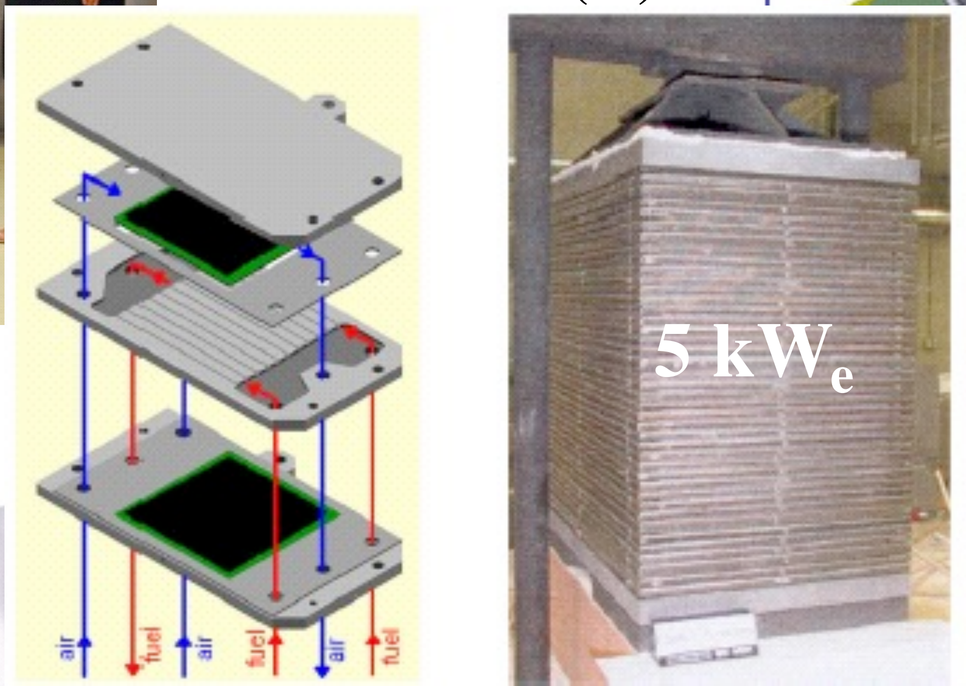
600-1000C

TOHO GAS
1 kW_e

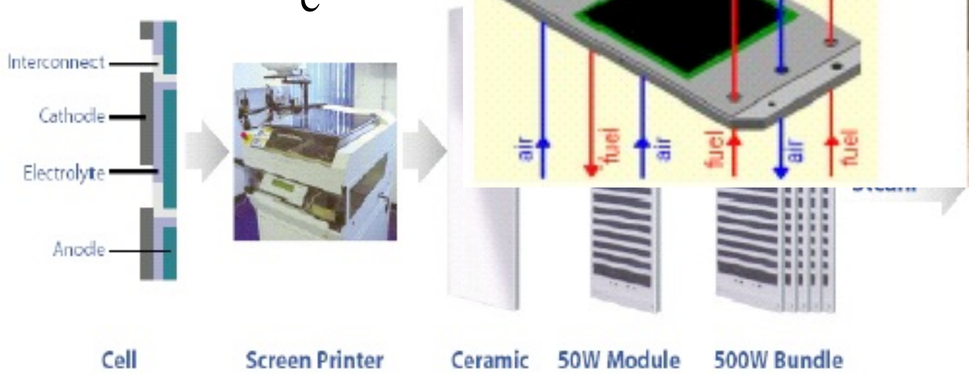
Kansai Electric
3 kW_e



FZJülich (D)



200 kW_e



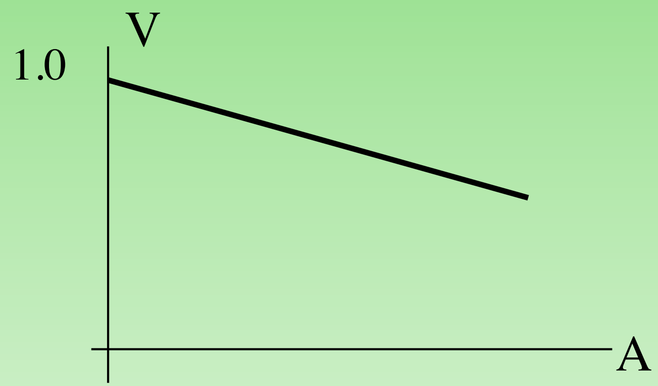
RollsRoyce Power (UK)

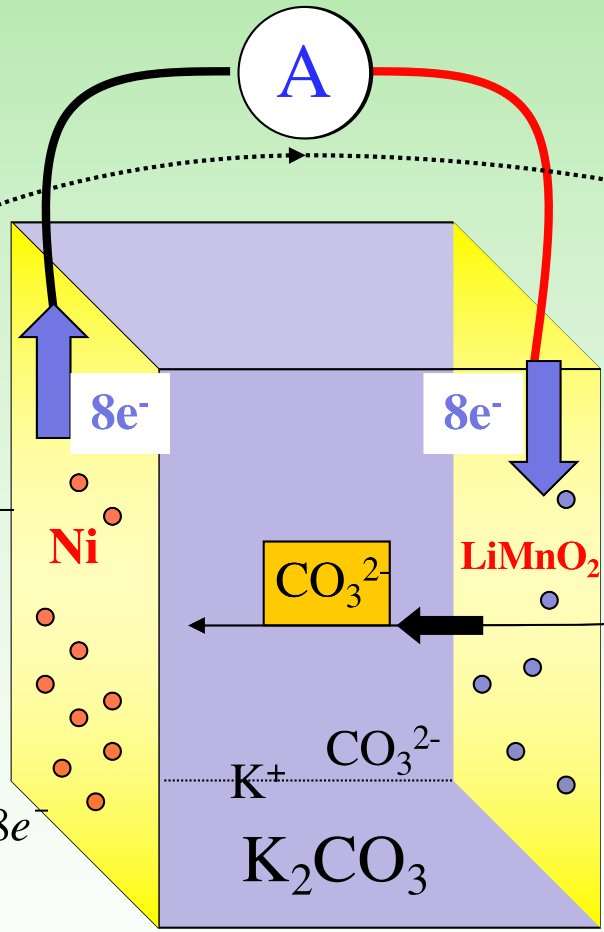
200 kW_e

Siemens-Westinghouse

Molten Carbonate Fuel Cell (MCFC) – type 5

< 1 V





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

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

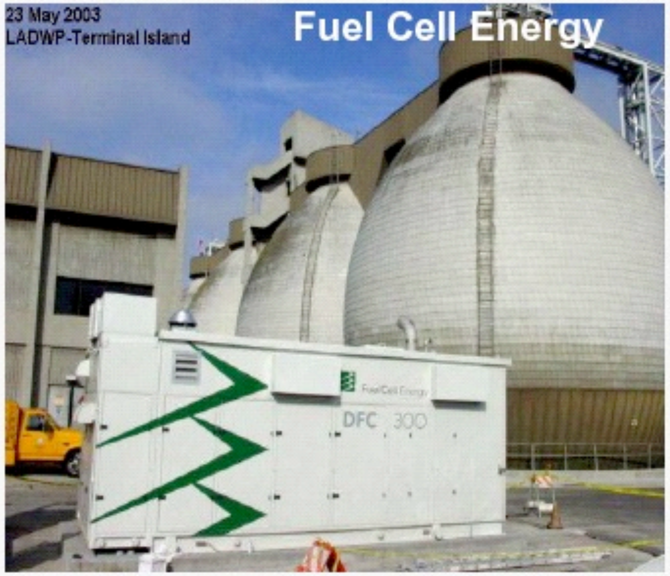
$$CH_4 + 4CO_3^{2-} \Leftrightarrow 2H_2O + 5CO_2 + 8e^-$$

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

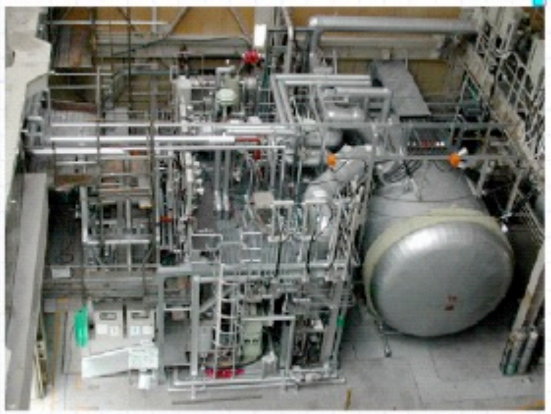
$$H_2 + \tfrac{1}{2}O_2 \Leftrightarrow H_2O$$

650C

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



NEDO



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

MCFC cogeneration units of 300 kW_e - 3 MW_e

Overview of the 5 fuel cell types

Type	Electrolyte	Temperature	Fuel
AFC	liquid alcaline	20-100° C	H_2
PEFC DMFC	membrane polymer	20-100° C	H_2 (or methanol)
PAFC	liquid acid	200° C	H_2 (from nat. gas)
MCFC	molten salt	650° C	**hydrocarbons**
SOFC	ceramic	600-1000° C	**hydrocarbons**

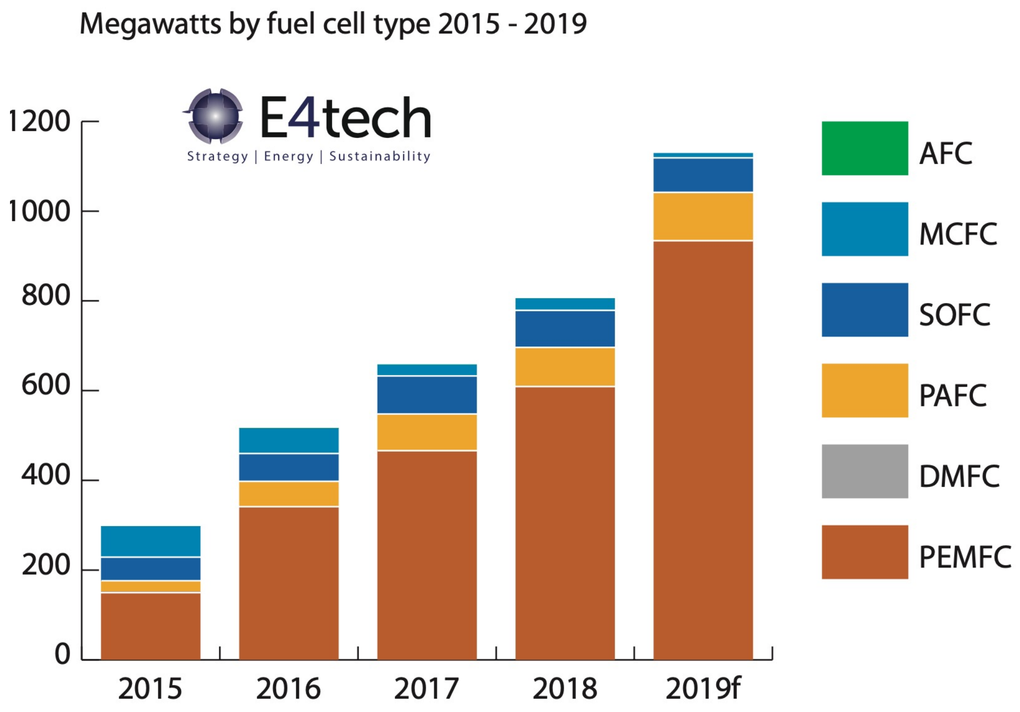
"direct" methanol ← DMFC

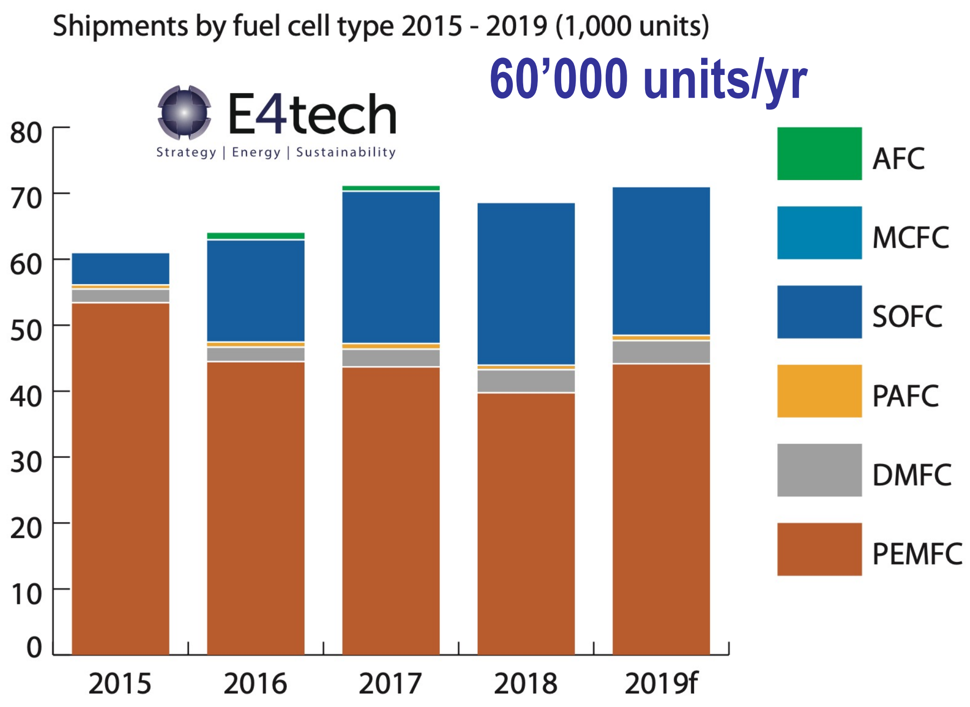
Current status

The 2 most developed types are:

- PEFC for electric mobility
  - almost all car companies have a FC development
  - Toyota, Hyundai, (Honda) most advanced
  - 10-30kWe in cars, 100-200kWe in trucks/buses
- SOFC for stationary (small scale) cogeneration
  - Europe, Japan: kWe-units for residential natural gas
  - USA: also MWe scale (clean distributed power on NG)

Fuel cell units and MW shipped





Installed power: >3.5 GW_{el}

>600’000 Units

especially mobility power

especially μ-CHP in Japan

Sources:
Fuel Cell Today,
E4Tech

Part 2: Fuel-to-electricity efficiency

- **Thermodynamics** (equilibrium or Nernst voltage), $i = 0$
  - Nernst equation

- **Losses** (real operating voltage), $i \neq 0$
  - ionic conduction loss (ohmic)
  - electrodes kinetics loss (non-ohmic: 'polarisation')
    - charge transfer (Butler-Volmer equation)
    - mass transfer (diffusion, adsorption,...)

- Fuel '**utilisation**' (u_F) or fuel conversion loss

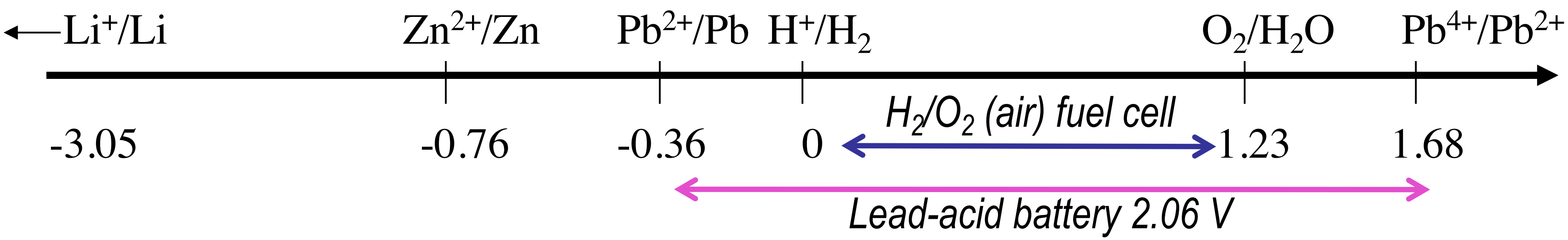
From chemical energy (total enthalpy ΔH) to electrical power ($P = V*I$)

$\Delta H_{reaction}$	*total* enthalpy = total chemical (**heat**) energy at inlet = heating value of the used fuel (kJ/mol, kJ/kg)
↓	
$\Delta G_{reaction}$	*free* enthalpy = theoretical useful **work** (kJ/mol, kJ/kg) ↓ *in a fuel cell: electrical work*
↓	
E_{Nernst}	*equilibrium* voltage (V) $i = 0$
↓	
V_{cell}	*operating* voltage (V) $i \neq 0$ - includes all **losses** in the internal circuit

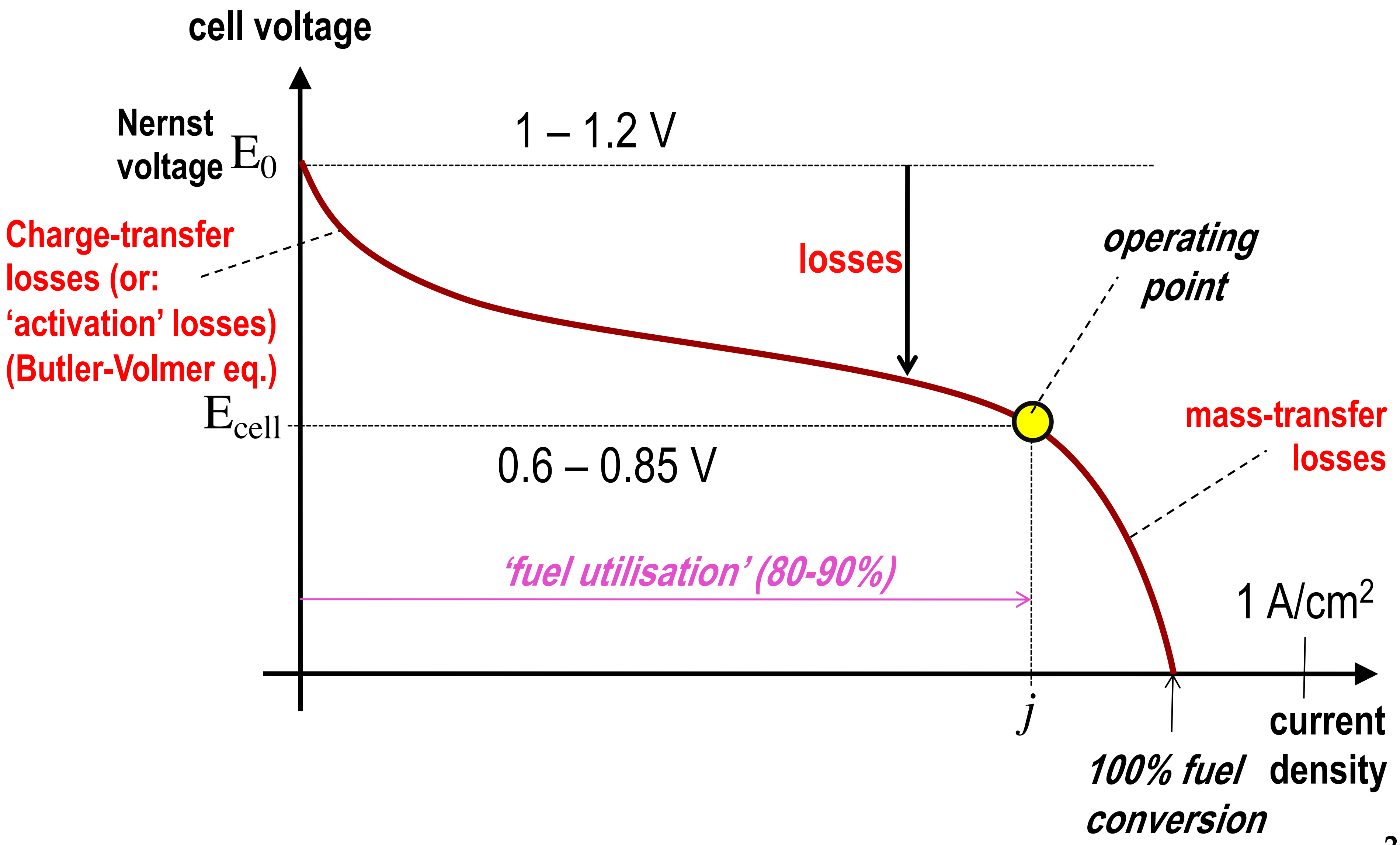
From Gibbs enthalpy to Nernst voltage

- a H_2/O_2 fuel cell at i = 0 creates an **equilibrium voltage of 1.23 V** (at 25° C, 1 bar)
- the Gibbs enthalpy of reaction ΔG_r (=theoretical maximal work) for
  $H_2 + 0.5\ O_2 \rightarrow H_2O$ is given by
  ΔG^0_r (25° C, 1 atm) = -237'150 J/mole
- The link between thermodynamics and voltage is given by
  $\Delta G^0_r = - nF.E^0$ (with n = exchanged electrons; n = 2 for H_2/O_2)
  energy (J/mol) = charge (C/mol) * voltage (V)
  with F = Faraday constant = the charge of 1 mol electrons (96484 C/mol)
  → therefore $E^0 = (\Delta G^0_r/2F)$ = 237150 / (2*96484) = 1.23 V at 298 K, 1bar
  (^{0} : standard concentration conditions: 1 atm, 1 mole/L,…)

Electrochemical series of elements



Characteristic i-V (current-voltage) curve



Useful electrical power from the fuel cell

$$P = \Sigma E_{cell} \bullet I$$

$$E_{cell} = E_{Nernst}(p,T) - I.\Sigma R_{ohmic} - \left|\Sigma \eta_{cathode}\right| - \Sigma \eta_{anode}$$

E_{Nernst} (1 atm, 200° C, I = 0 A) = 1.1 V
@ typical current density = 0.4 A/cm^2 :
=> typical operating voltage E_{cell} = 0.7 V

R_{ohmic} = 0.25 Ωcm^2
$\eta_{cathode}$ = 0.2 V, η_{anode} = 0.1 V
power density = 0.28 W/cm^2

Example of phosphoric acid fuel cell (PAFC) :
160 cells in series → 160 * 0.7 V = 112 V
electrodes 0.7 m * 0.7 m = 0.49 m^2 → 4900 cm^2 * 0.4 A/cm^2 = 1960 A
⇒ Power = 112 V * 1960 A = 220 kW$_e$ *dc* gross

The module (0.5 m^3) delivers 200 kW$_{el}$ *ac* net (+ 200 kW$_{thermal}$) with an electrical efficiency of 40% and a total cogeneration efficiency of >80%.
(natural gas input: 500 kW)

Fuel cell electrical efficiency

$$\eta_{cell} = \frac{P[W]}{\dot{f}[mol/s] \bullet \Delta H_{293K}[J/mol]}$$

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

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

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

η_I: **current efficiency, “fuel utilisation”**

η_V: **voltage efficiency**

η_{THDYN}: **thermodynamic efficiency**

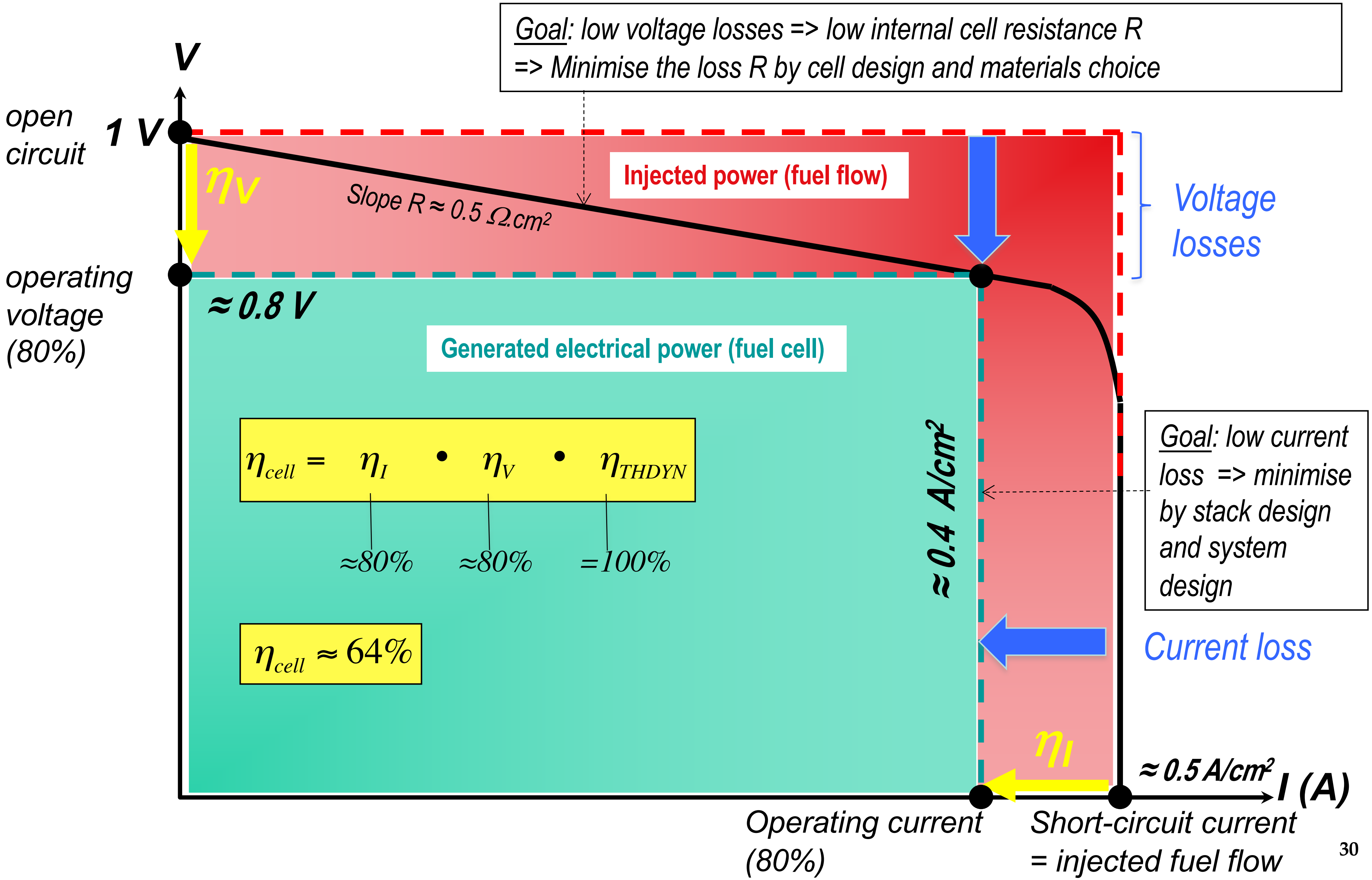
Example: H_2 vs. CH_4, with air

	H_2, 80° C (PEFC)	H_2, 800° C (SOFC)	CH_4, 800° C (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

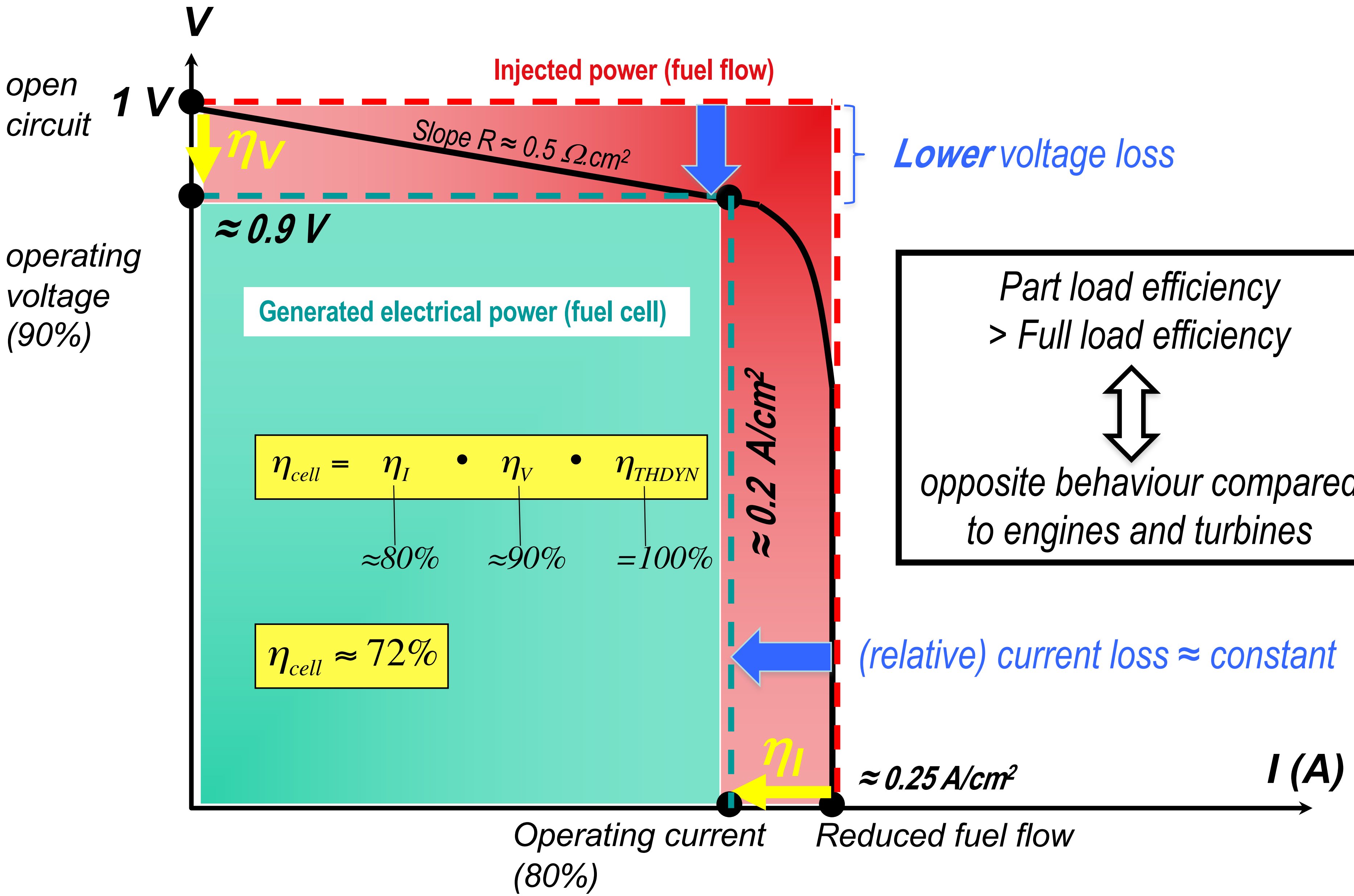
- Such values have been achieved in real systems.
- There will usually be co-generation of useful heat, for total efficiencies of ≈ 90%.
- CH_4 has the intrinsic benefit of presenting **no entropy loss**.
- H_2 carries an additional intrinsic loss as it has to be synthesized first.

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

Current-voltage characteristic, full load



Current-voltage characteristic, part load



Part load efficiency
> Full load efficiency

⇕

opposite behaviour compared to engines and turbines

Comparison with direct combustion

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

emissions

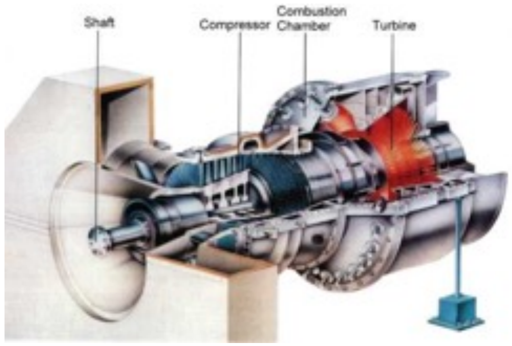
ENGINES

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

0.1 – 5 MW_{el}
η_{EL} 33-45%

TURBINES

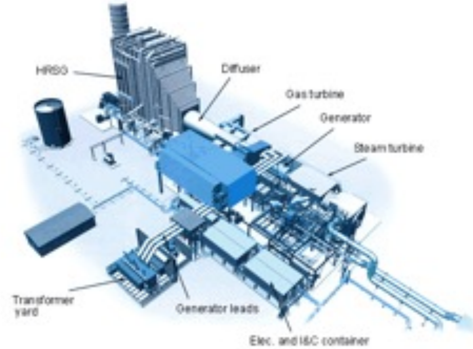
http://www.wartsila.com/sv/kraftverk/learning-center/gas-turbine-for-power-generation



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%

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no polluting emissions

CH_4 + $4\ O^{2-}$ ← $4\ O^{2-}$

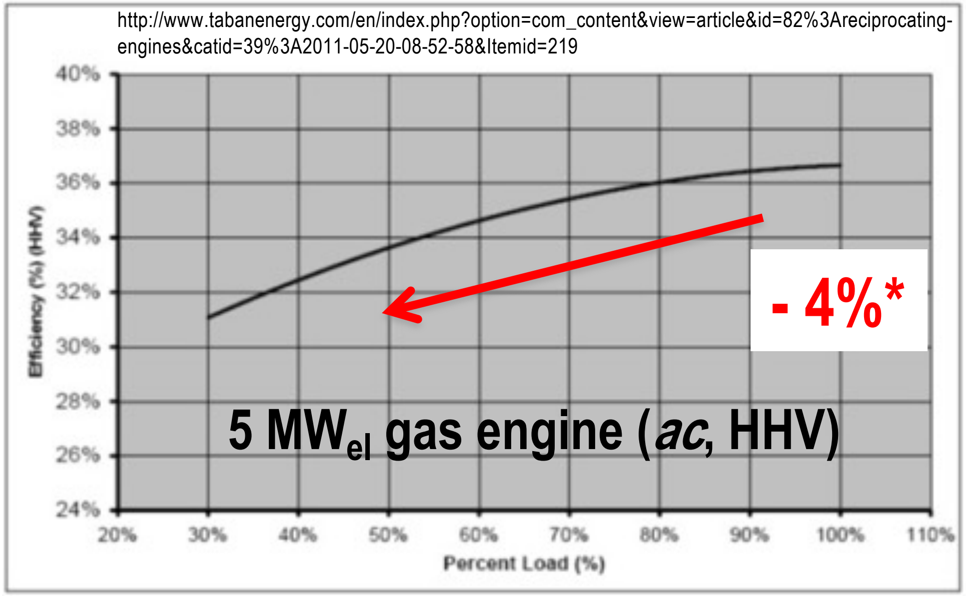
$H_2O + CO_2$ + **$8e^-$** → **$8e^-$** + air (O_2, N_2)

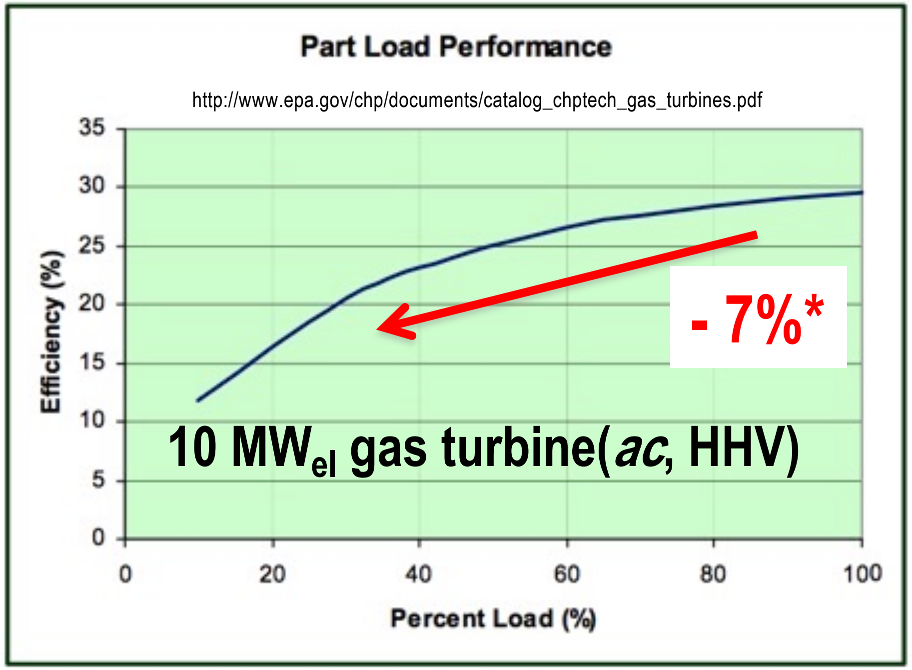
electrochemical "combustion"

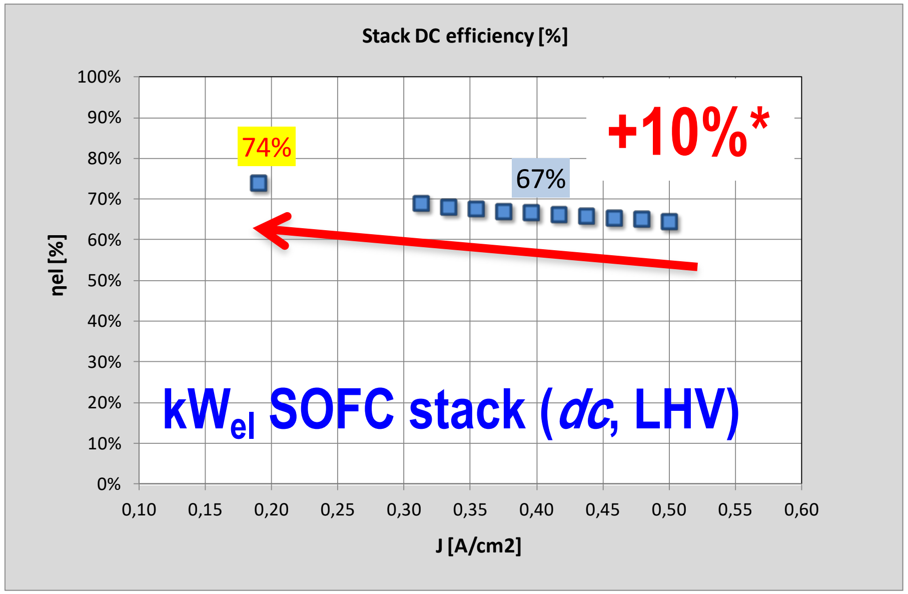
1 – 100 kW_{el}
η_{EL} 50-60%

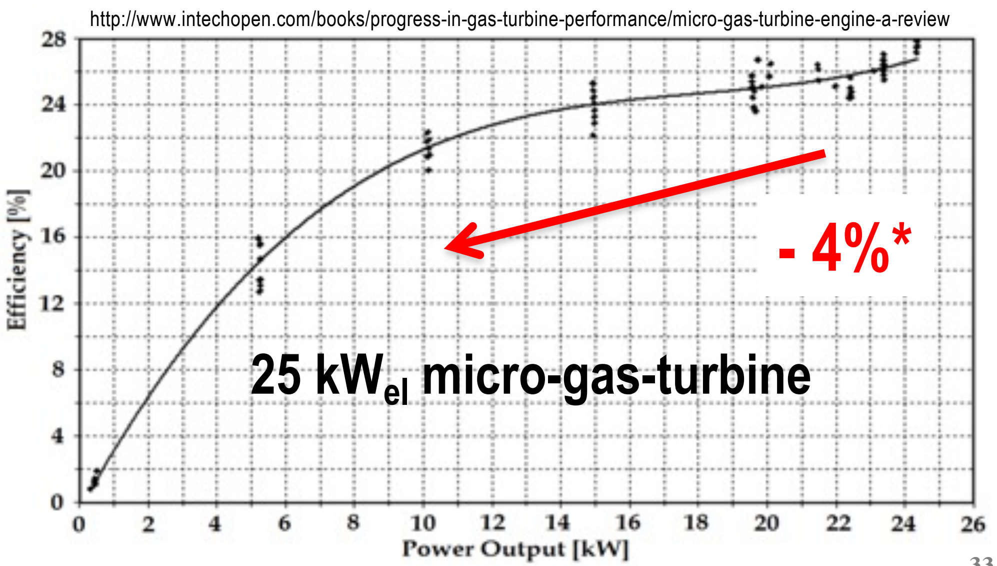
CH_4 + air => $H_2O + CO_2$ + ***dc* current** + cogenerated useful heat

Part load comparison









*from 100% to 40% power modulation

Which fuel cell for which application ?

Portable	1-100 W	electronics (3C market)	DMFC, PEFC
Small cogen.	10 kW - 100 kW	"UPS" (reduced competition from μT or diesel engine)	PEFC, SOFC
Transport	20 kW - 200 kW > 1 MW	vehicles, buses ships	PEFC, DMFC, AFC MCFC, SOFC
Medium cogen.	0.5 MW - 10 MW	offices, schools, universities, supermarkets, hotels, data centers, hospitals, industry (chem/steel/ food/WW/telecom)	PAFC MCFC SOFC

size

2 kW_e net 60% *ac* efficiency (SOFC)

= world record,
at this small power scale

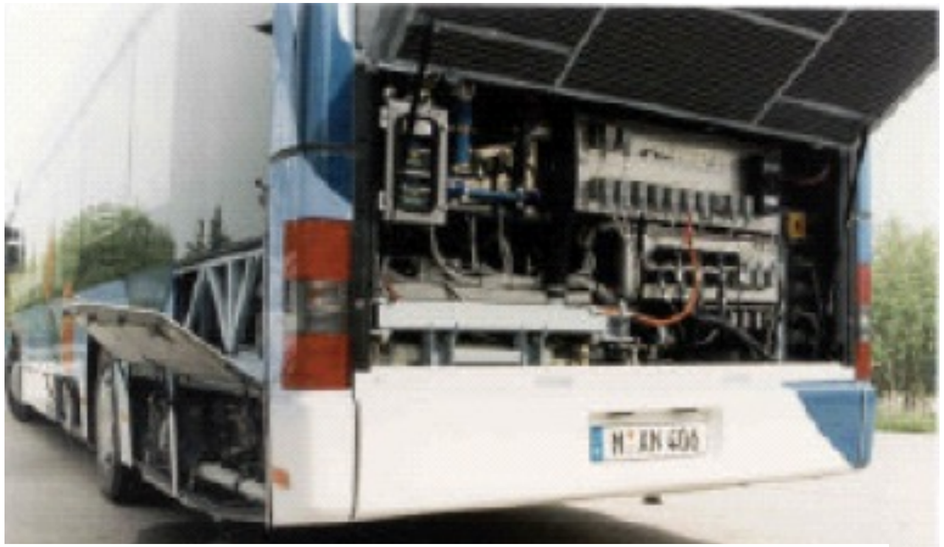
Performance			
	Min	Optimum	Max
Electrical Output	500 W	1500 W	2000 W
Electrical Efficiency	36 %	60 %	57 %
Thermal Output	Approx. 400 W*	Approx. 540 W*	Approx. 1000 W*
	* Based on exhaust gas cooled to 30 °C		
Power Output Modulation	From 0 % to 100 %		
System Efficiency	60 % to 85 % Depending on heat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

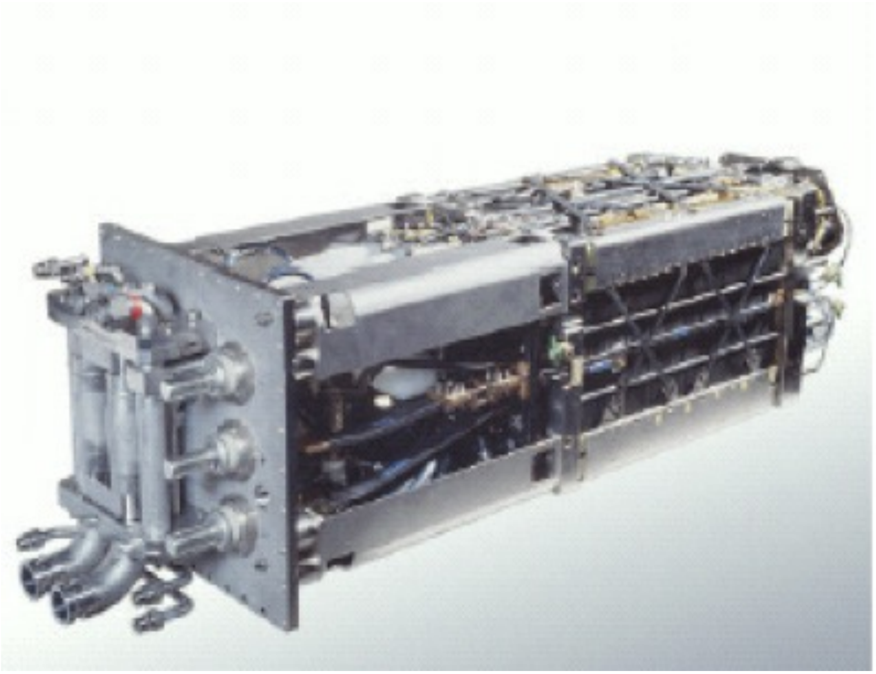
Multi-100 kWe Bloom Energy Box (SOFC)

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

Siemens: MAN City Bus (PEFC)

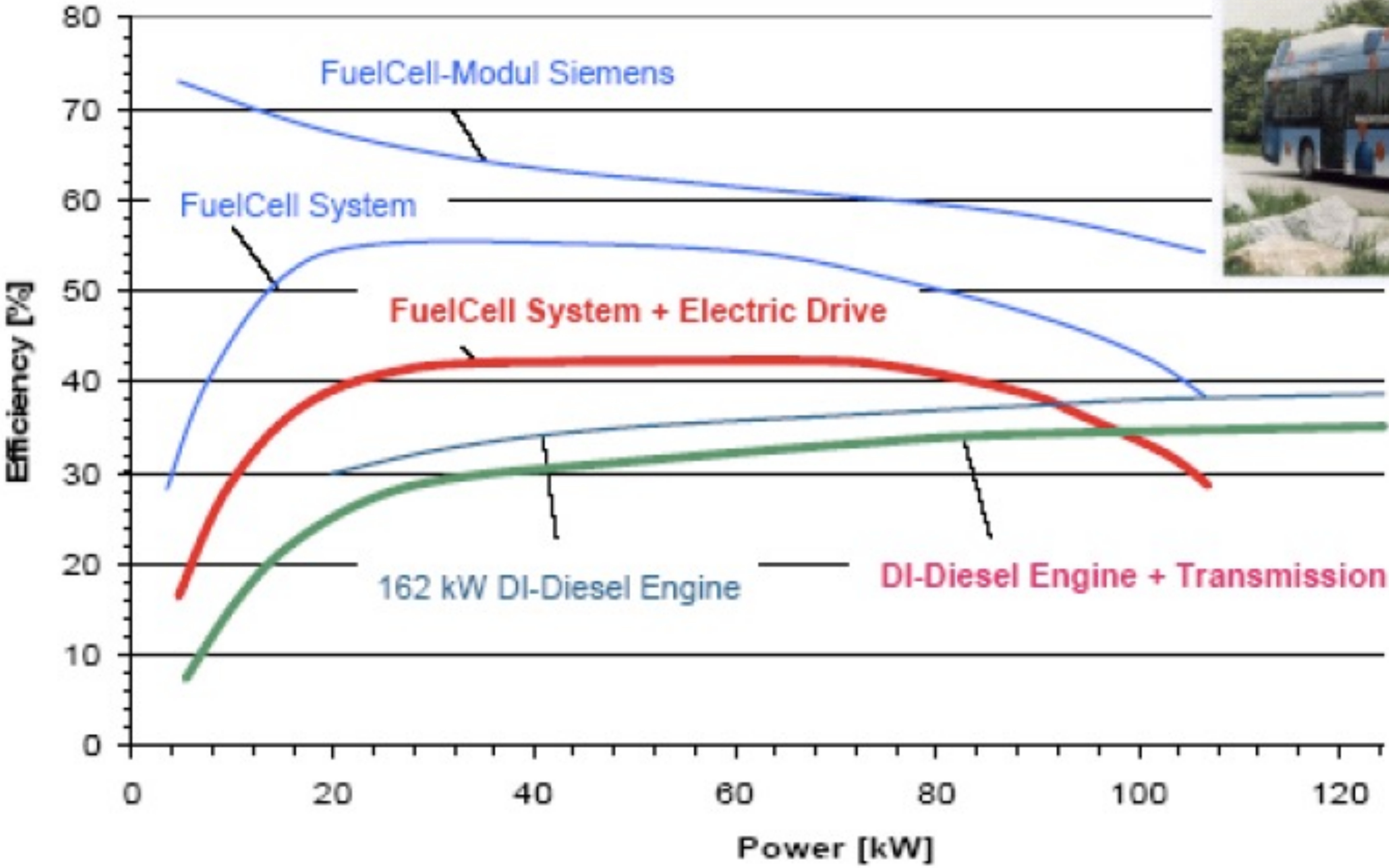




number of cells		320
rated power	≈	120 kW
rated current		560 A
rated voltage	≈	215 V
operating temperature		80° C
dimension	≈	176x53x50 cm^3
weight	≈	900 kg
Rated efficiency (at 20% load)	≈	68 %
(at rated load)	≈	56 %

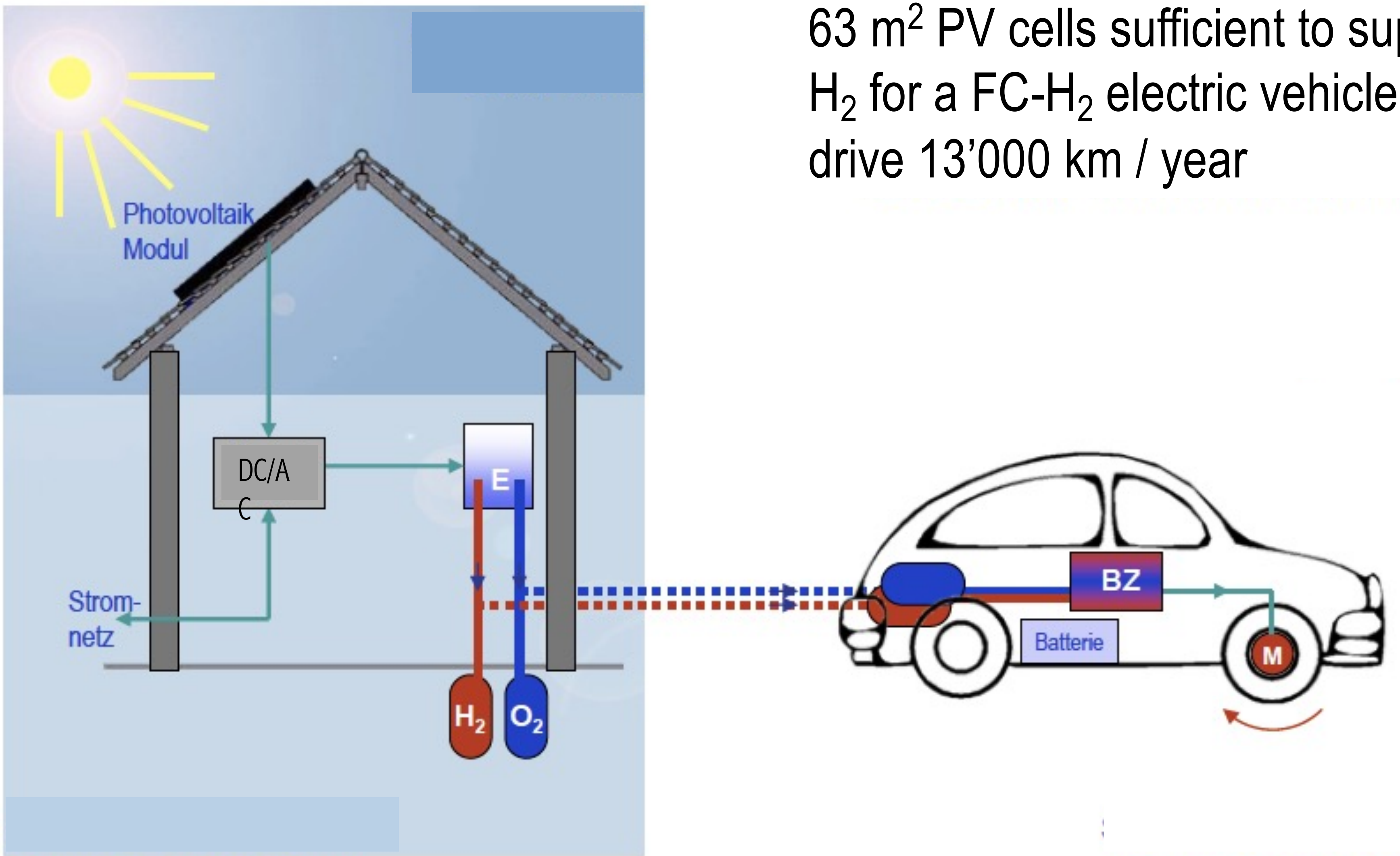
(Copied from G.G. Scherer, Tutorial, European Fuel Cell Forium, July 2011, Lucerne)

Measured efficiency (MA City Bus)



(Copied from G.G. Scherer, Tutorial, European Fuel Cell Forium, July 2011, Lucerne)

H_2-Mobility: Swisshydrogen

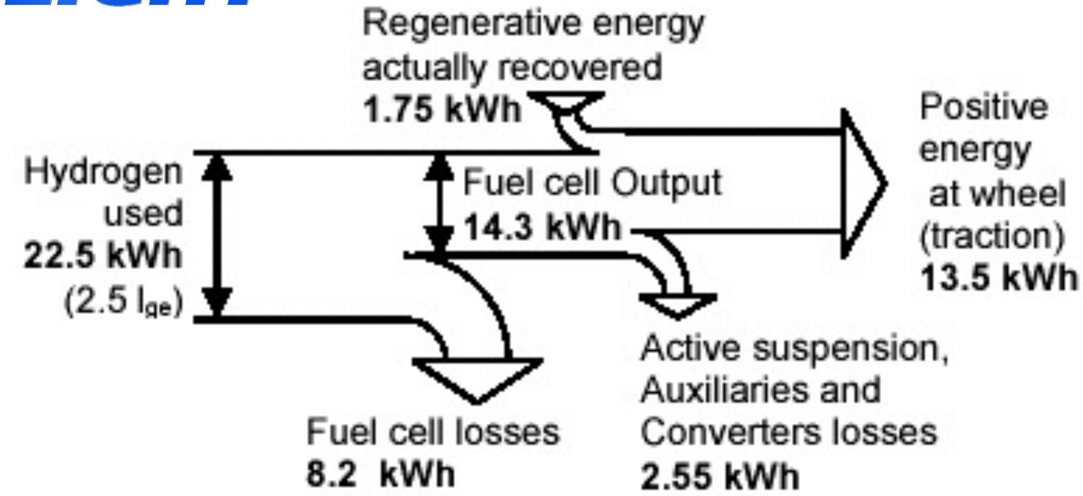


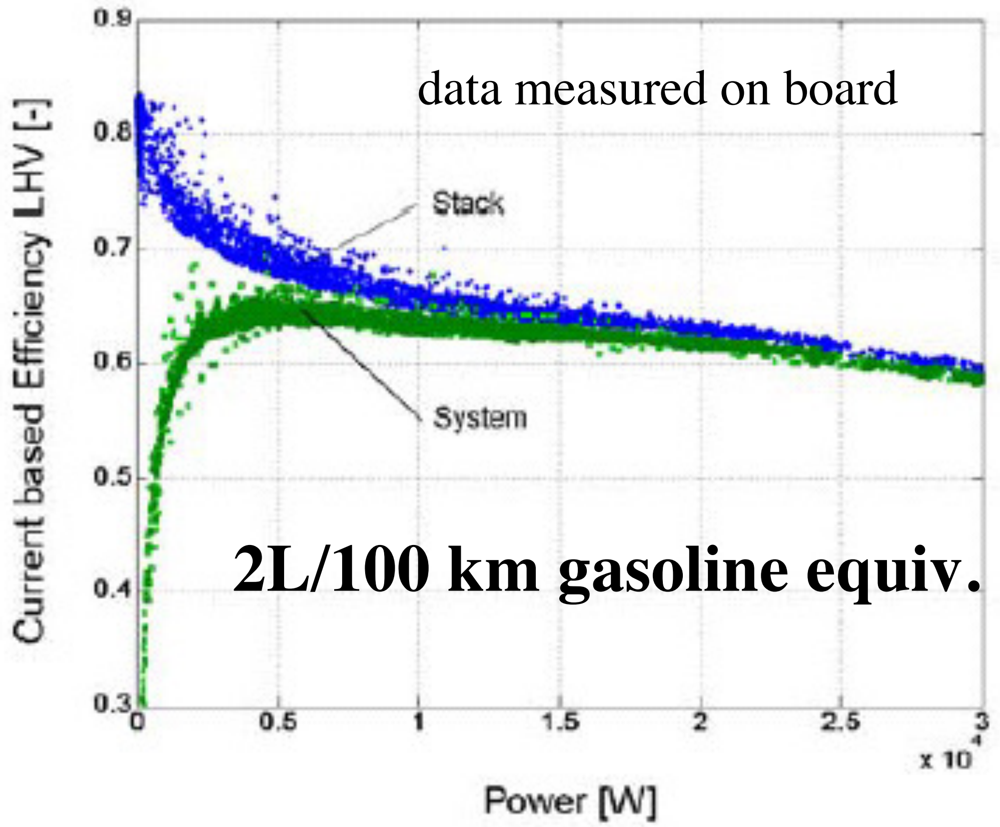
63 m^2 PV cells sufficient to supply H_2 for a FC-H_2 electric vehicle to drive 13'000 km / year

PAUL SCHERRER INSTITUT PSI

MICHELIN A better way forward

HY-LIGHT



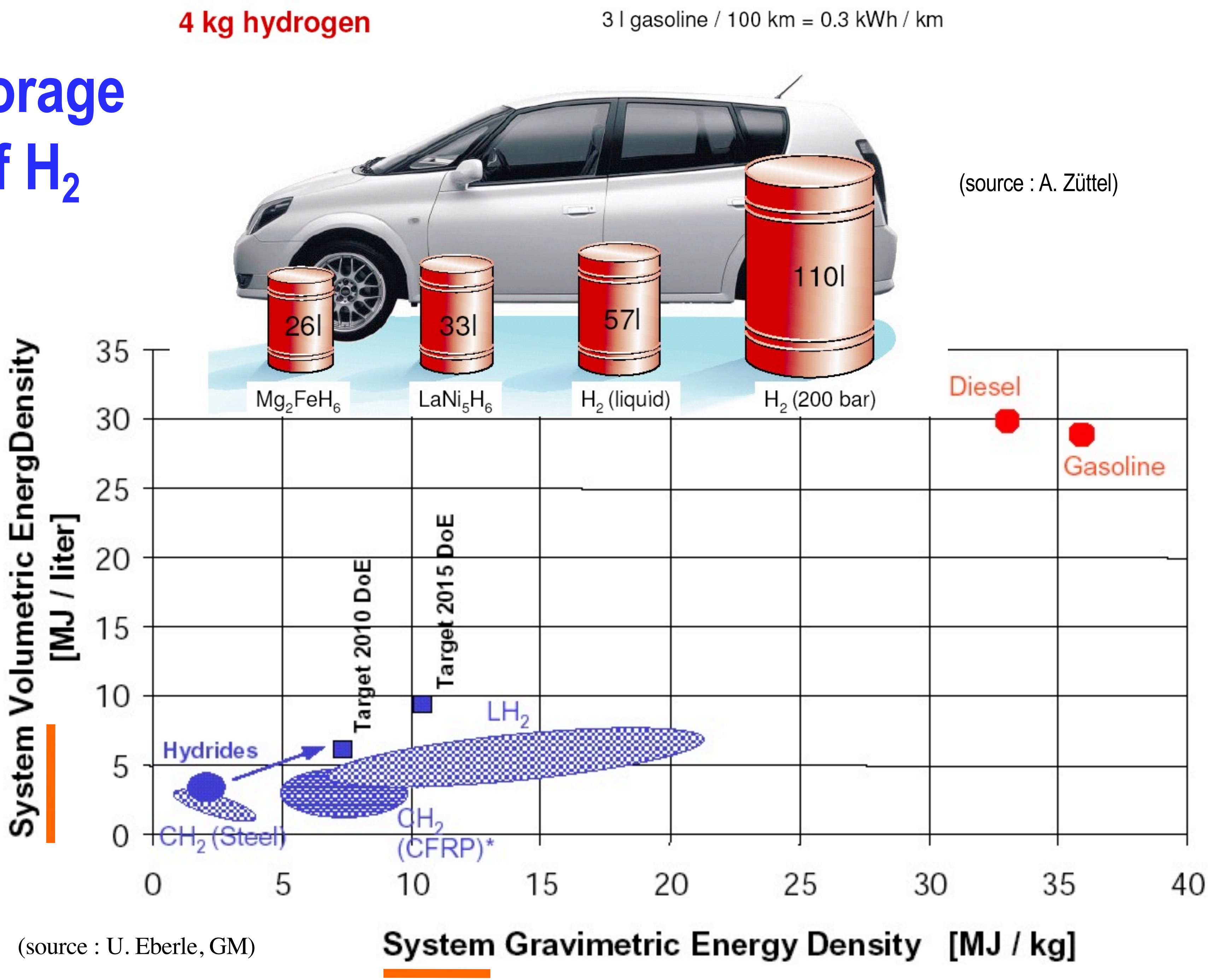


(source : F. Büchi, PSI)

The fuel issue

- Operating **temperature** as decisive parameter
- Fuel ‘processing’ (= fuel preparation)
- H_2 as **mobility** fuel
- Hydrocarbons for **stationary** application
- Importance of <u>integrated</u> fuel cell <u>systems</u>

Storage of H_2



(source : U. Eberle, GM)

Fuel cell processing basics

- any hydrocarbon fuel (CH_x) is converted to syngas (H_2, CO)
- syngas can directly feed high temperature FC
- to feed low temperature FC, chemical steps are necessary to reduce CO content to only traces, as CO blocks the Pt-catalyst

=> *fundamental difference between low and high T - fuel cells :*

	Low T	**High T**
Fuel	H_2	CH_x
Catalyst	**Pt**	**Ni**
CO	= poison	= fuel

Main fuel chemical reactions

✔ *methods to transform a primary hydrocarbon (e.g. natural gas, biogas,..) into syngas (the mixture of H_2, CO)*

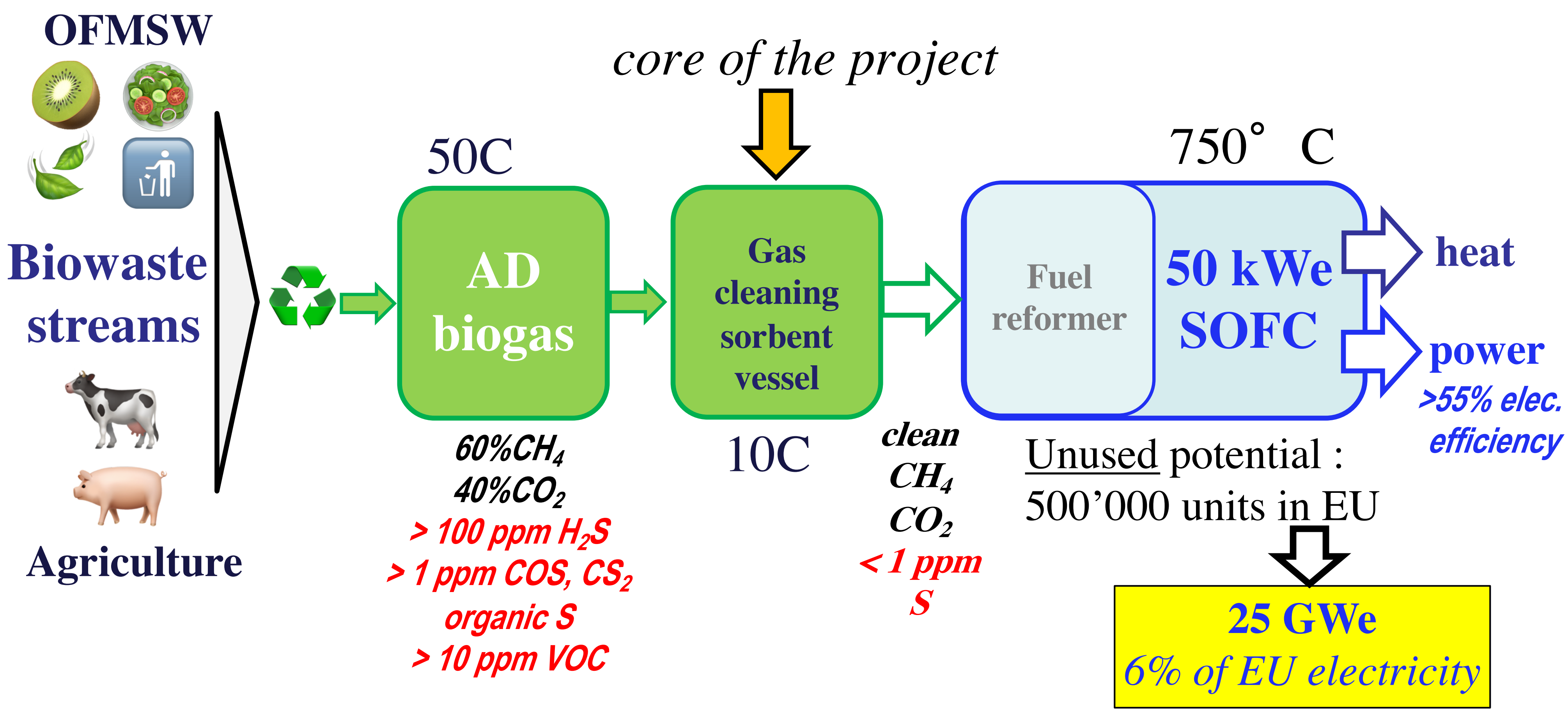
Steam reforming SR	$CH_4 + H_2O \leftrightarrow 3H_2 + CO$
Dry reforming	$CH_4 + CO_2 \leftrightarrow 2H_2 + 2CO$
Partial Oxidation POX	$CH_4 + \frac{1}{2}O_2 \Rightarrow 2H_2 + CO$
(Water gas) shift	$CO + H_2O \leftrightarrow H_2 + CO_2$
Pyrolysis ("cracking")	$CH_4 \Rightarrow 2H_2 + C$
Boudouard	$2CO \Leftrightarrow CO_2 + C$
Reverse gasification	$CO + H_2O \leftrightarrow H_2O + C$

☒ *reactions that deposit solid carbon (to be avoided!)*

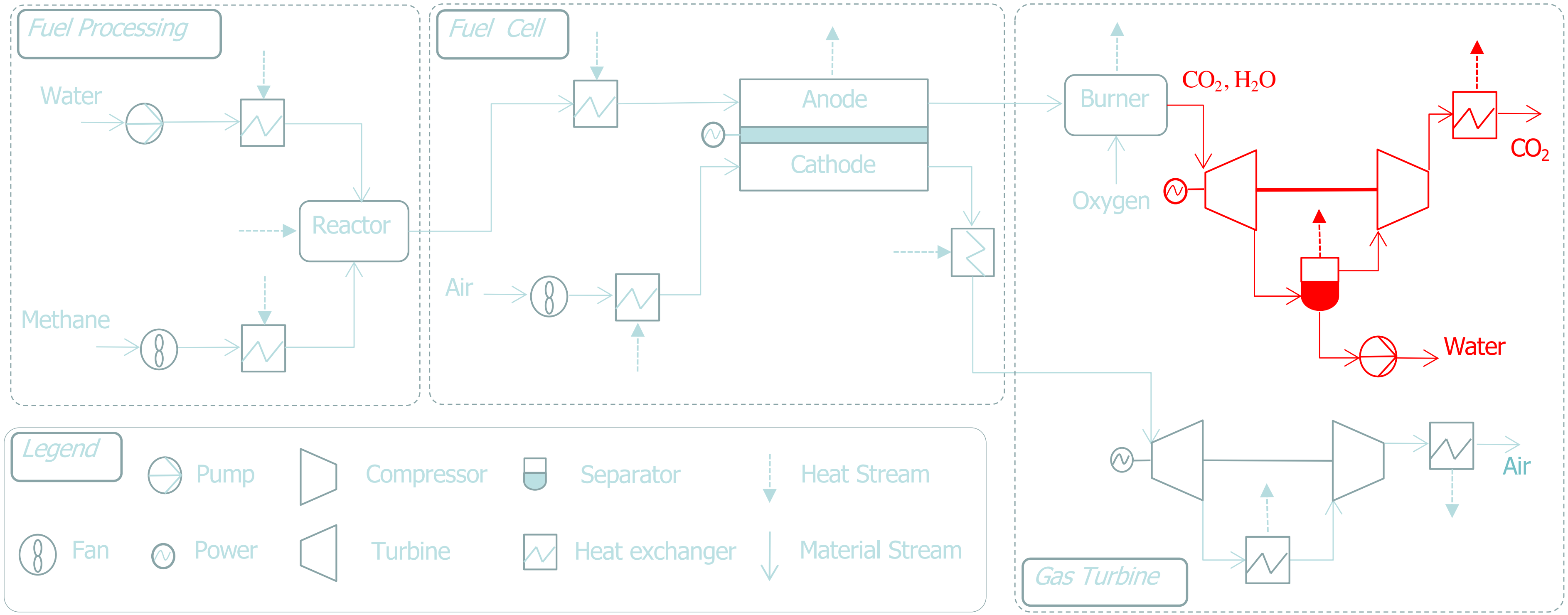
✔ *method to transform CO into H_2*

Waste2Watts EU project

- **low cost biogas cleaning** for coupling with **low cost SOFC** to prepare biogas market entry for Solid Oxide Fuel Cells



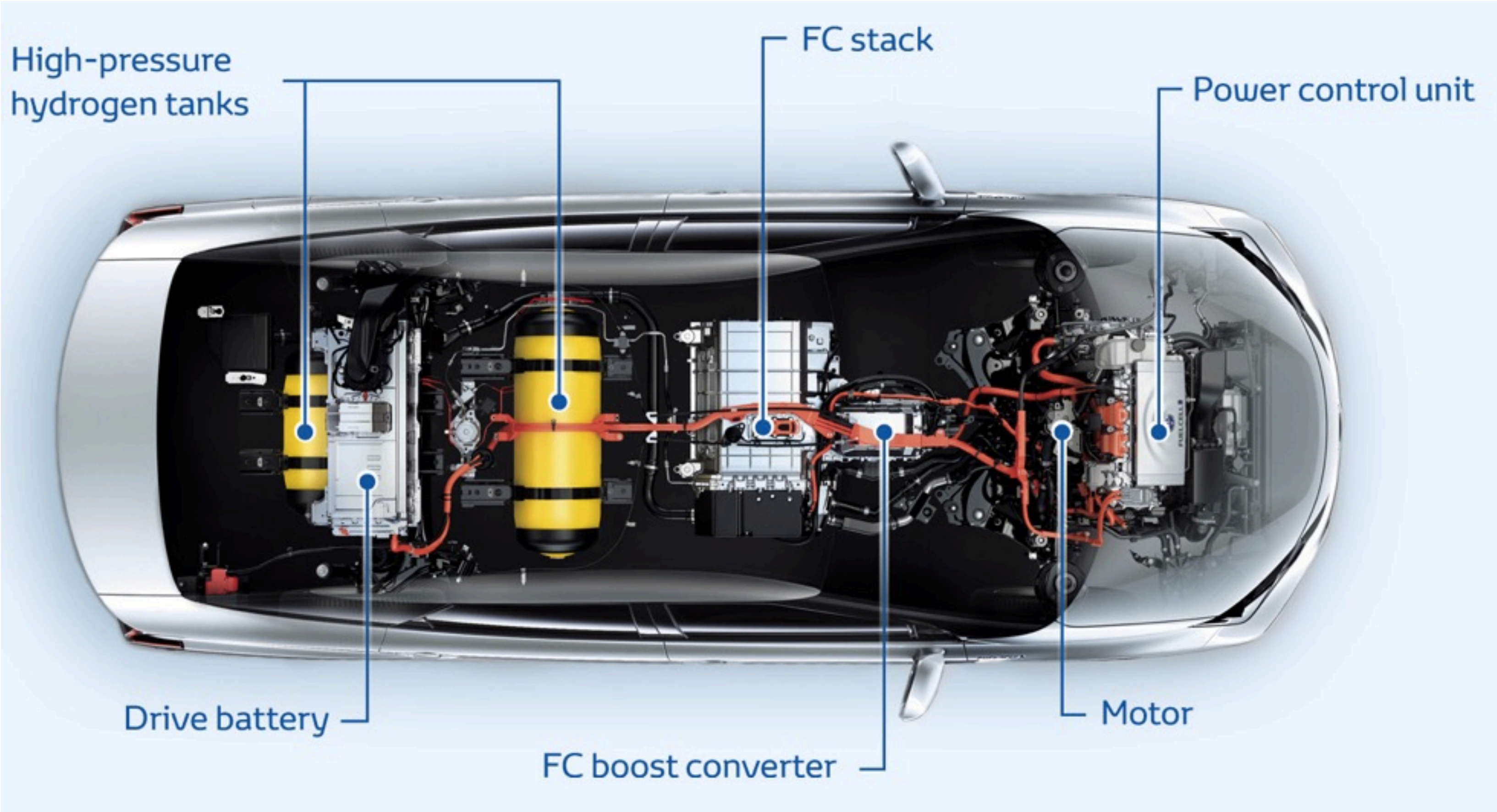
HYBRID SOFC-GT FUEL CELL SYSTEM WITH CO_2 SEPARATION



- **A SOFC is inherently a separator of oxygen and nitrogen of air**
- **Anodic flow is mainly CO_2 and H_2O that can be used in a sub-atmospheric Brayton cycle improving the overall electrical efficiency (up to 80%) with an efficient CO_2 recovery**

Toyota Mirai

650 km range - H_2 700 bar - 3 min refill - 114 kW max



http://www.toyota-global.com/innovation/environmental_technology/fuelcell_vehicle/

http://www.theverge.com/2014/11/18/7242785/toyotas-new-hydrogen-powered-mirai-sedan-will-be-on-sale-next-year

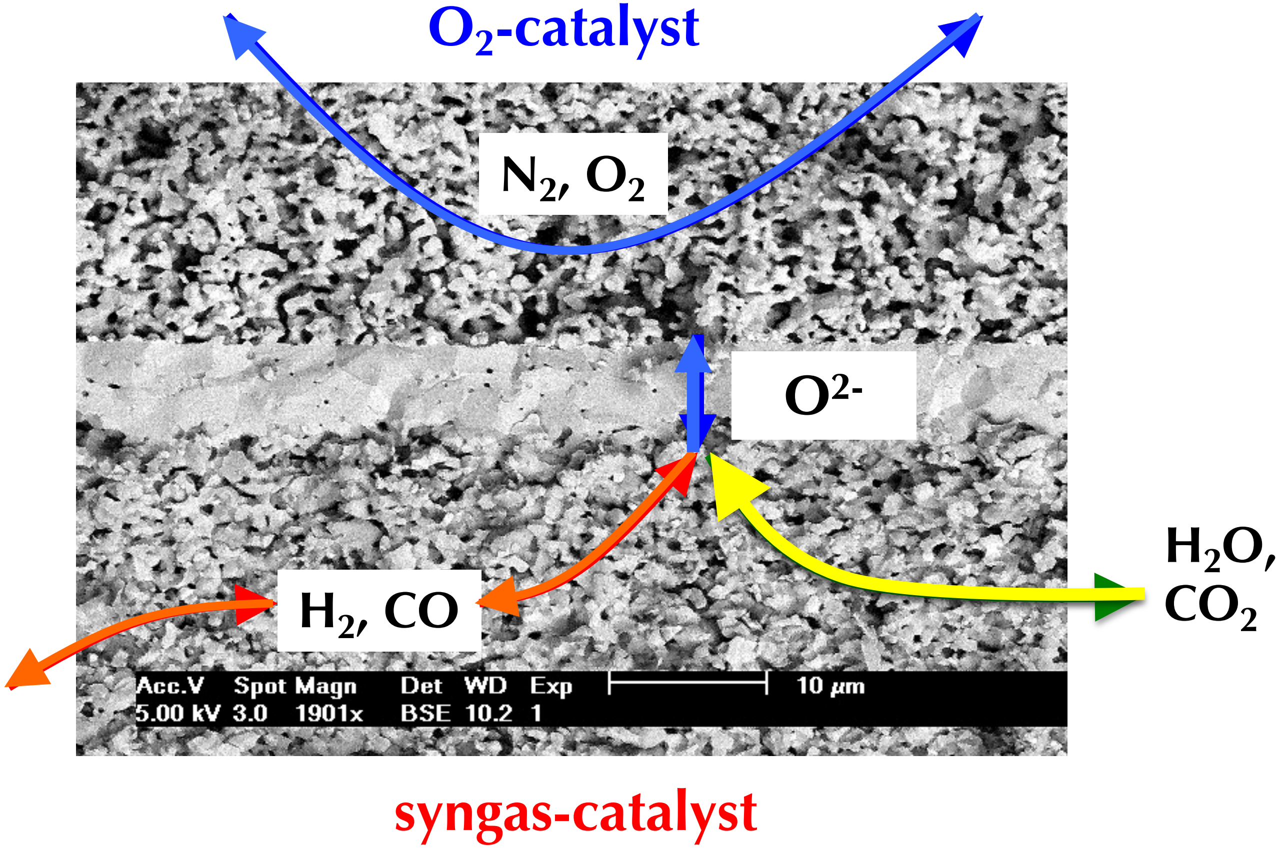
Electricity Storage

- the electrical grid has virtually no storage capacity
- **seasonal** electricity demand varies significantly
- the difference (summer-winter) is exacerbated when replacing base-load (nuclear, coal) with renewables like PV and hydro (summer-excess, winter-deficit)

→ long term storage is required

- as **fuel** by electrolysis (H_2, CH_4, …) => **"Power-to-Gas"**
- in batteries

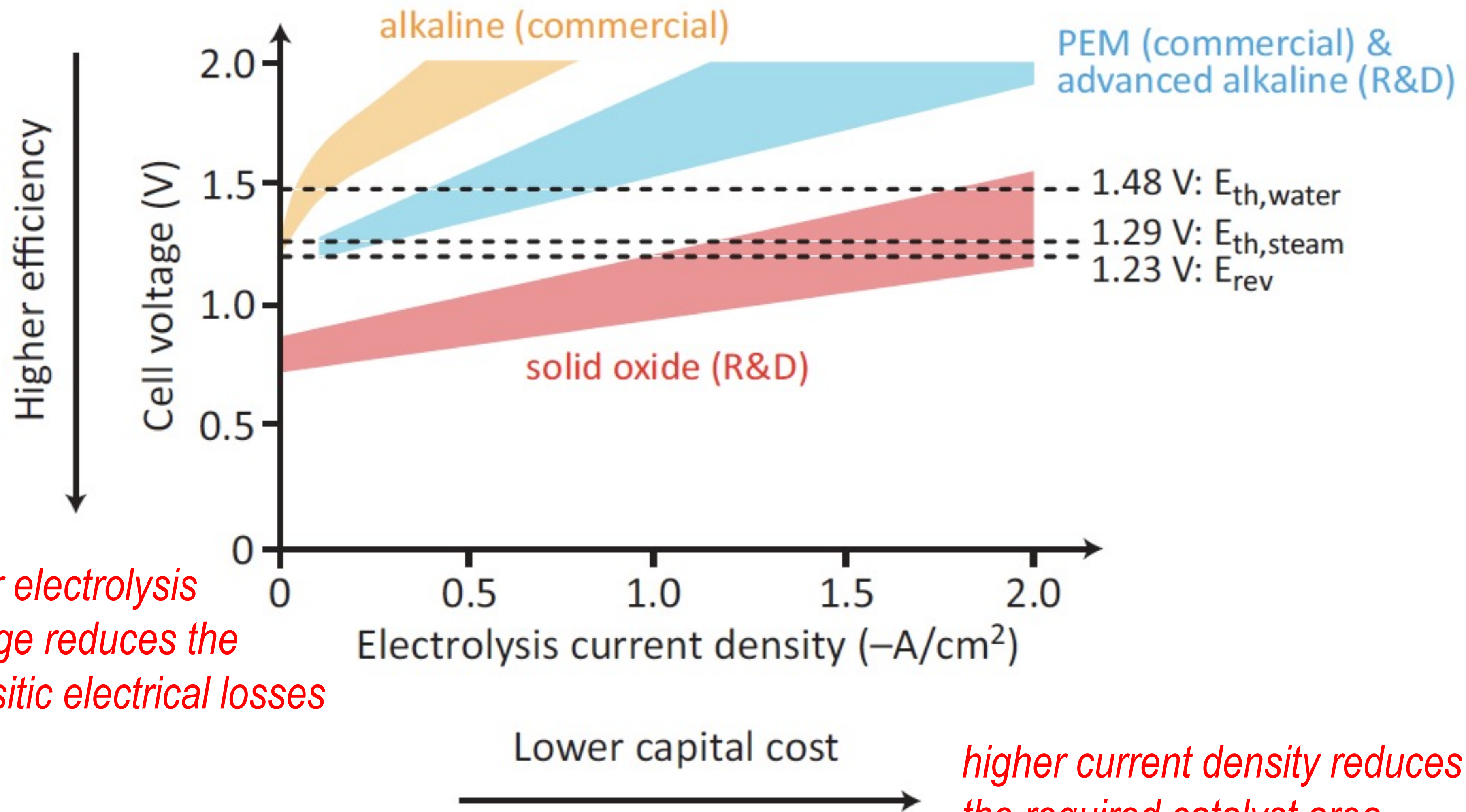
Reverse fuel cell = electrolyzer



<u>Operating regime</u> :
700-800C
1 bar (to 5 bar)

FUEL CELL
ELECTROLYSER

Electrolysis technology comparison



lower electrolysis voltage reduces the parasitic electrical losses

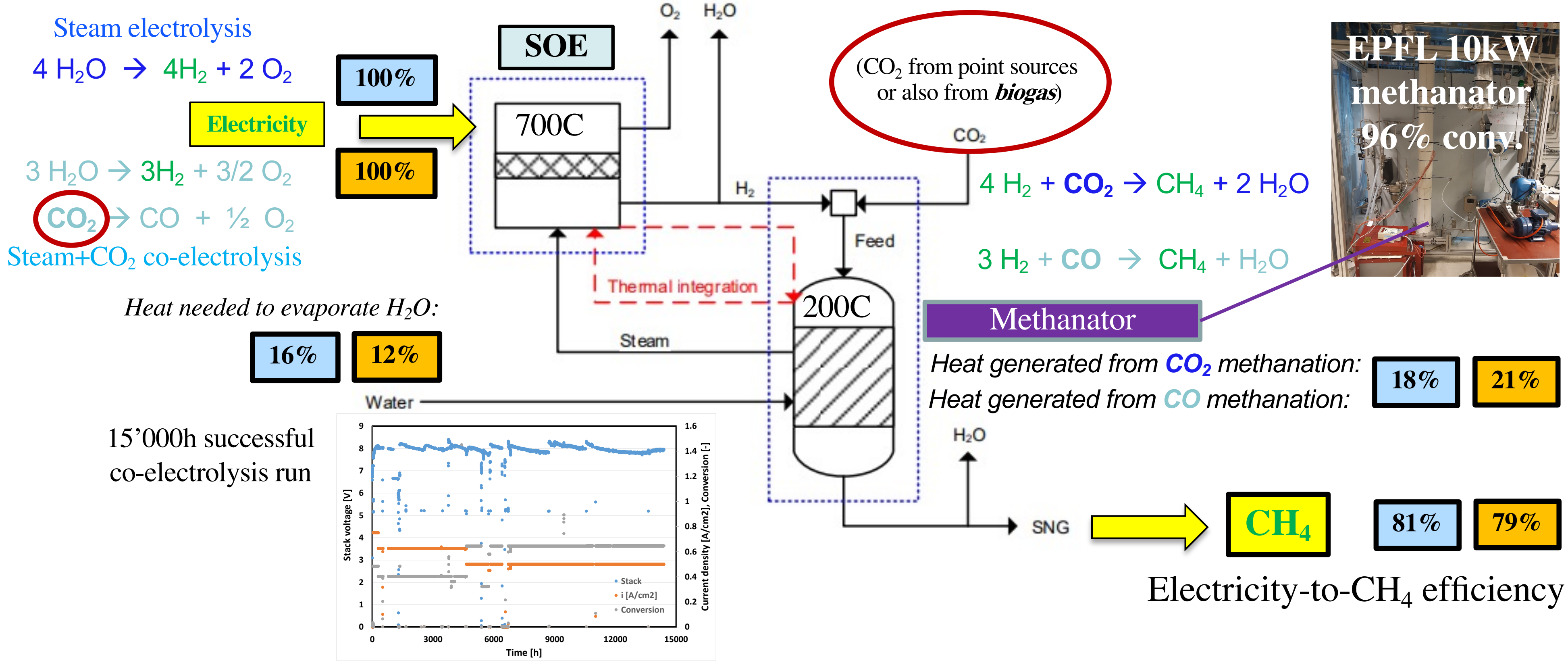
higher current density reduces the required catalyst area

Sustainable hydrocarbon fuels by recycling CO2 and H2O with renewable or nuclear energy
Christopher Graves, Sune D. Ebbesen, Mogens Mogensen, Klaus S. Lackner
Renewable and Sustainable Energy Reviews 15 (2011) 1–23

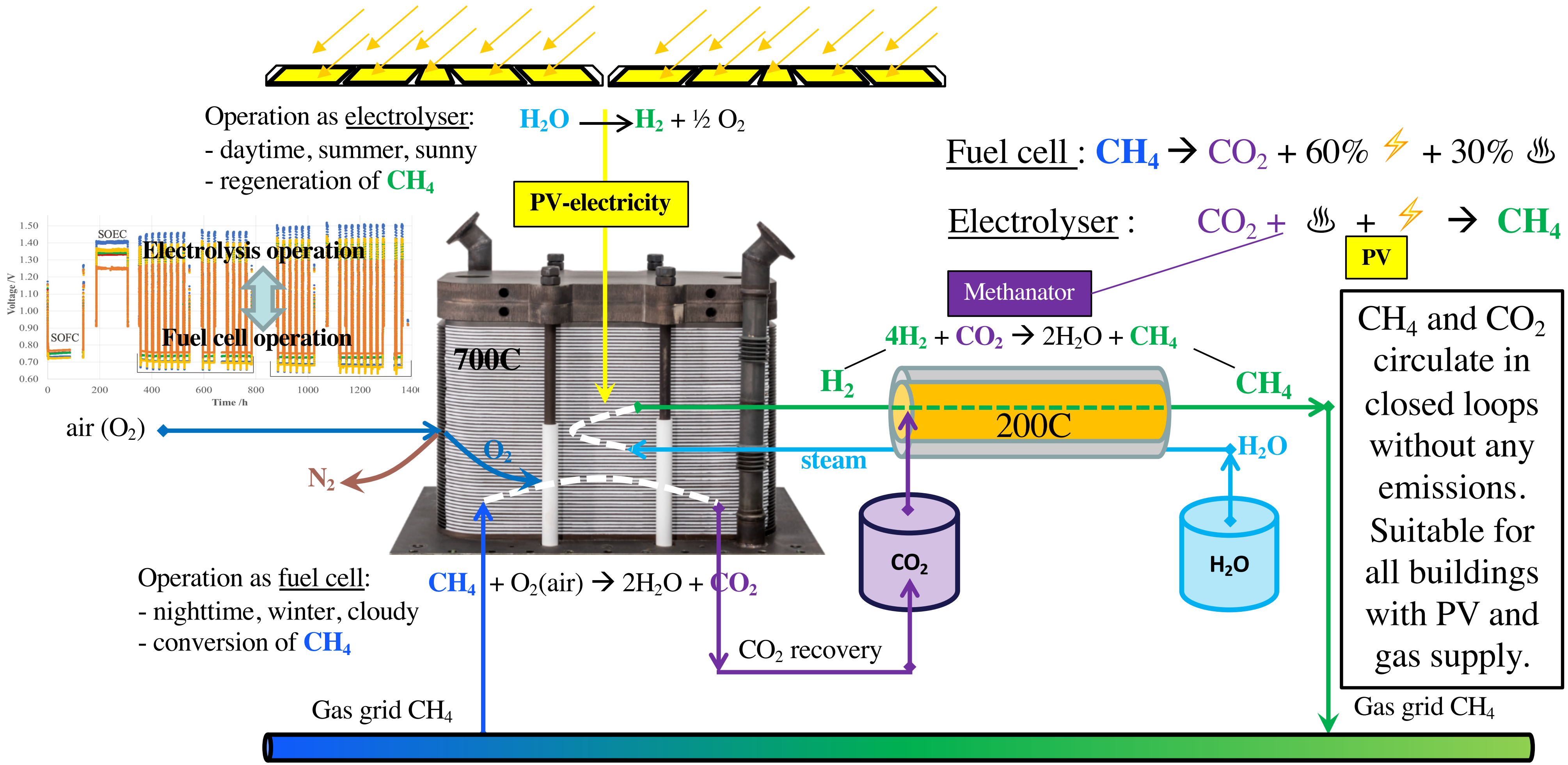
CO_2-to-CH_4 via methanation coupled with solid oxide (co)electrolysis (SOE)

Motivation:

1) (Green) H_2 is needed to methanate CO_2 to CH_4
2) The most efficient electrolysis to provide H_2 is from steam (30% less electricity need than water electrolysis)
3) The steam is provided from the methanation heat itself => integrated system => highest efficiency



CH_4–to–CO_2–to–CH_4 with *reversible* solid oxide cell technology (*r*SOC)



Key Issues

- Great progress in Fuel Cells since 2 decades
  - H_2-cars and buses (10 – 200 kW_e PEFC)
  - residential micro-CHP (1-2 kW_e SOFC, natural gas)
  - efficient clean cogeneration plants (MW_e-sized MCFC, incl. biogas)
- big effort in reliability and cost reduction still to accomplish
- competition (engines, batteries,…) progresses too!
- issue of the H_2-storage & distribution