The Abdus Salam
International Centre for Theoretical Physics

United Nations
Educational, Scientific
and Cultural Organization

International Atomic
Energy Agency

Workshop on "Physics for Renewable Energy"
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301/1679-32

"Fuel Cells"

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Italy

FUEL CELLS: BASIC AND TECHNOLOGY

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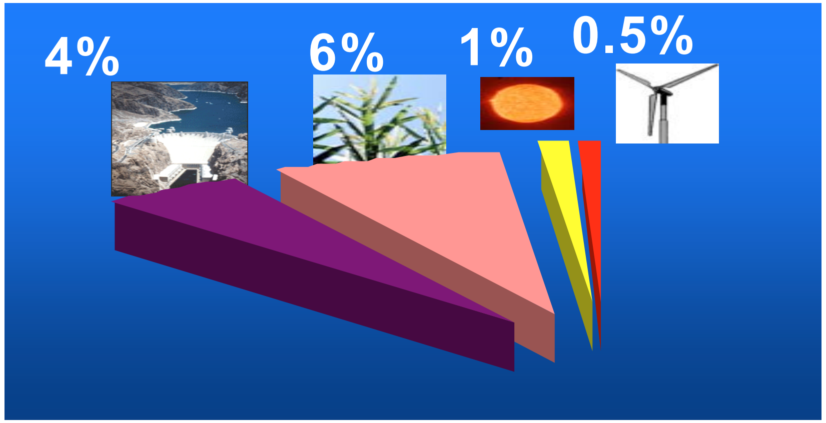
and Fuel Cell Technology

LAB-FCT

Dipartimento di Chimica,
Università "La Sapienza" Rome, Italy

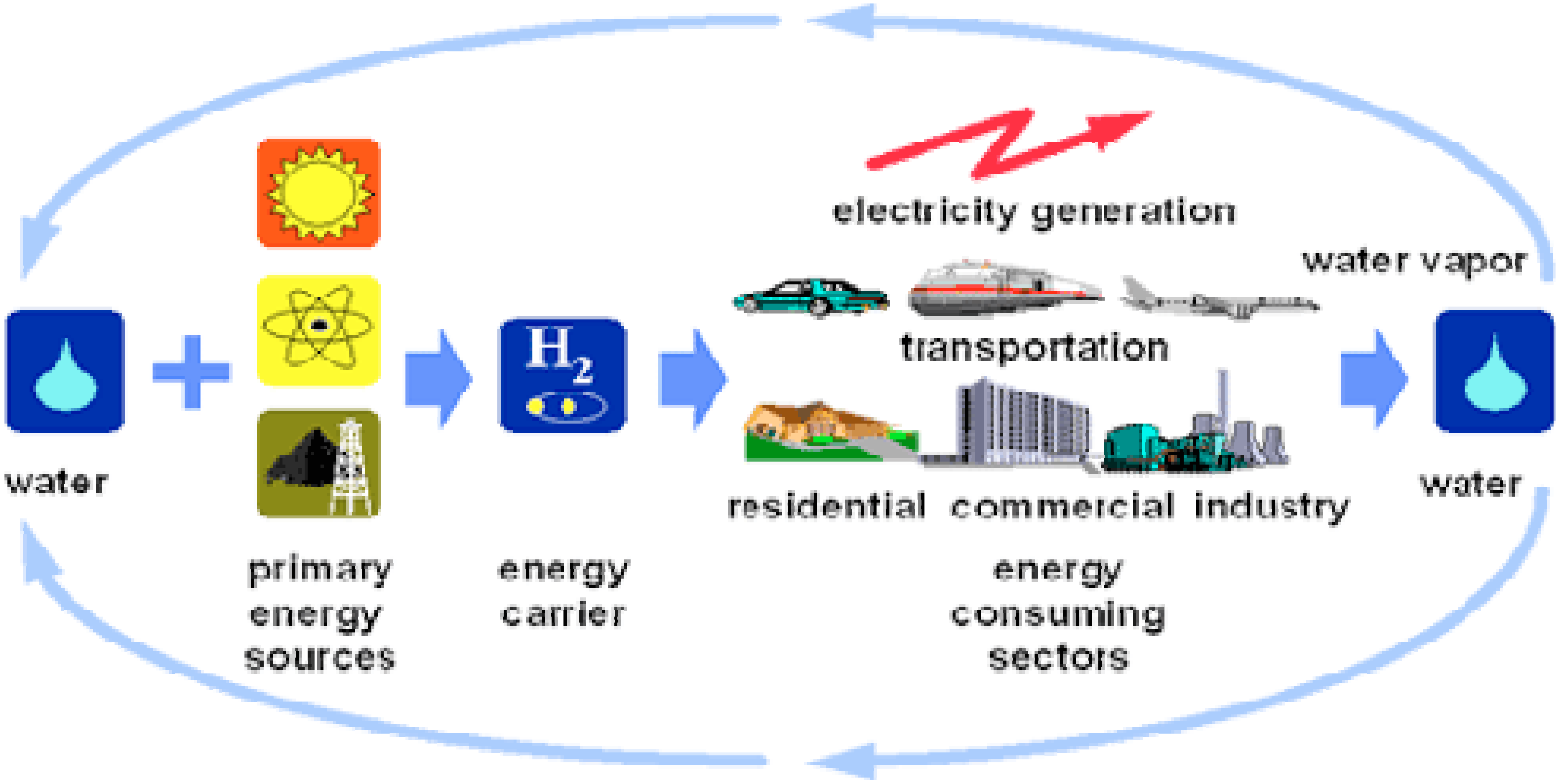
To control environment pollution and..

..to better implement renewable energies in our day-to-day lives
Sun doesn't shine on demands...
Wind doesn't blow every days..



Cost-efficient, long-life, high-power energy electrochemical power sources (e.g. batteries or fuel cells) are urgently needed!

Renewable and clean energy: the hydrogen cycle



Electrochemical devices able to recombine hydrogen and oxygen, i.e. fuel cells, are crucial to close the loop!

The Promise of Fuel Cell Vehicles

Environmentally Clean

On-Board Power

High Performance

Design Freedom

Low Maintenance

High Efficiency

Reliability

Low Noise

Comfort (no vibration)

Hydrogen is a clean and renewable vector for energy conversion and for high-performance, zero emission cars.

The question is: why hydrogen energy is still not in force and hydrogen cars are not in the road?

Fuel cells

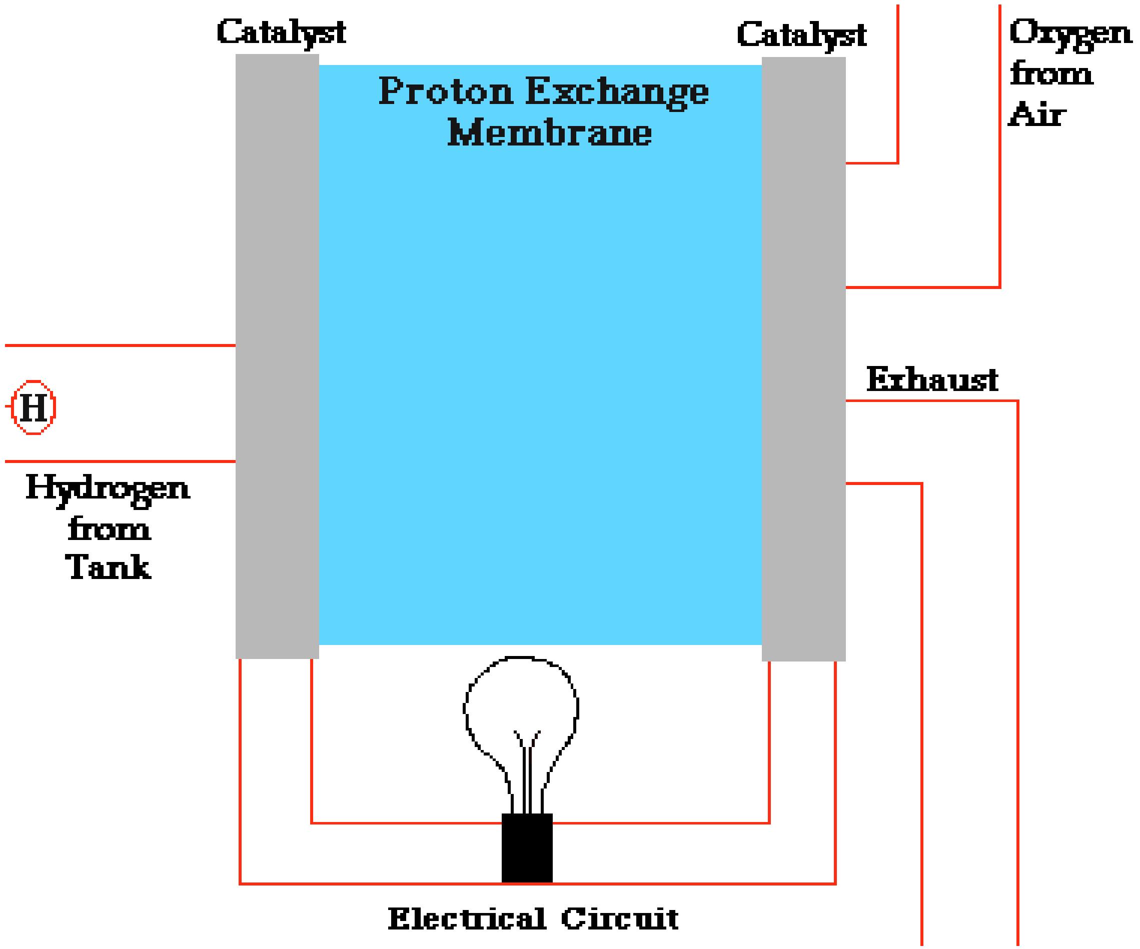
Devices for directly converting the chemical energy of a fuel into electric energy.

In the most classic configuration, the fuel cell reaction involves the combustion of hydrogen with oxygen to form water:

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

Thermodynamic potential, E: 1.23 V

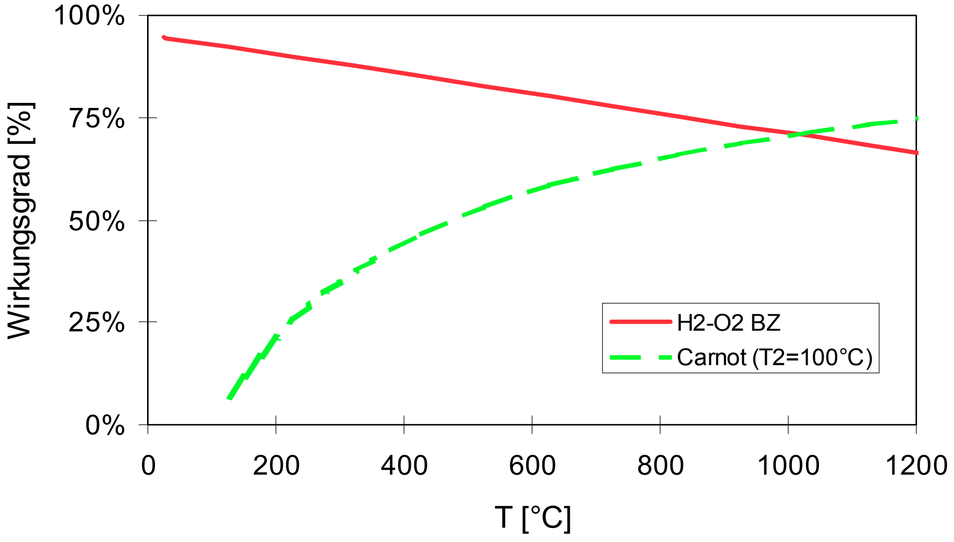
Fuel cell operation scheme



A fuel cell is an electrochemical power source with advantages of both combustion engine and a battery.

Like a combustion engine, a fuel cell will run as long as it is provided fuel; like a battery, fuel cells convert chemical energy directly to electrical energy.

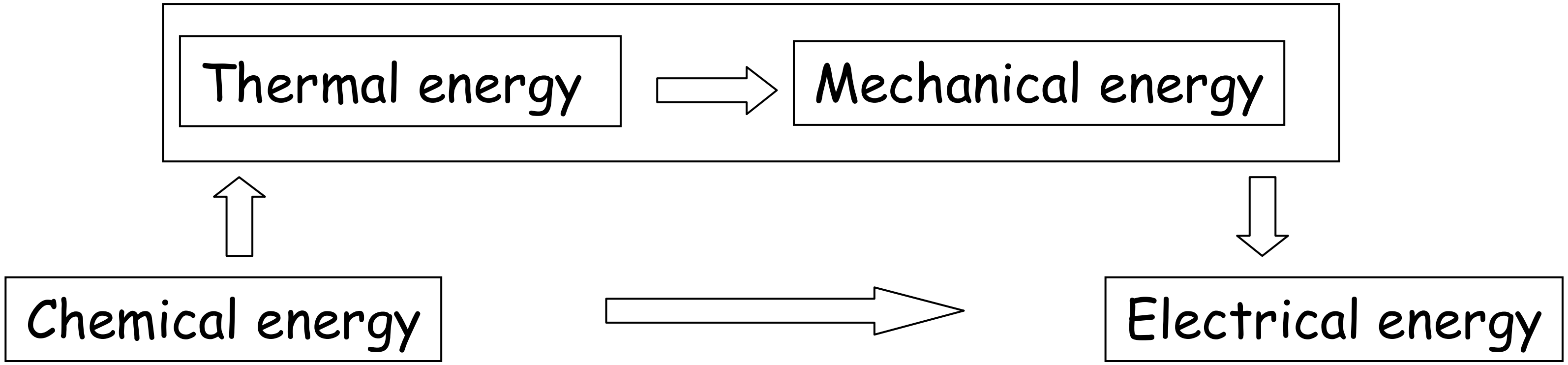
However, being electrochemical reactors, fuel cells are not subject to the Carnot limitations of combustion (heat) engines.



BATTERY ⟺ FUEL CELL

- Direct conversion from chemical to electrical energy
- Reagent gas continuously provided from an external source

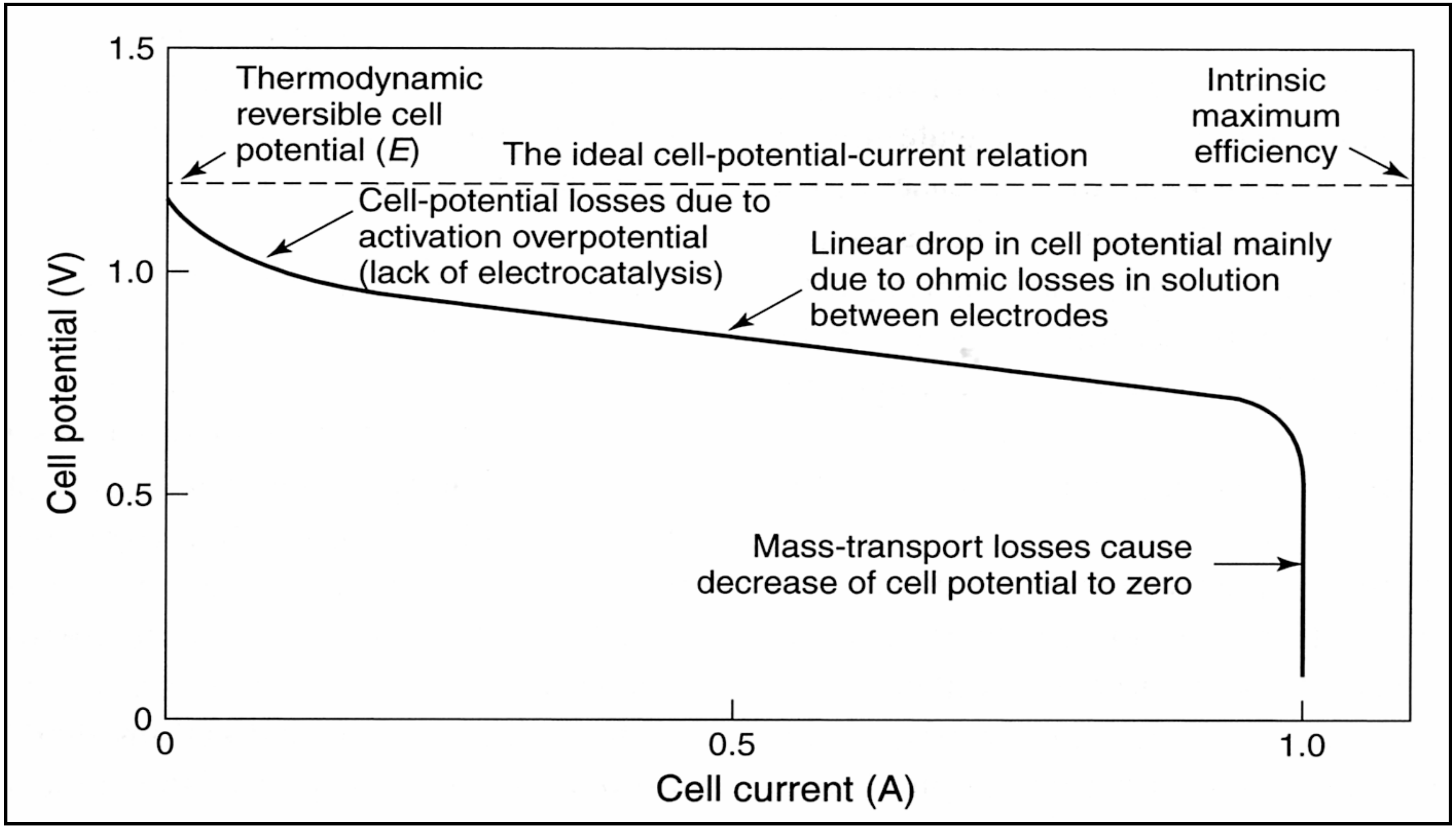
FUEL CELL ⟺ INTERNAL COMBUSTION ENGINE


Thermal energy
Mechanical energy
Chemical energy
Electrical energy

efficiency:

🙂 $\varepsilon_{teor} = \dfrac{\Delta G}{\Delta H}$ $\Leftrightarrow$ 🙁 $\varepsilon_{Car} = \dfrac{T_1 - T_2}{T_1}$ $(\sim 40\%)$

Fuel cell operation
Current-potential curve

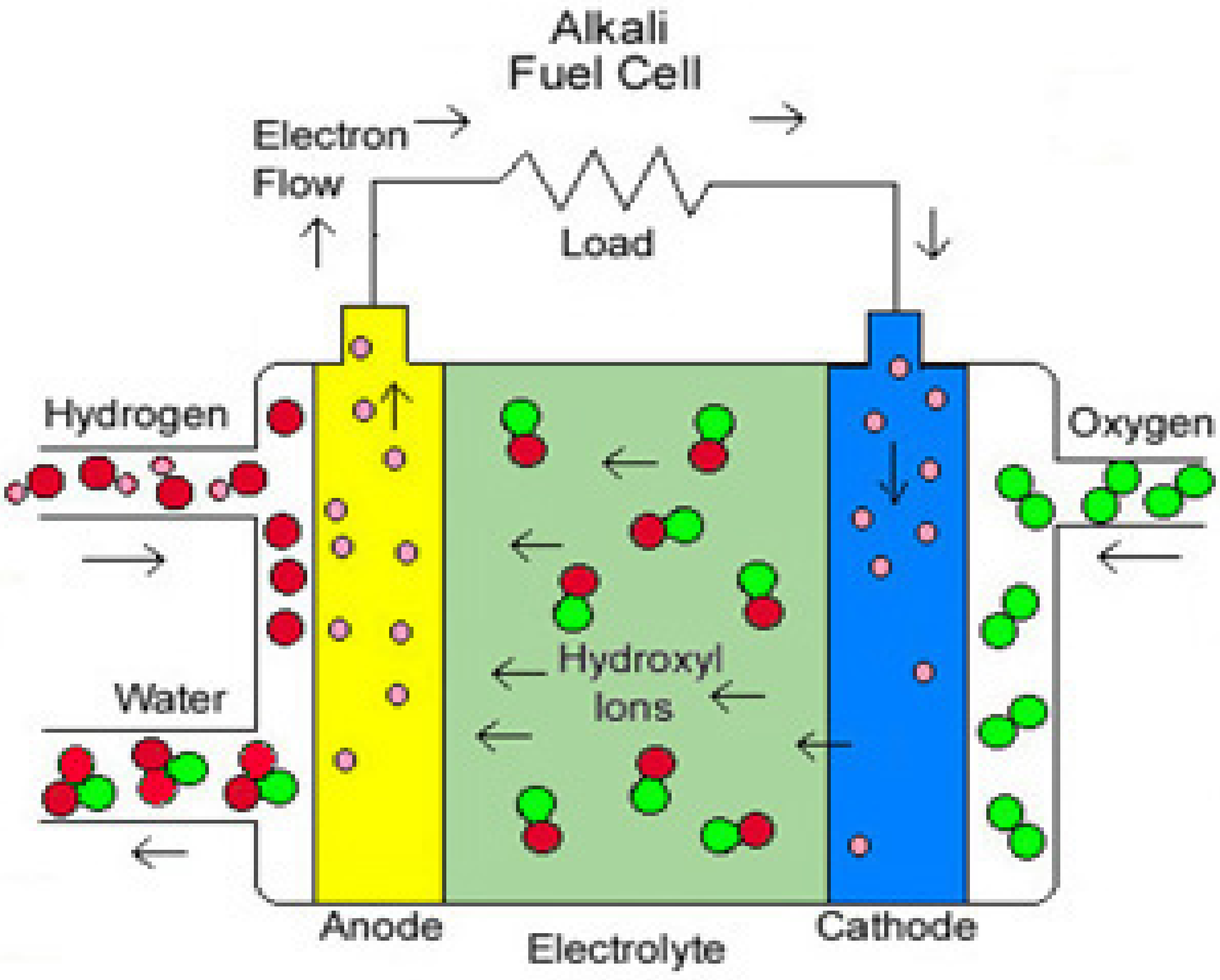


Fuel Cells

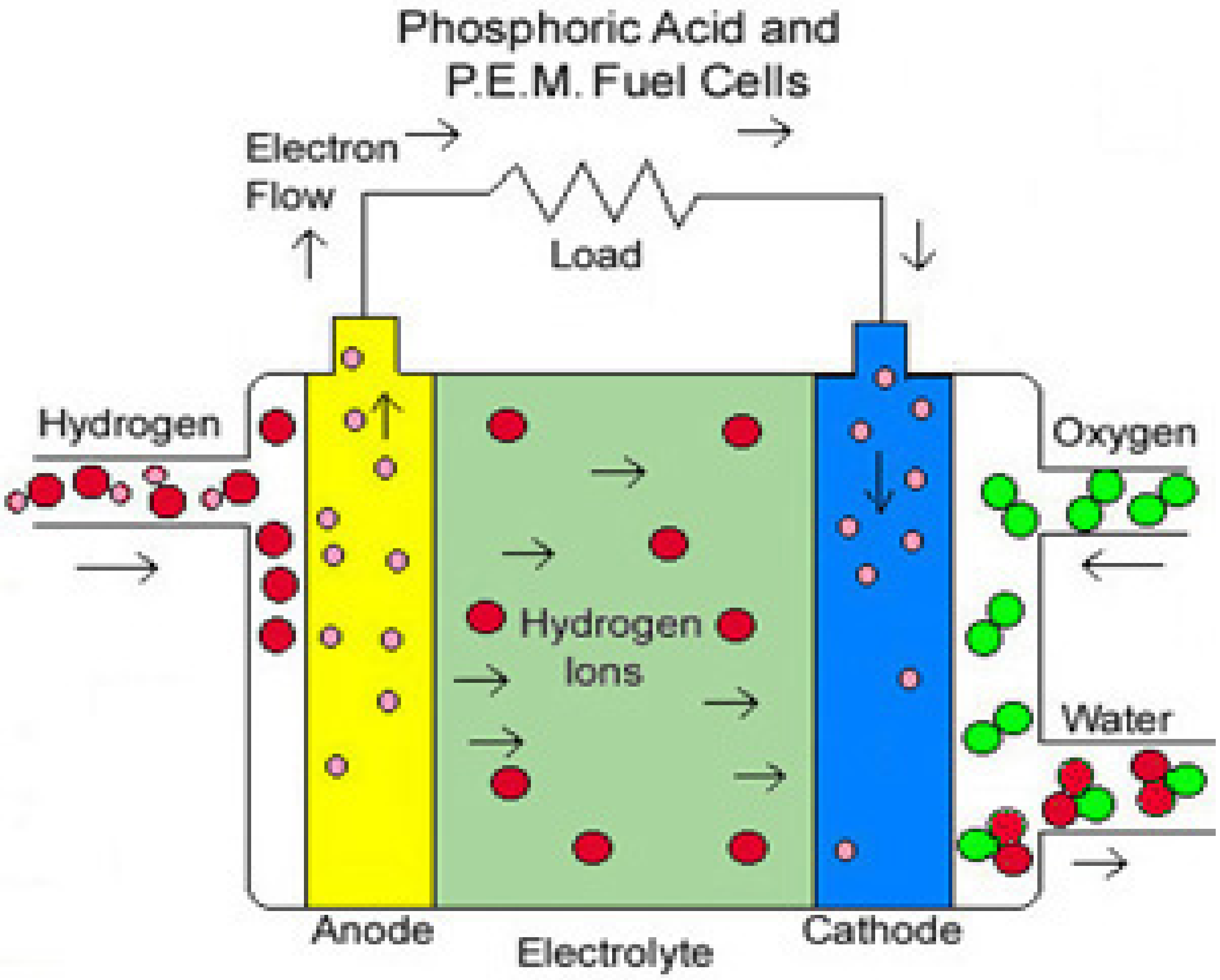
There are various types of fuel cells, mainly differing by the type of electrolyte used and accordingly, by the temperature of operation.

	Fuel cell types		operat. temp
-	Alkaline FC	AFC	80 °C
-	Polymer Membrane FC	PEFC	80 °C
-	Phosphoric Acid FC	PAFC	180 °C
-	Molten Carbonate FC	MCFC	600 °C
-	Solid Oxid FC	SOFC	800 °C

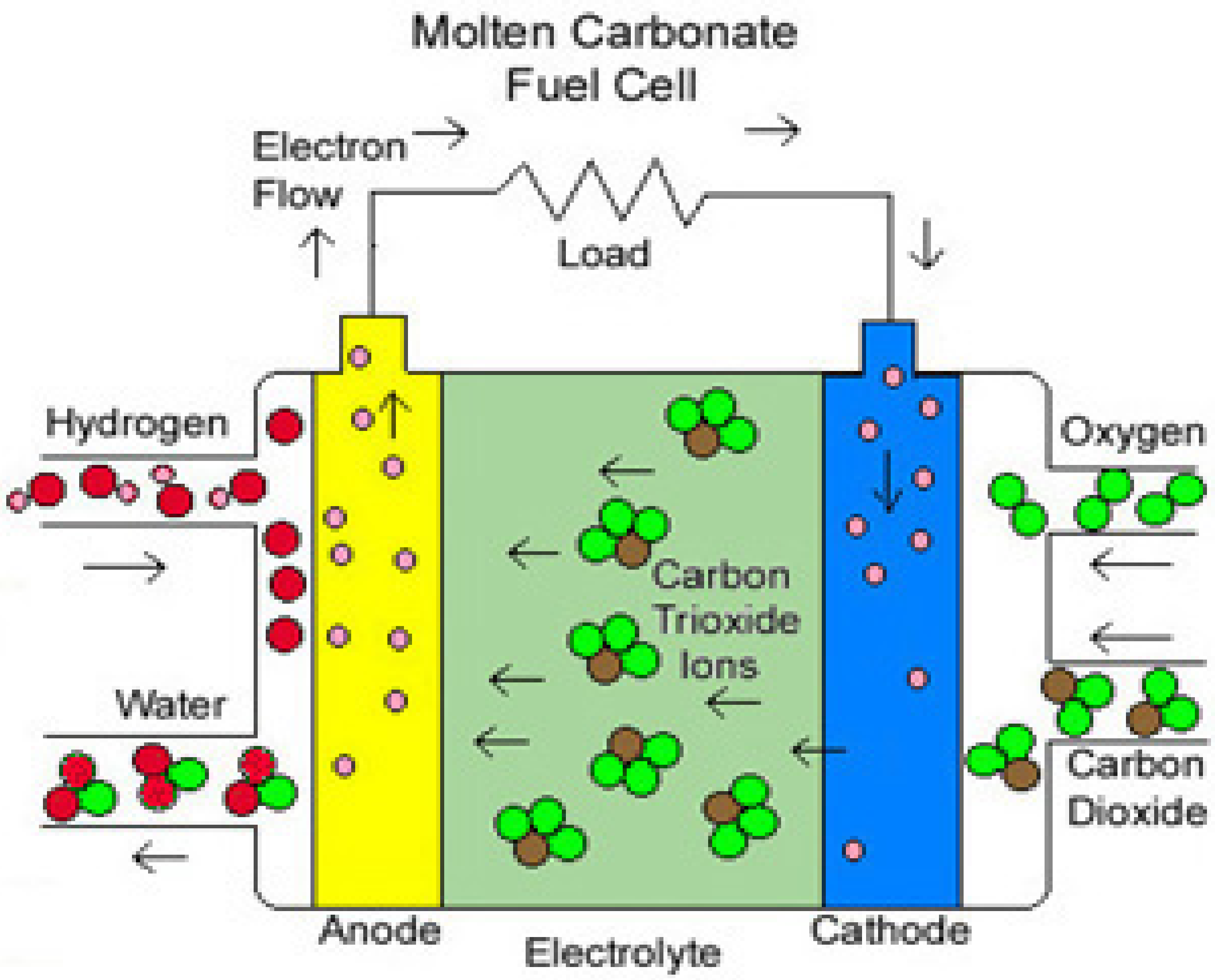
Drawing of an alkaline fuel cell, AFC



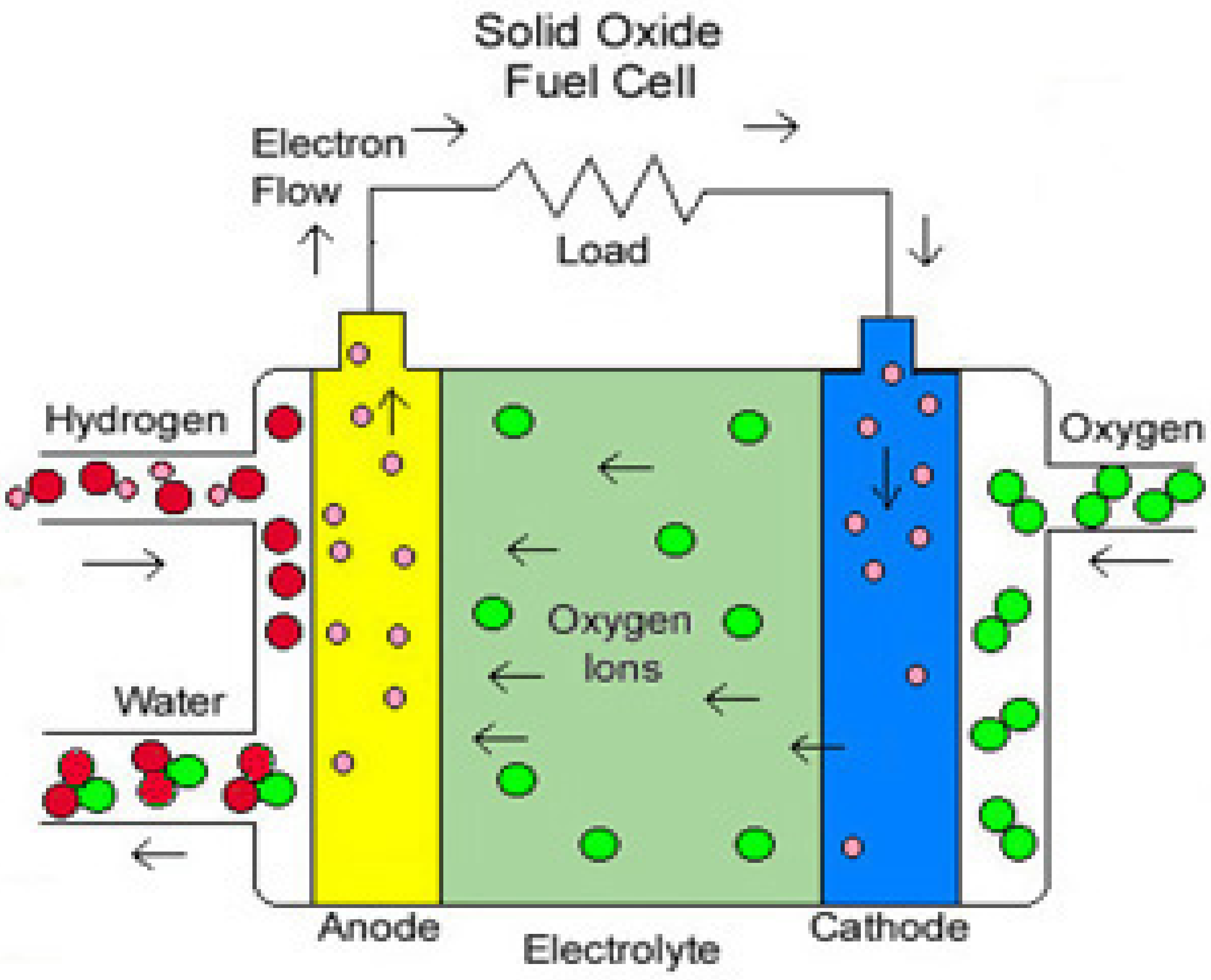
Drawing of phosphoric acid fuel cells, PAFC



Drawing of a molten carbonate fuel cell, MCFC



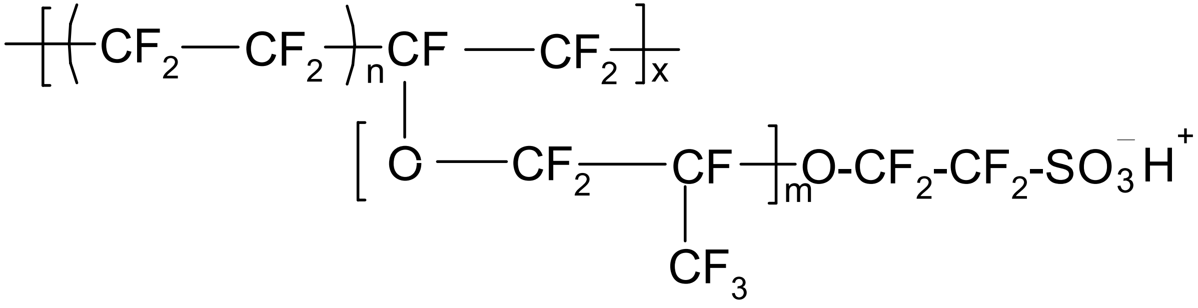
Drawing of a solid oxide fuel cell, SOFC



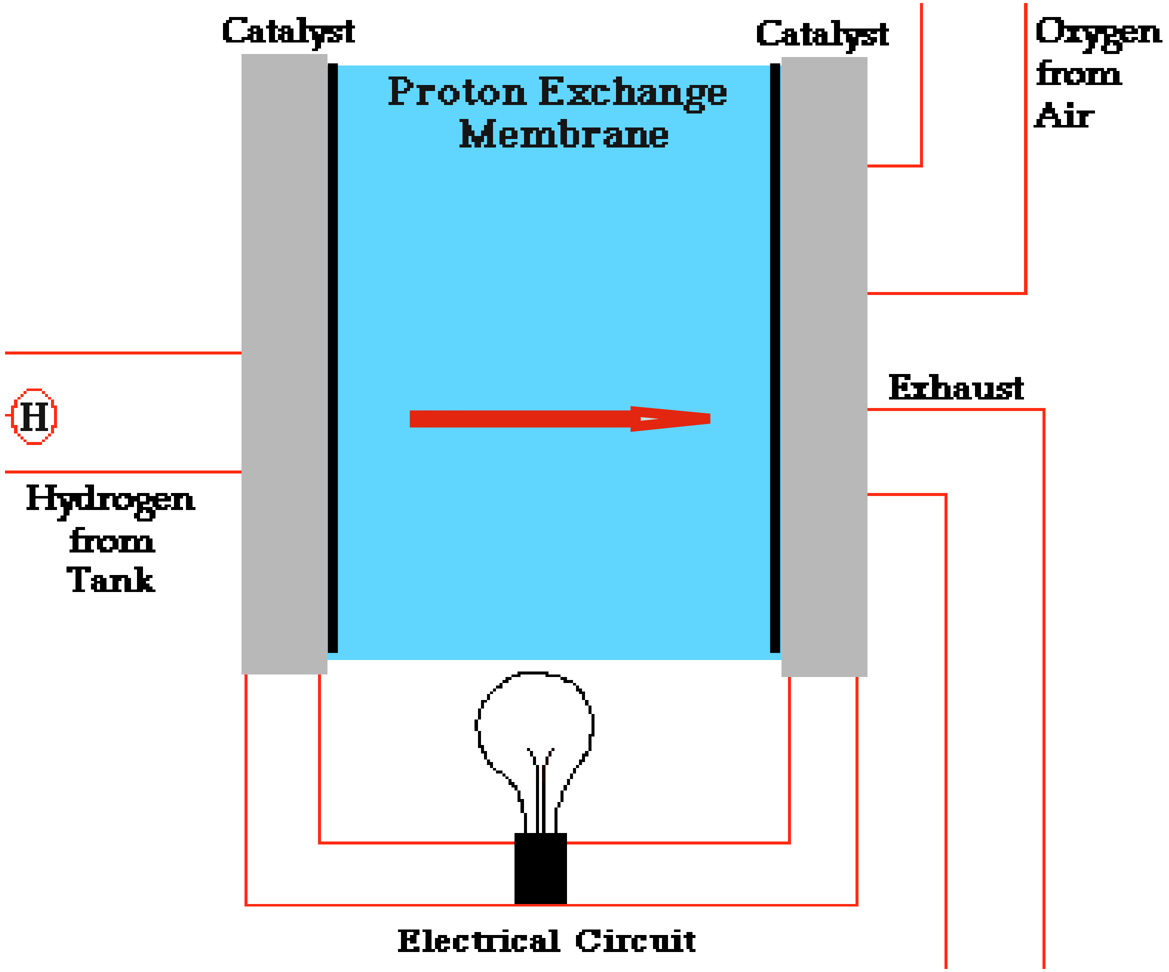
Fuel Cells

There are various types of fuel cells, mainly differing by the type of electrolyte used and accordingly, by the temperature of operation.

The most common are polymer electrolyte fuel cells (PEMFCs) which use as separator a proton conducting, perfluorosulphonate membrane, typically Nafion®.



Fuel cell operation



anode

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

cathode

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

Polymer electrolyte fuel cells

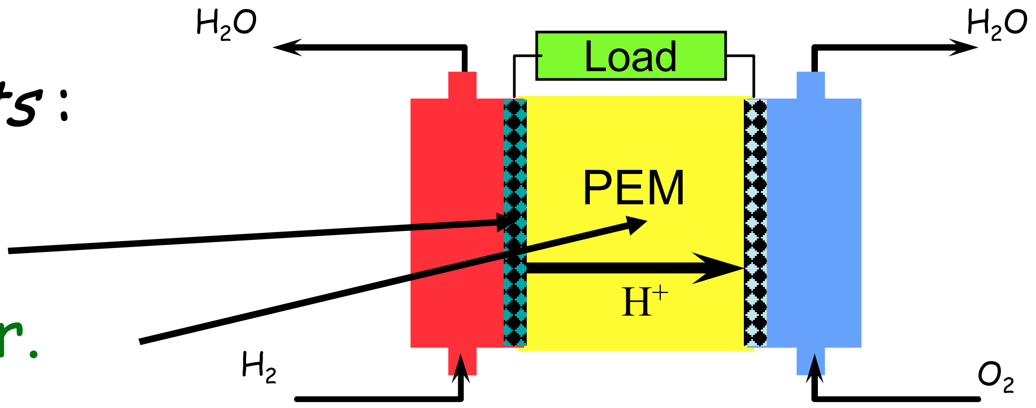
Fuels : hydrogen or alcohol
(e.g methanol, DMFCs)

Comburent : oxygen or air

Two main distinctive components :

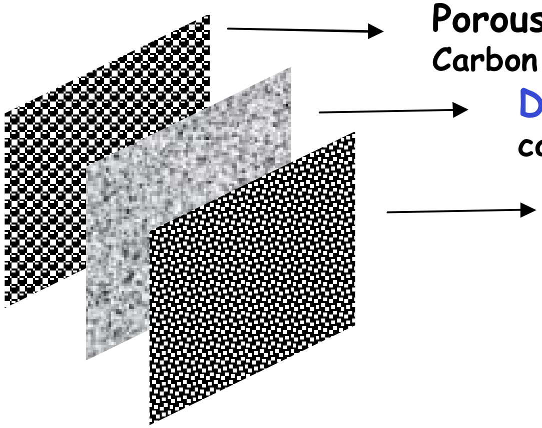
☞ Electrode structure (MEA)

☞ Polymer electrolyte separator.



Electrode structure

The electrodes are typically constructed by making a catalyst layers applied to porous carbon substrate containing the membrane and heat pressed to form the so called Membrane Electrode Structure (MEA)



Porous backing layer
Carbon Paper

Diffusion Layer
carbon particles + Teflon

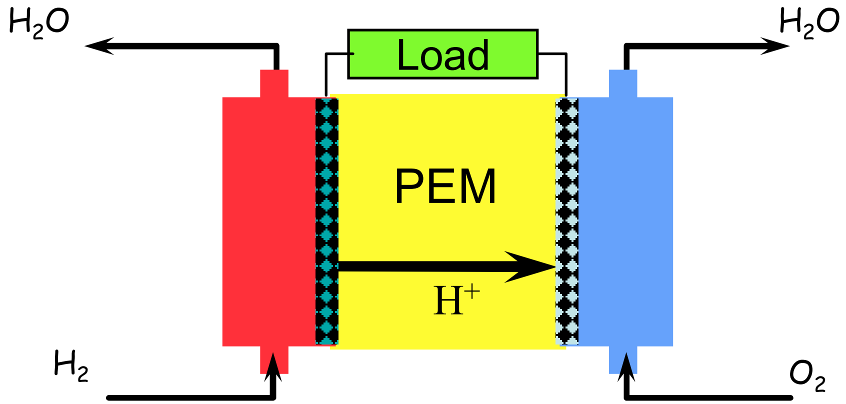
Catalytic Layer
catalyst+porous carbon +
protonic membrane

Noble metal catalysts, usually Pt or Pt alloys

Polymer electrolyte fuel cells, PMFCs

Energy renewal
(*hydrogen-economy*)

Environmental control
(*No-emission vehicles*)



Major drawback:
cost of the catalyst (noble metals) and of the polymer electrolyte membrane (Nafion™ -type)

The catalyst (Pt)

Pt world production: just 165 tons (2002 figure)

Cost of Pt catalyst in fuel cell: \$18/kW
(assuming \$ 35/g_{Pt} for a Pt/C catalyst)

Industrial target :<< \$10/kW, equivalent to <0.2 g_{Pt}/kW !

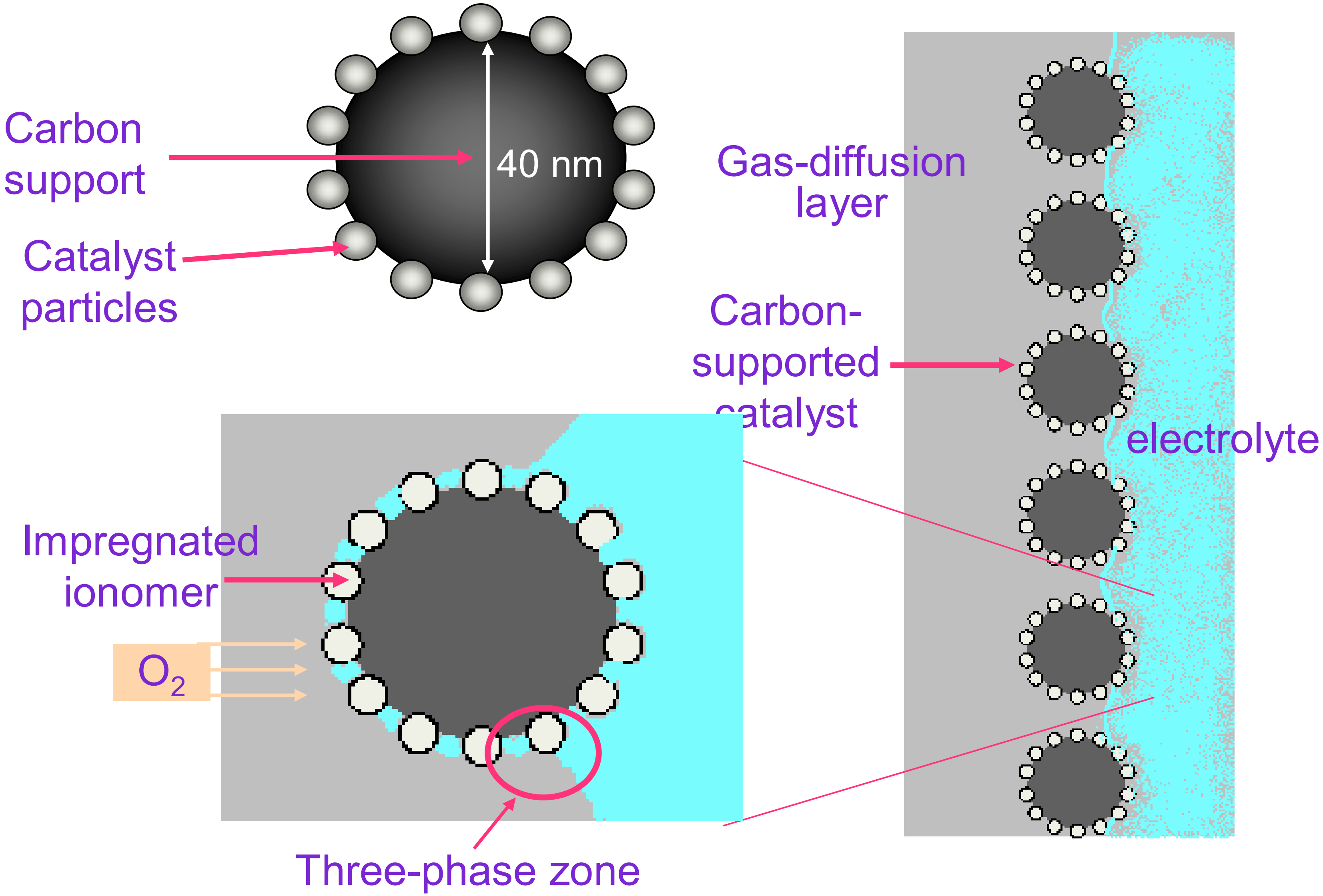
Intensive research on electrocatalysts for H_2 and O_2 reduction!

Increasing of Pt mass-specific activity

new carbon supports for catalyst
optimized morphology

Main tasks: reduce the Pt loading or discover alternative not-noble metal catalysts!

Electrode structure



40 nm

Carbon support

Catalyst particles

Gas-diffusion layer

Carbon-supported catalyst

electrolyte

Impregnated ionomer

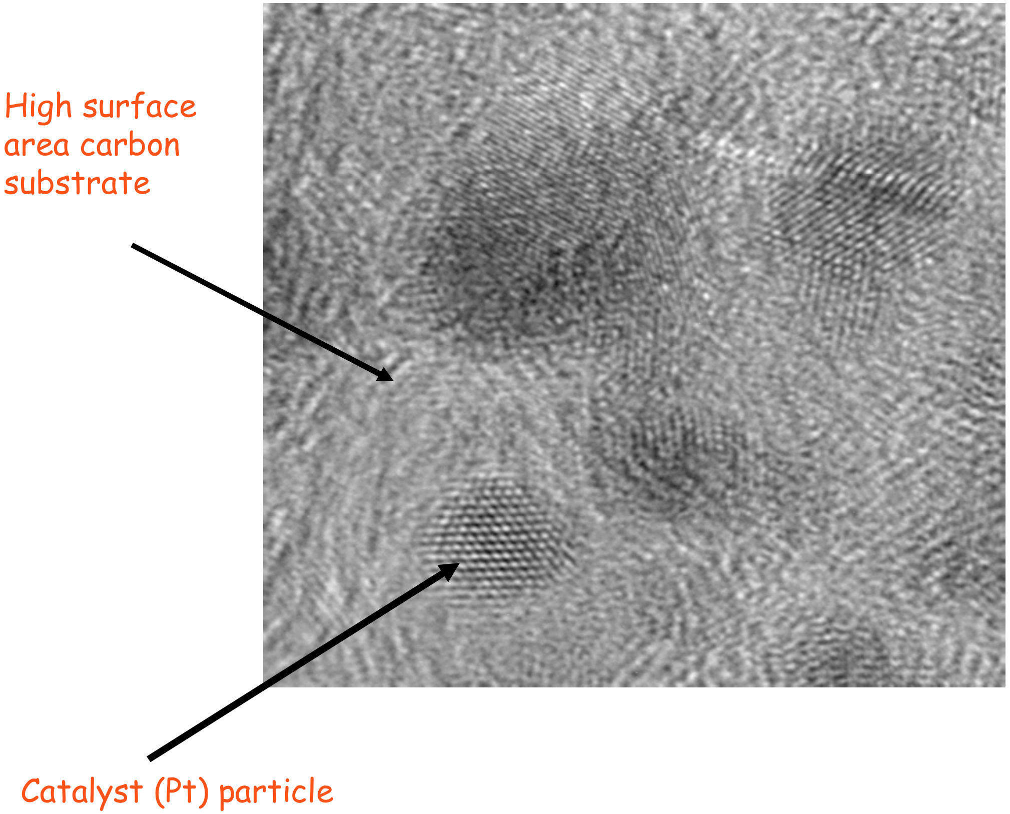
O_2

Three-phase zone

Courtesy of Professor E.Peled, Tel Aviv University

Fuel cell electrode structure

The cost of the electrode structure may be controlled by using high surface area substrates on which nanoscale catalyst (Pt, Pt-Ru) particles may be dispersed.

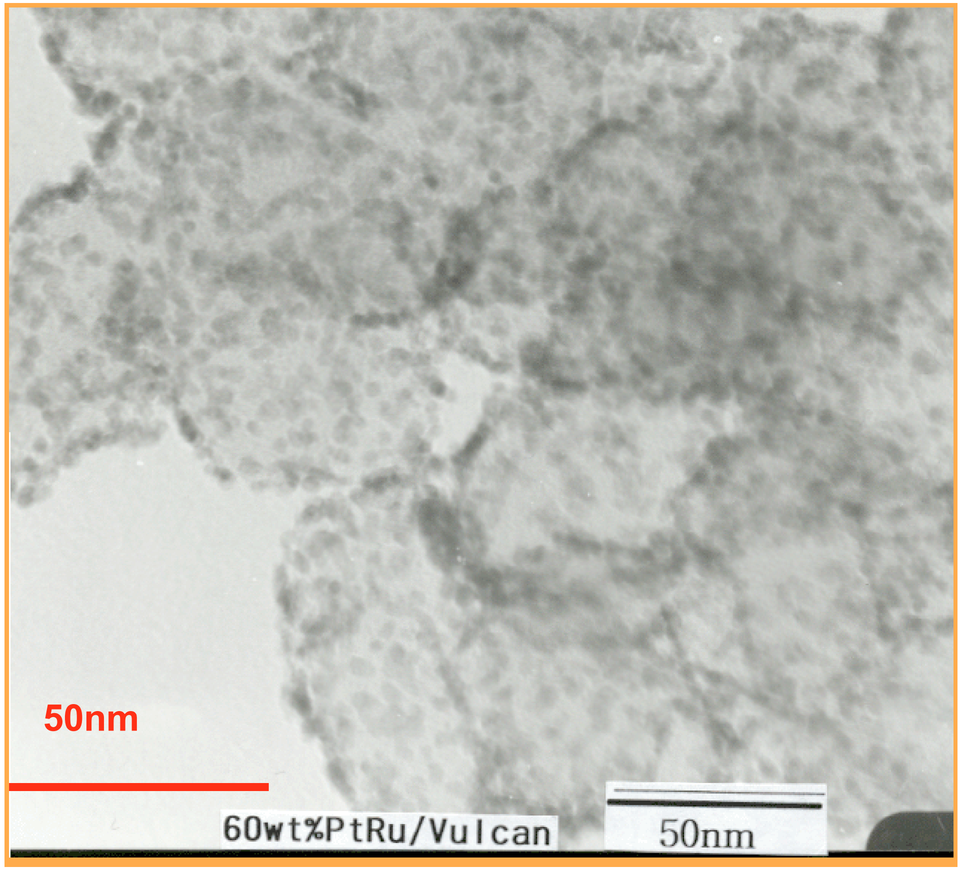


With this approach, the precious metal loading may be reduced to very low levels, e.g few mg/cm^2 and, with the new technologies, to 0,5 mg/cm^2.

The goal of the car companies is to reach Pt loadings even lower than this limit.

Courtesy of Prof. Tom Zavodinski, Case Western University, Cleveland, USA

Fuel cell electrode structure



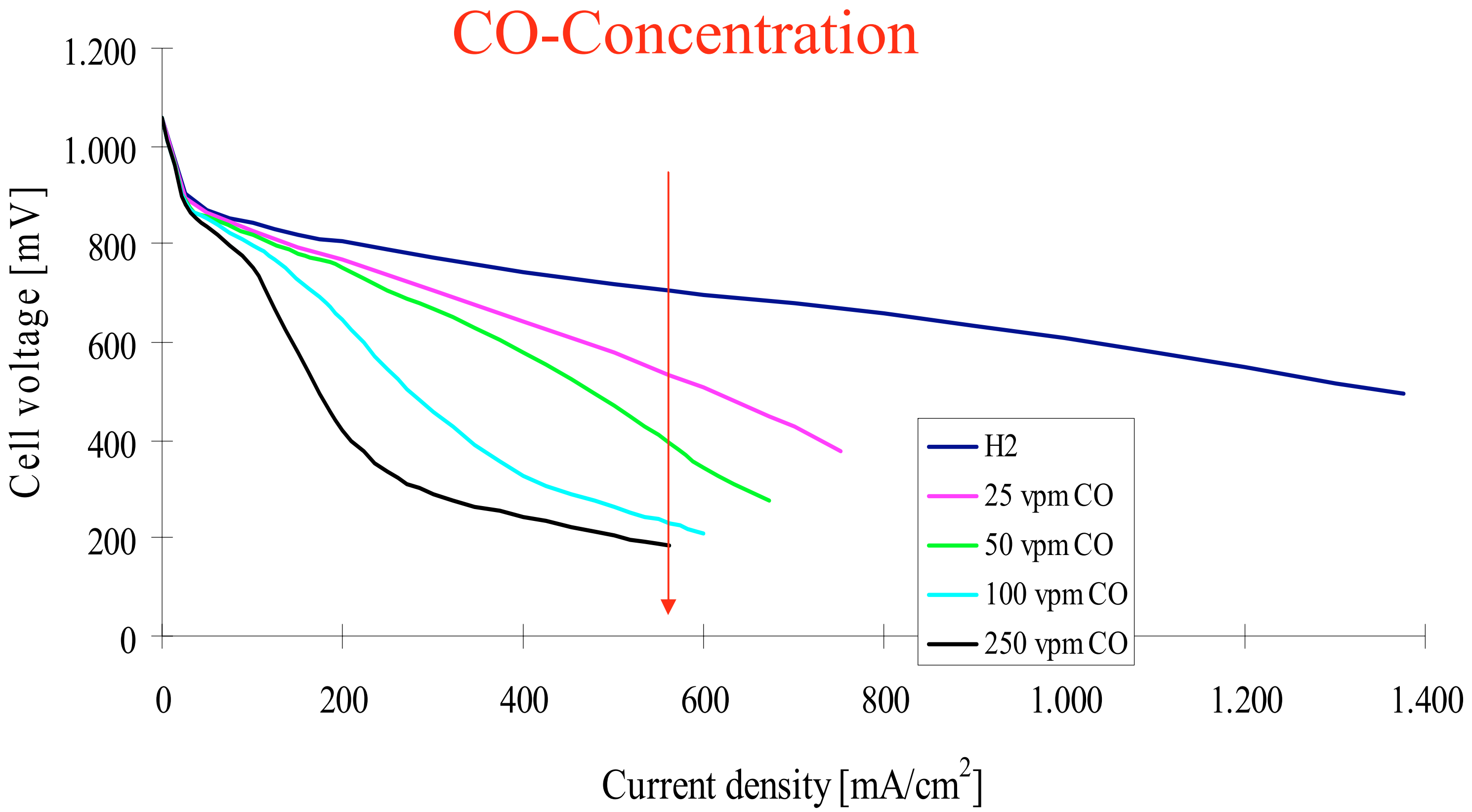
60 wt% PtRu / Vulcan XC-72

Courtesy of Prof. Yung-Eun Sung, *Kwangju Institute of Science & Technology (K-JIST)*, Korea

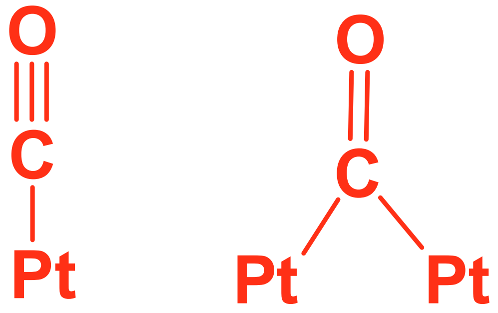
Succesful R&D Work
Pt-Catalyst Content

Time	**Pt content [mg/cm²]**
1997	4
2002	0.1
Today (labotatory results)	0.007

CO impurity effect on PEMFC



The catalyst is very sensible to impurities in the fuels, e.g. CO impurities, since they can be adsorbed on the active sites! For this reason Pt is often used in conjuntion with other metals (e.g., Pt-Ru alloys) that reduce the CO coverage of active particles.

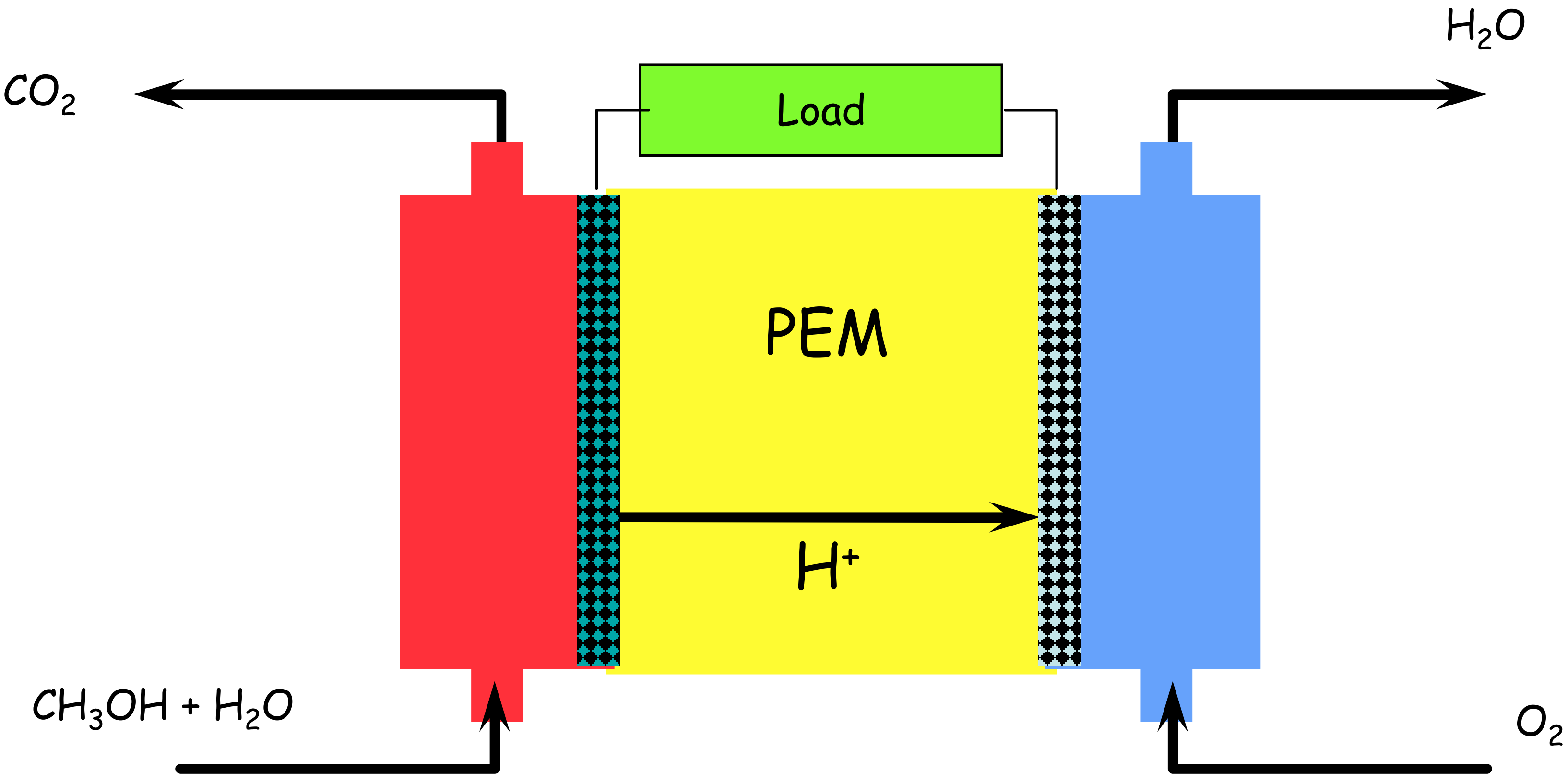


Large efforts are devoted to fuel cell catalyst R&D throught the world!

Direct Methanol Fuel Cell (DMFC)

Polymer electrolyte fuel cells using methanol rather than hydrogen as a fuel:

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



$H_3COH + H_2O \rightarrow 6\ H^+ + 6\ e^- + CO_2$

$6\ H^+ + 6\ e^- + 3/2\ O_2 \rightarrow 3\ H_2O$

Direct Methanol Fuel Cell (DMFC)

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

The electrocatalyst for CH_3OH oxidation is PtRu which has a bifunctional mechanism:

$Pt + CH_3OH_{(aq)} \rightarrow Pt\text{-}CH_3OH_{(ads)} \rightarrow Pt\text{-}CO_{(ads)} + 4H^+ + 4e^-$

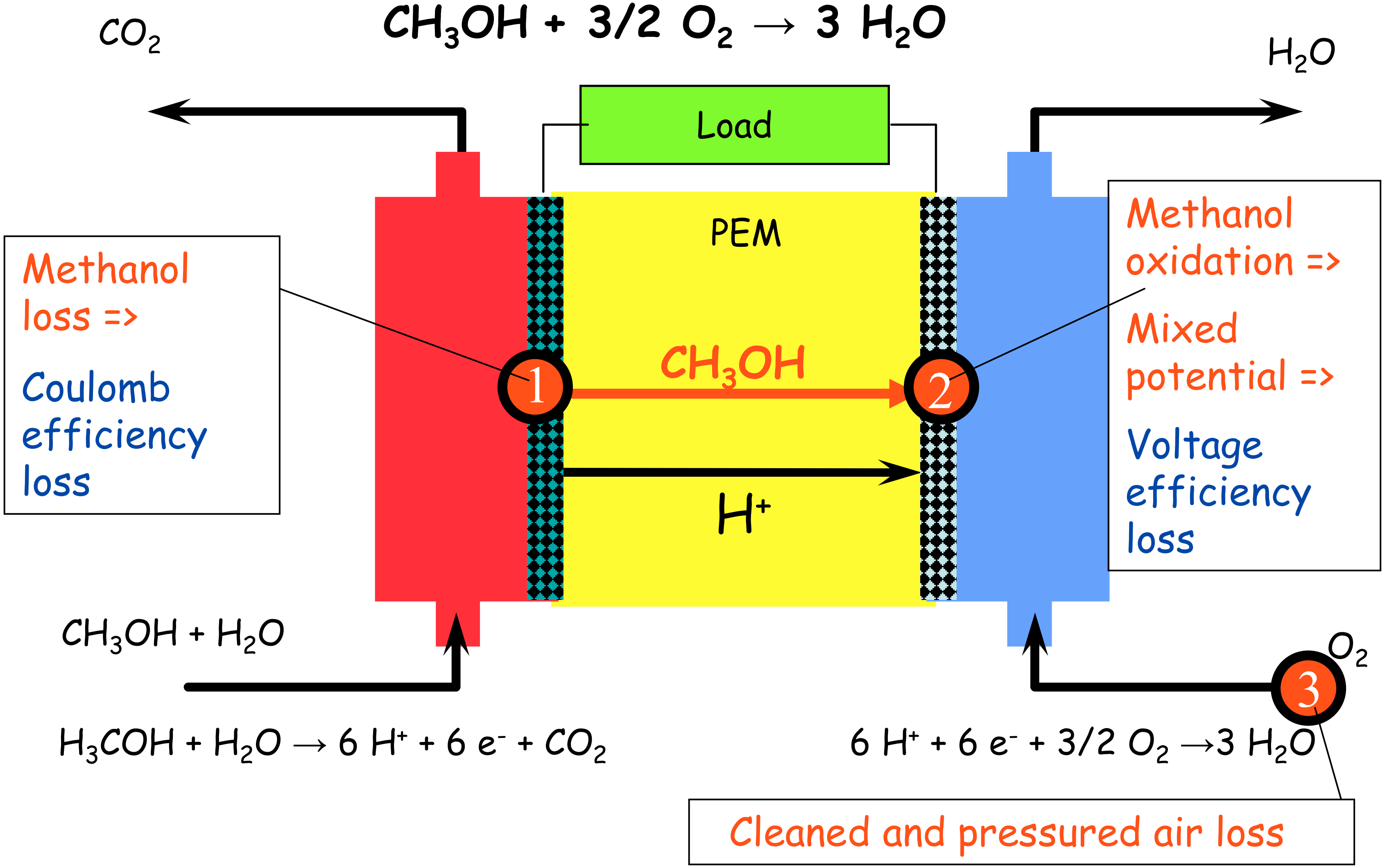
$Ru + H_2O \rightarrow Ru\text{-}OH_{(ads)} + H^+ + e^-$

$Pt\text{-}CO_{(ads)} + Ru\text{-}OH_{(ads)} \rightarrow Pt + Ru + CO_2 + H^+ + e^-$

For a high catalytic activity of PtRu/C at low Pt content:

- atomic ratio Pt/Ru$\geq$1.5
- nanosized PtRu particles
- uniform distribution of PtRu on the carbon support

DMFCs serious problem: methanol crossover



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

Methanol loss =>

Coulomb efficiency loss

Methanol oxidation =>

Mixed potential =>

Voltage efficiency loss

$H_3COH + H_2O \rightarrow 6\ H^+ + 6\ e^- + CO_2$

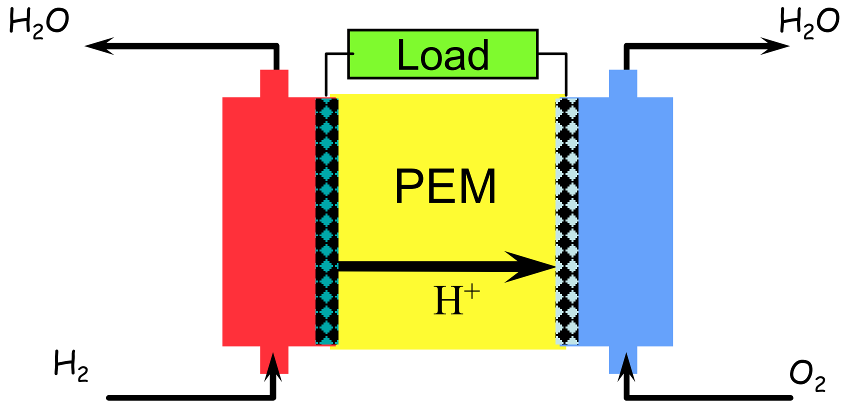
$6\ H^+ + 6\ e^- + 3/2\ O_2 \rightarrow 3\ H_2O$

Cleaned and pressured air loss

Polymer electrolyte fuel cells, PMFCs

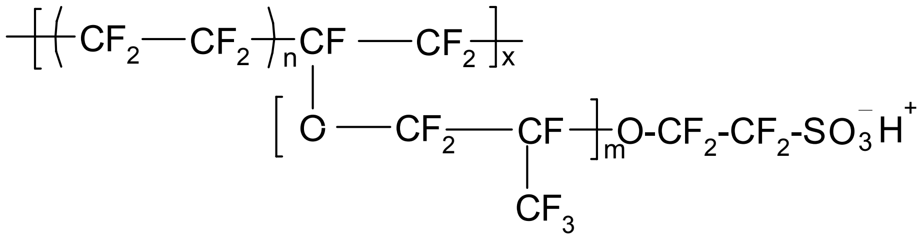
Energy renewal
(*hydrogen-economy*)

Environmental control
(*No-emission vehicles*)



Major drawback:
cost of the catalyst (noble metals) and of the polymer electrolyte membrane (Nafion™ -type)

Common electrolyte membrane: *NAFION®*



- ☺high chemical stability
- ☺ good conductivity

- ☹ high cost (\$ 5,000/kg ~ \$250/m^2)
- ☹ transport dependent on hydration state
- ☹ methanol crossover

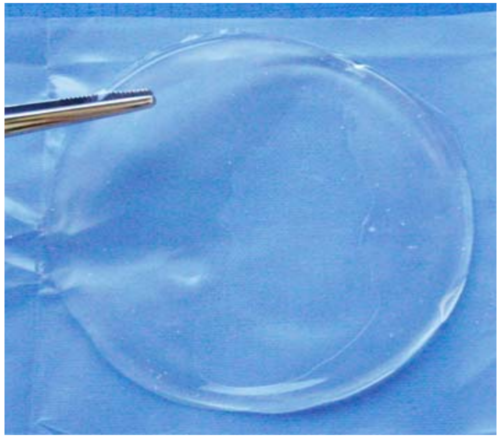
Membranes alternatives to Nafion are needed.

Approach in our laboratory: composite "gel-type" protonic membranes prepared by readapting synthesis procedures which have been proven to be successful in the lithium polymer technology.

The concept was first introduced by Peled
E. Peled, T. Duvdevani, A. Melman, *Electrochem. Solid State Lett.*, 1, 210 (1998)
and further developed in our laboratory
S. Panero, F.Ciuffa, A.D'Epifano and B. Scrosati,
Electrochim. Acta, 48,2009 (2003)

Strategy

***In lithium battery technology*:**
lithium conducting membranes formed by trapping liquid solutions (e.g., a $LiPF_6$-PC-EC solution) in a suitable polymer matrix (e.g. a poly(vinylidene fluoride), PVdF matrix) ***Gel polymer electrolytes*.**

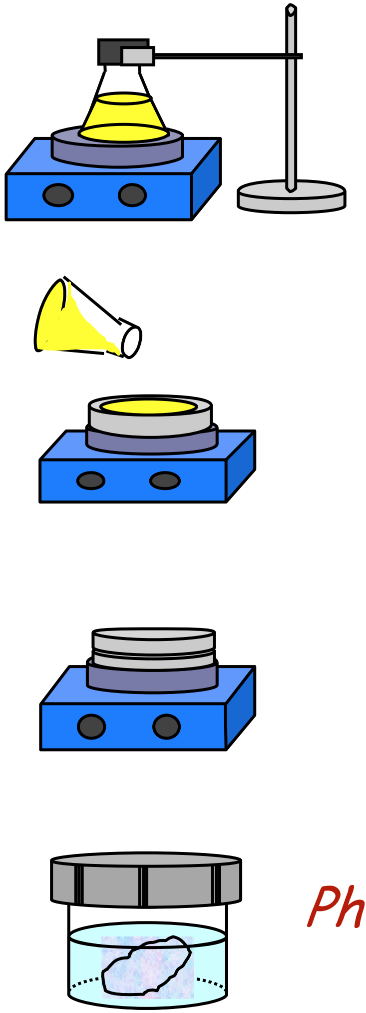


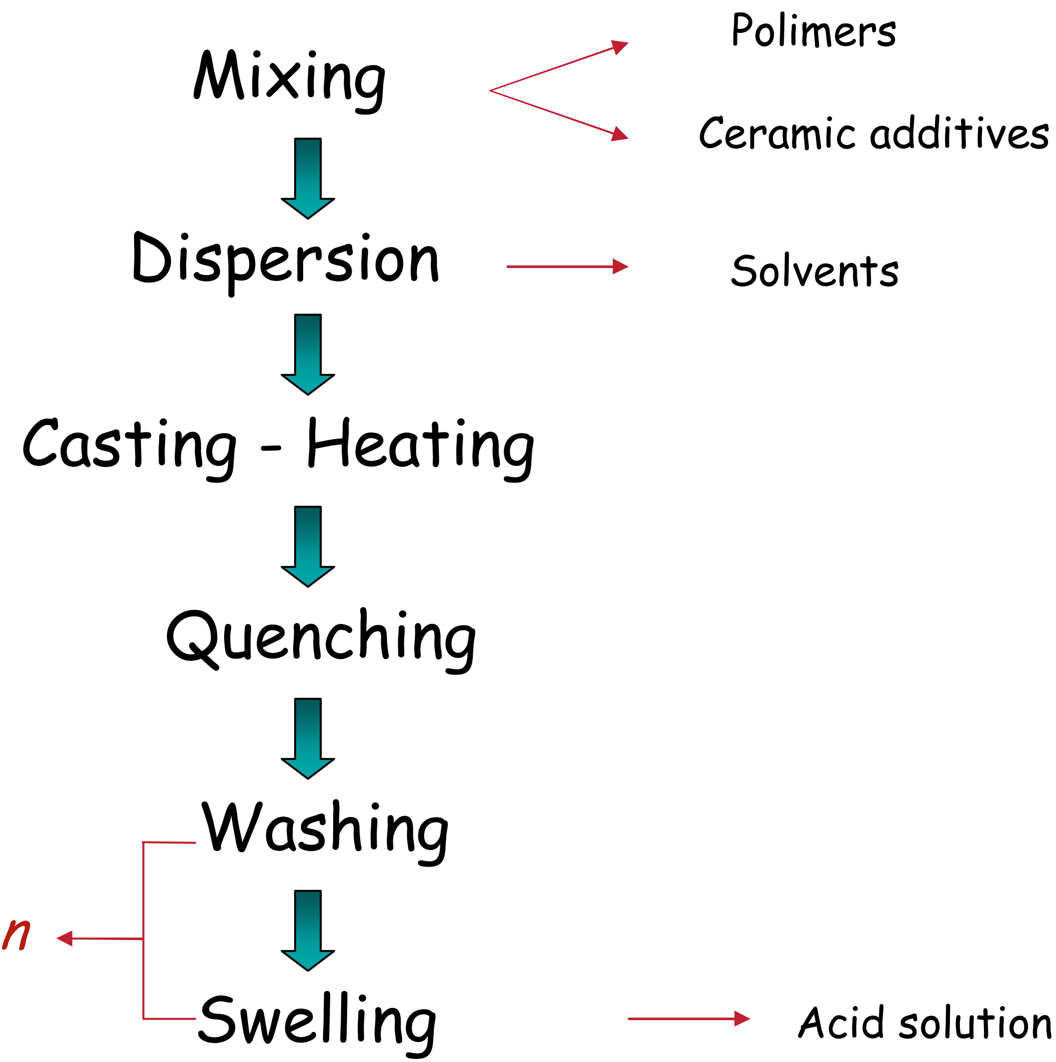
↓

***Extension to fuel cell technology*:**
proton conducting membranes formed by trapping acid solutions (e.g., H_2SO_4 solutions) in suitable composite (polymer + ceramic filler) matrices.
***Composite gel electrolyte membranes*.**

The main goal is to develop low-cost, low-methanol-permeability, temperature-resistant composite membranes for PEMFCs (DMFCs).

Synthesis procedure





Mixing

Polimers

Ceramic additives

Dispersion

Solvents

Casting - Heating

Quenching

Washing

Phase inversion

Swelling

Acid solution

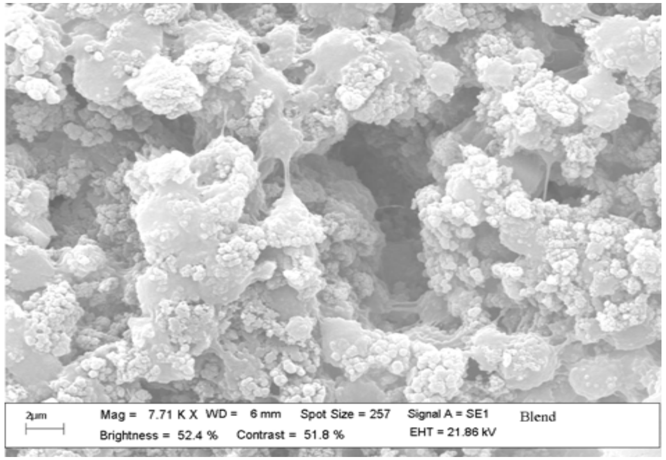
Composite PVdF-PAN- based membranes

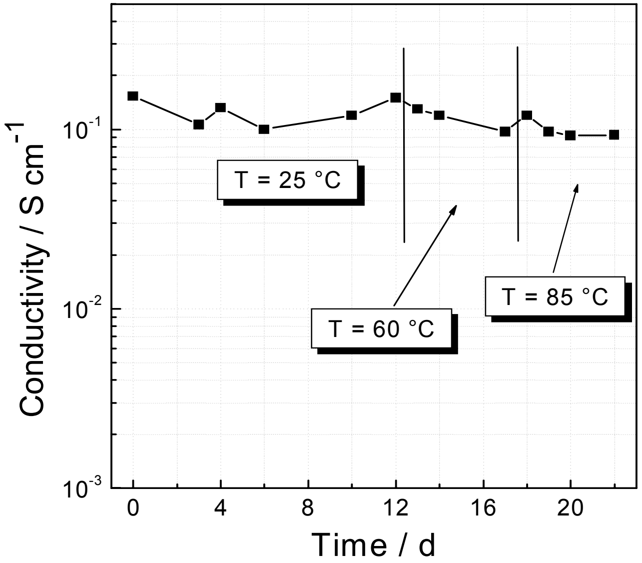
Nanosize-ceramic-added (e.g., Al_2O_3 or SiO_2) membrane obtained by the gelification of a poly(vinylidene)fluoride, PVdF - poly(acrylonitrile), PAN blend polymer matrix.

The membrane is activated by swelling it with an aqueous acid (e.g. H_2SO_4 or H_3PO_4) solution .

High conductivity!

The ceramic filler has a key role in assuring proper liquid-phase exchange and in retaining the liquid solution!

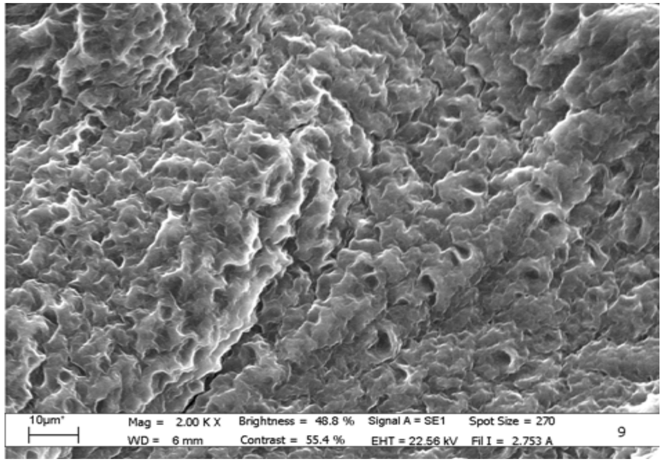


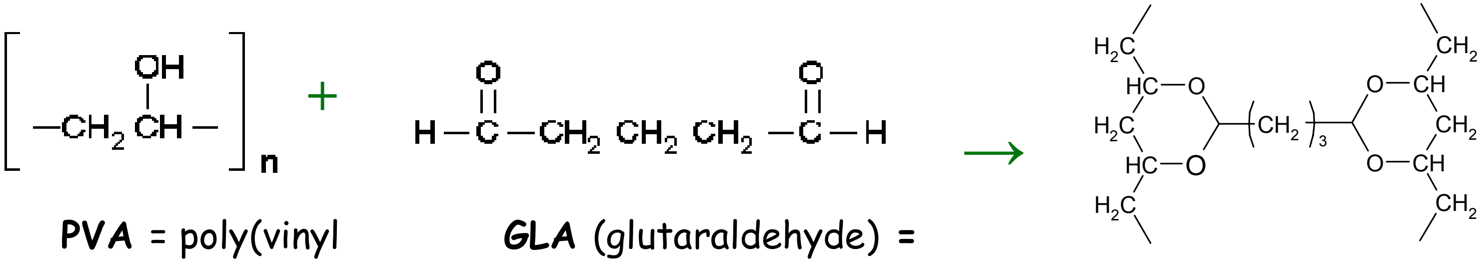


M.A. Navarra, S. Panero, B.Scrosati, *J.Solid State Electrochem.*, 8, (2004)804.

Composite PVA- based membranes

The membranes have been prepared using an innovative cross-linking process of poly(vinylalcohol), PVA with glutaraldehyde ,GLA, and with a dispersion of a surface functionalzed SiO_2-SO_3H ceramic filler.




$$\left[-CH_2\overset{\overset{OH}{|}}{C}H-\right]_n + H-\overset{\overset{O}{||}}{C}-CH_2\,CH_2\,CH_2-\overset{\overset{O}{||}}{C}-H \longrightarrow$$

PVA = poly(vinyl alcohol)

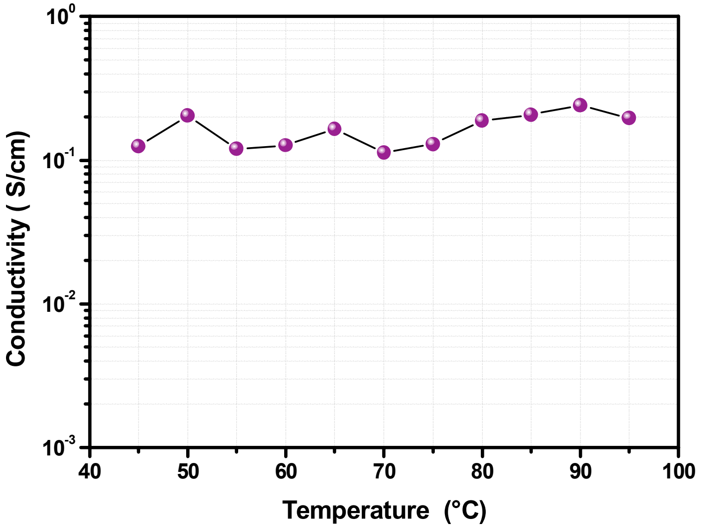
GLA (glutaraldehyde) = Pentane-1,5-dial

Acetal rings

M.A. Navarra,S.Panero, J. Romanowska, P. Fiorenza, B. Scrosati, J.Electrochem. Soc, in press

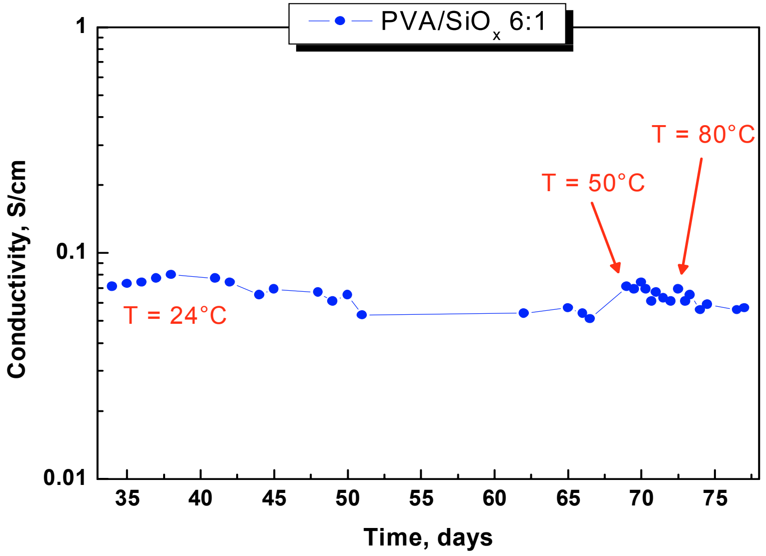
Composite PVA- based membranes

The membrane is activated by swelling it with an aqueous acid (e.g. H_2SO_4) solution.



Conductivity vs. time. Room temperature

The crosslinking and the dispersion of the functionalized ceramic give high porosity, favor liquid retention and ultimately high conductivity with good thermal stability.



Conductivity versus temperature.

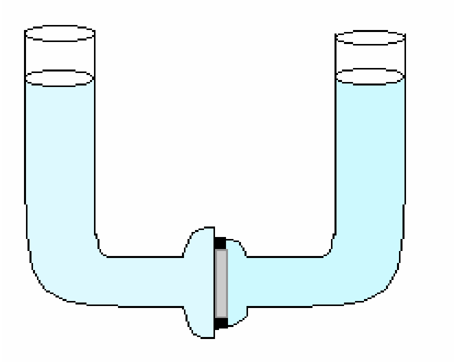
Gel-type membranes

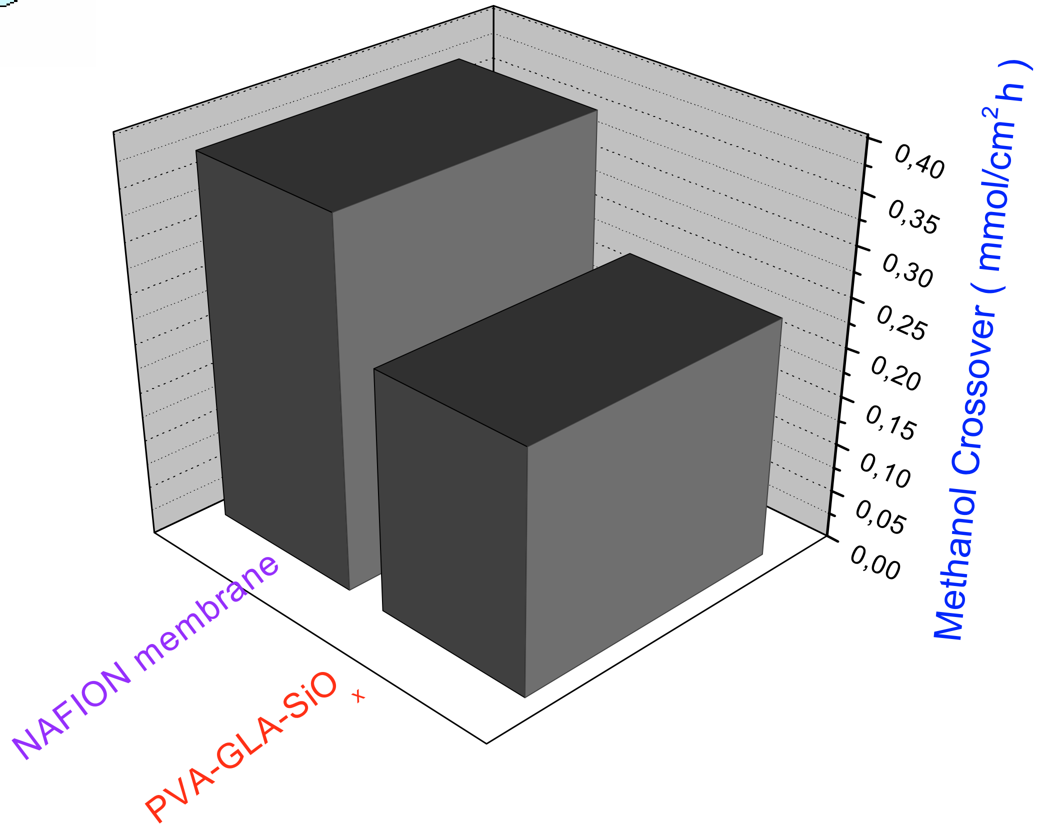
Transport mechanism

The conductivity mechanism is substantially different from that occurring in Nafion-type systems where the presence of water is vital for assisting proton transport (*Grotthuss mechanism*).

In the gel-type membranes the proton transport is intrinsically assured by the swollen acid solution (*free-acid mechanism*), so that the conductivity is expected to be less dependent on external relative humidity.

Methanol crossover in PVA – GLA – SiO_x membranes





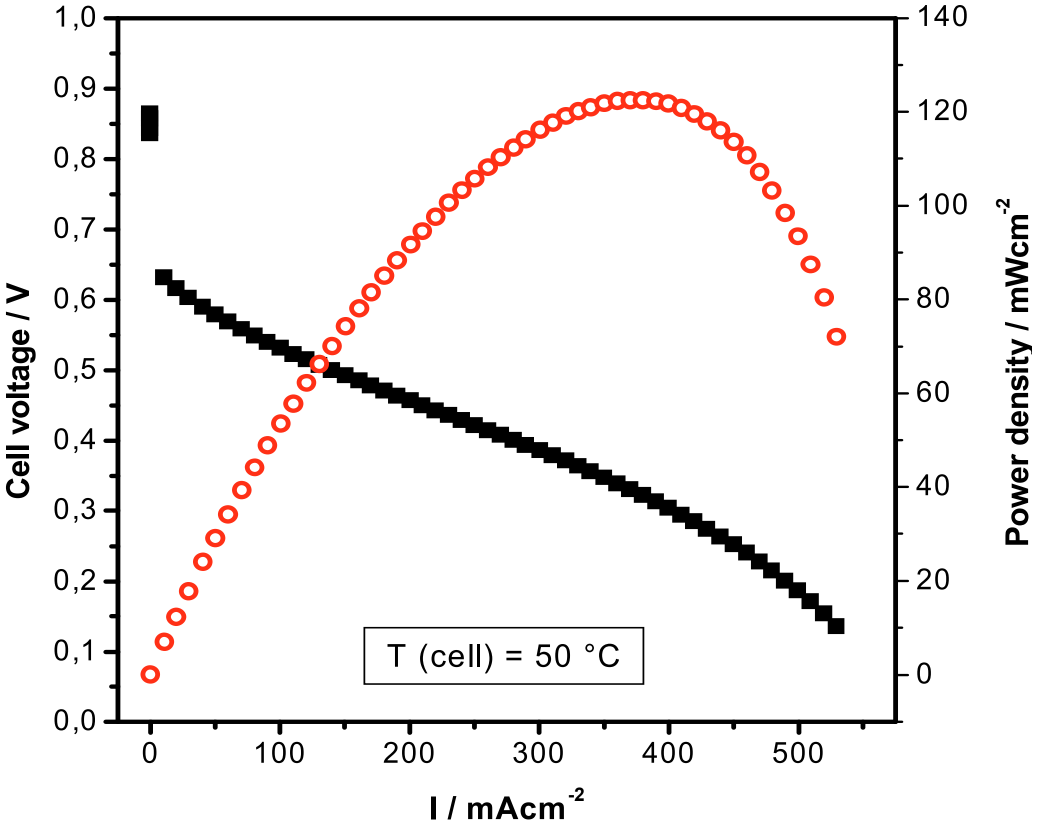
The PVA – based membrane seems to be more selective than Nafion for proton over methanol!

Fuel cell test with a PVA-GLA membrane

H_2 / air, 100% RH
P = 1 atm
Gas fluxes = 0.1 L / min

E-TEK Pt / C electrodes

Pt loading 0.4 mg / cm^2



The high open circuit voltage 0.85V indicates a small gas permeability though the membrane

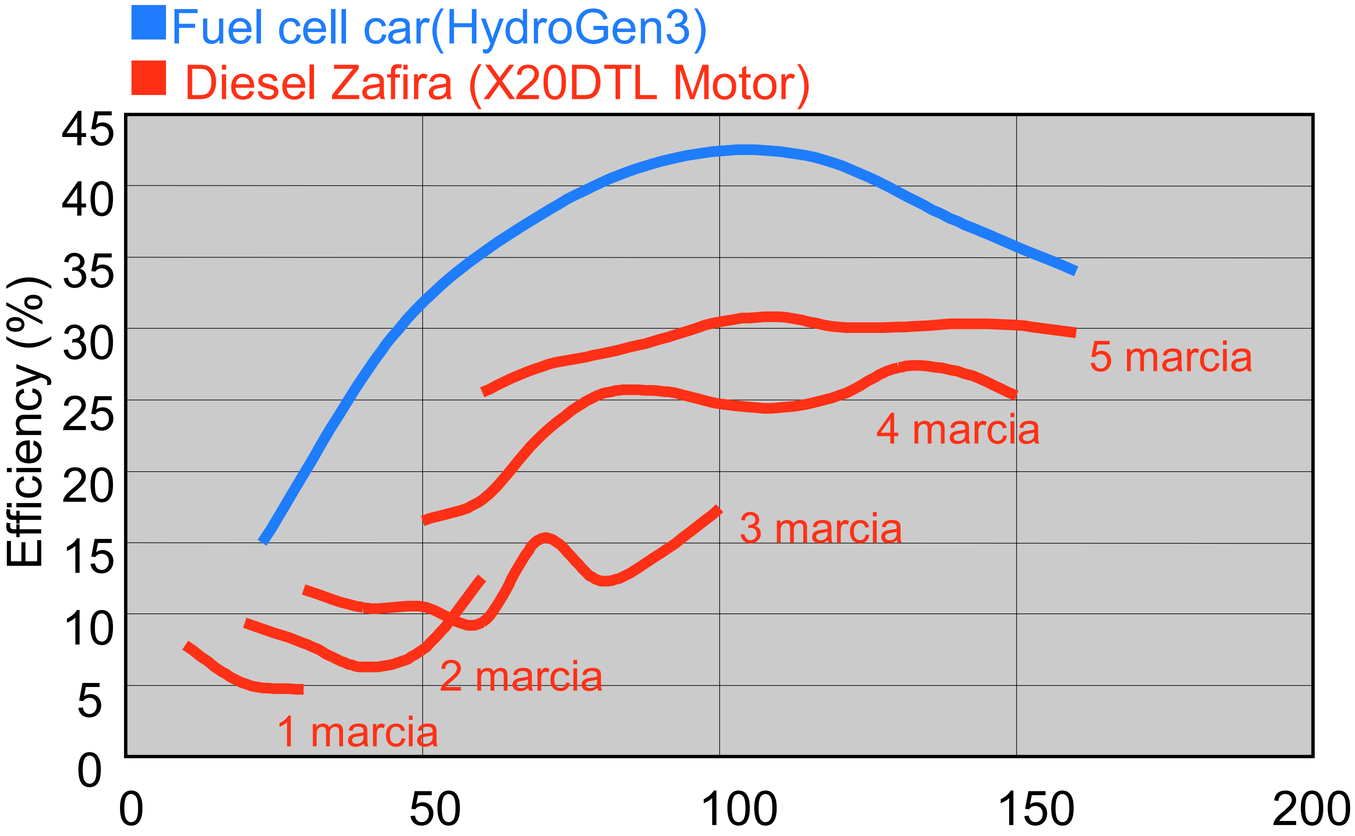
Maximum power density of about 120mW / cm^2 at 400 mA / cm^2 and 0.3 V

Substantial progresses have been obtained both on the electrode formulation and in the development of new types of membranes.

The question on whether or when fuel cells can be effectively used for powering electric vehicles still remains.

Are fuel cell cars ready to enter in the transportation market?

Efficiency



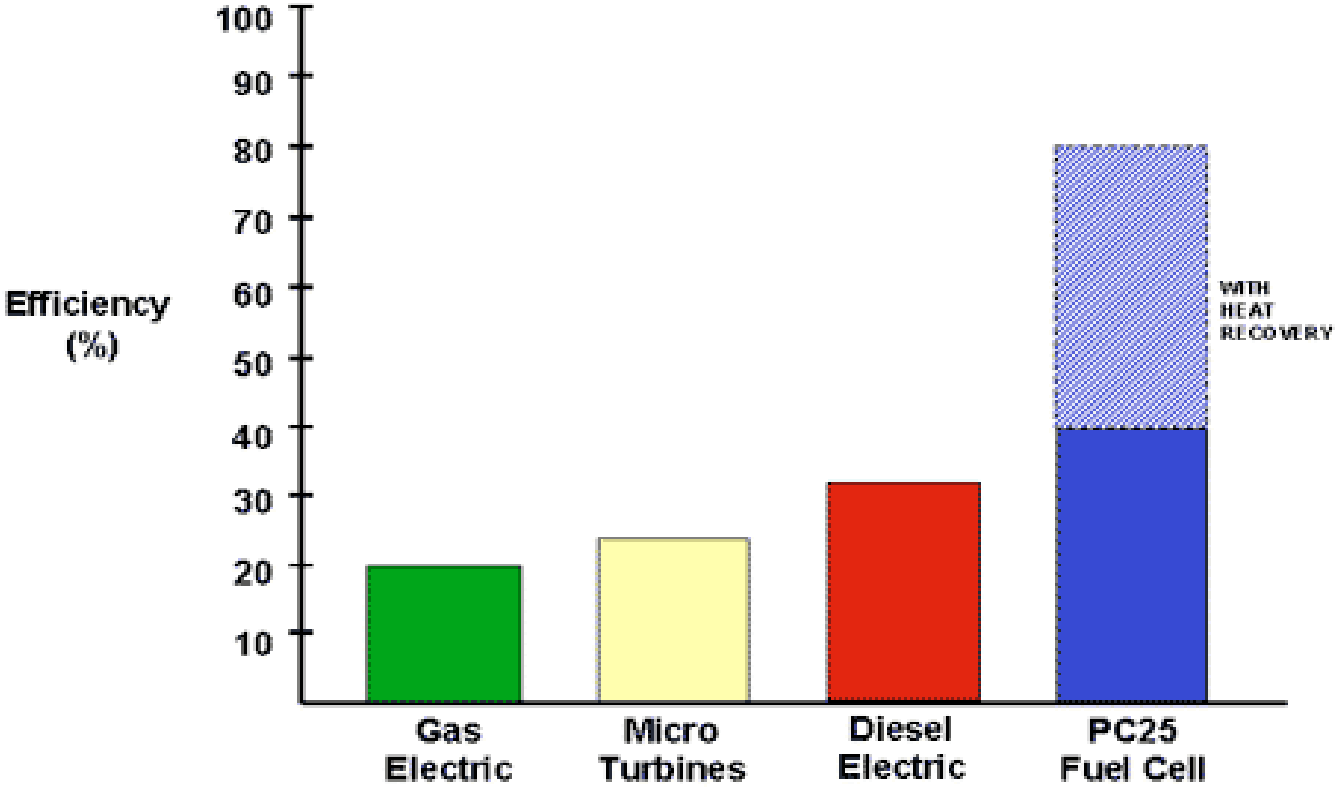
→ Medium (European Drive Cycle):

Efficiency: **36 %** / **22 %**

CO_2 emission (direct): **0 g/km** / **177 g/km**

Source: Opel GAPC-J.Garche, ZSW, Ulm, Germany

Efficiency of fuel cells in comparison with other combustion systems



General Motor's ELECTROVAN (1967)

(with 400V, 160 kW UCC Alkaline FC System, liquid H_2 und O_2)


Ford
fuel cell vehicle
zero emissions
www.fuelcelltoday.com


driving the future
Fuel
F-Cell

FC Cars Today

Ford

Fuel: CH2
Veh.basis: Focus
Stack: Ballard

GM/Opel

Fuel: CH2
Veh.basis: Zafira
Stack: GM/Opel

Hyundai

Fuel: CH2
Veh.basis: Santa Fé
Stack: IFC

Honda

Fuel: CH2
Veh.basis: EV Plus
Stack: Ballard / Honda

Nissan

Fuel: CH2
Veh.basis: XTerra
Stack: Ballard / IFC

Toyota

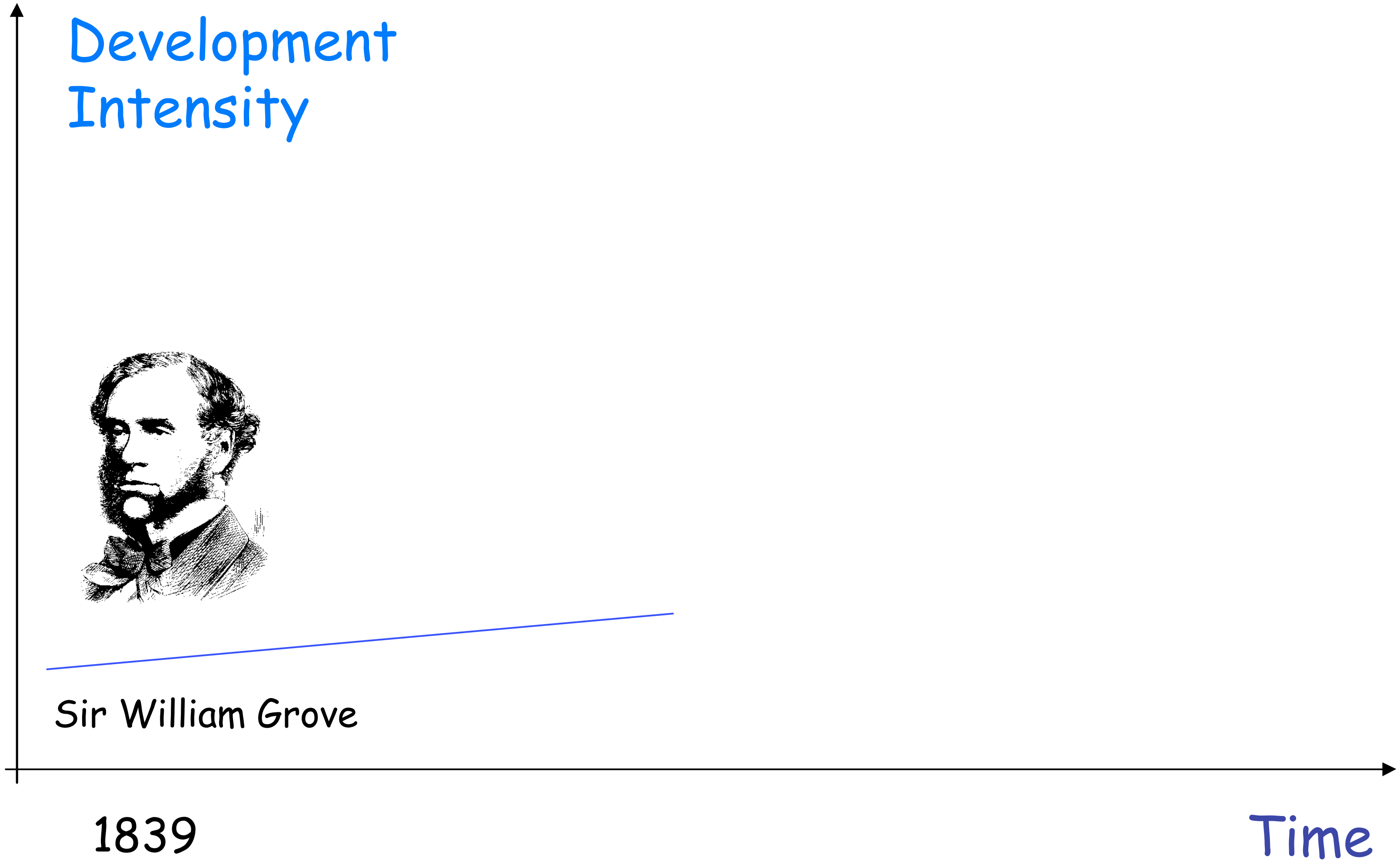
Fuel: CH2
Veh.basis: Kluger V
Stack: Toyota

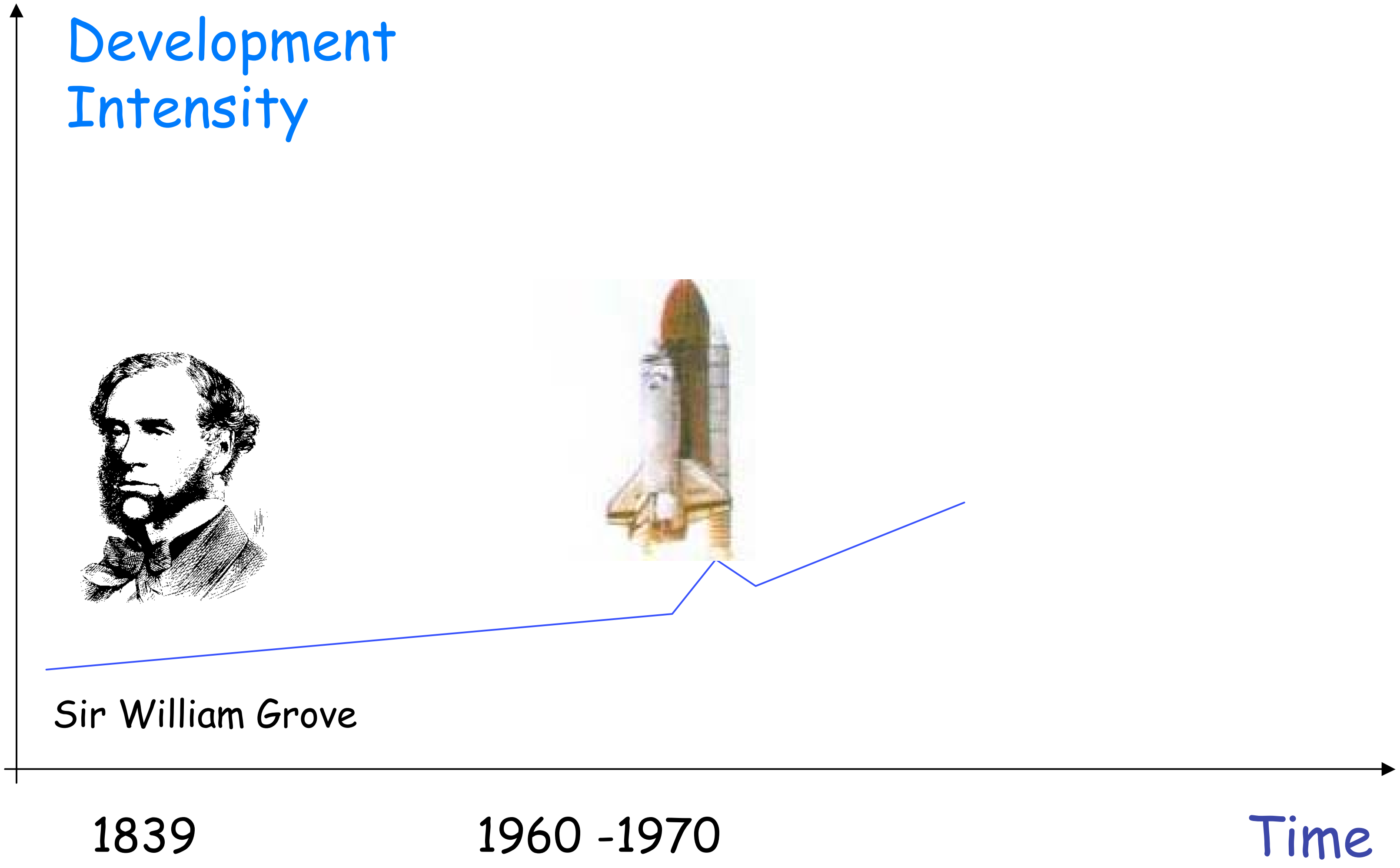
VW

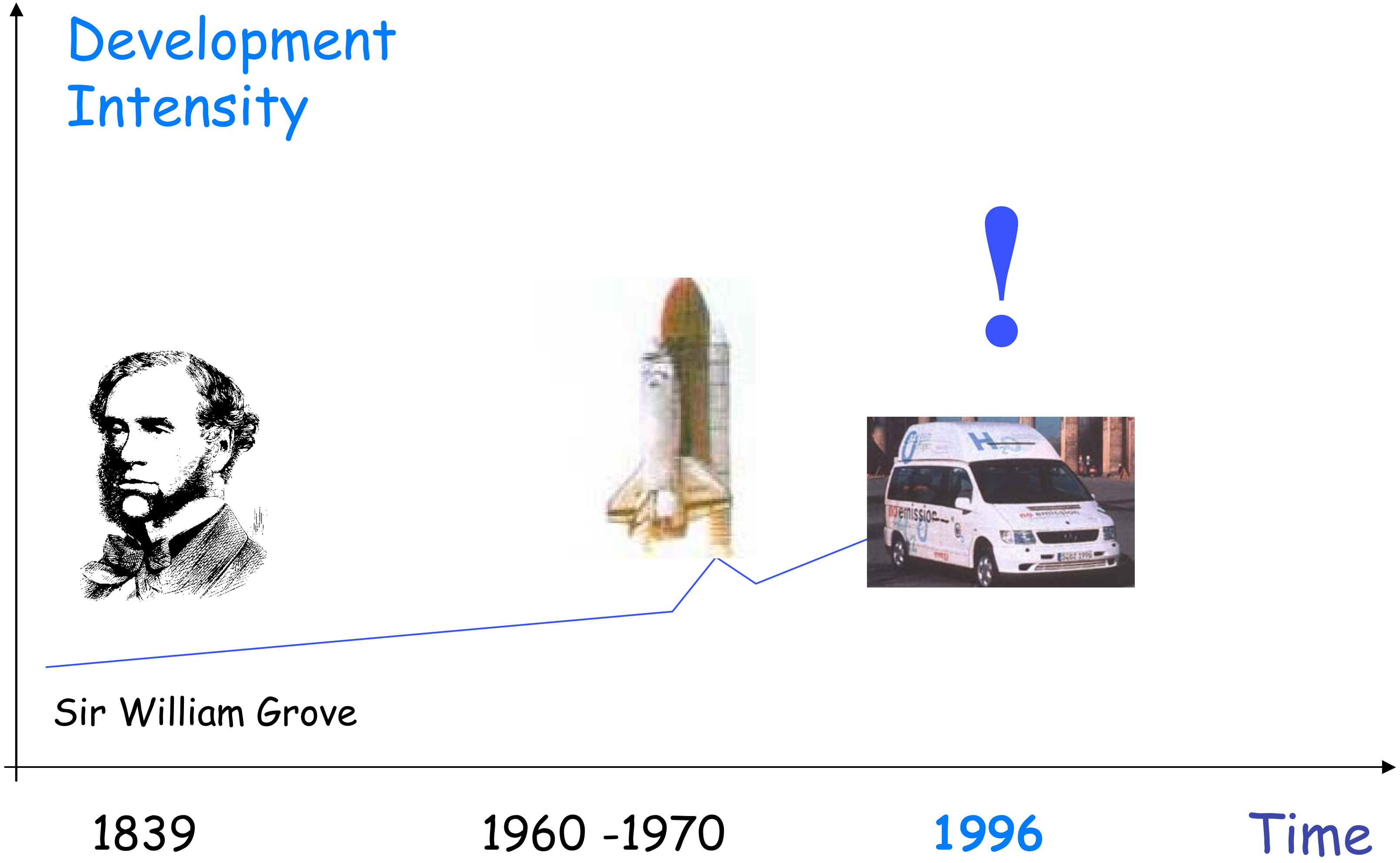
Fuel: CH2
Veh.basis: Bora
Stack: Ballard / PSI

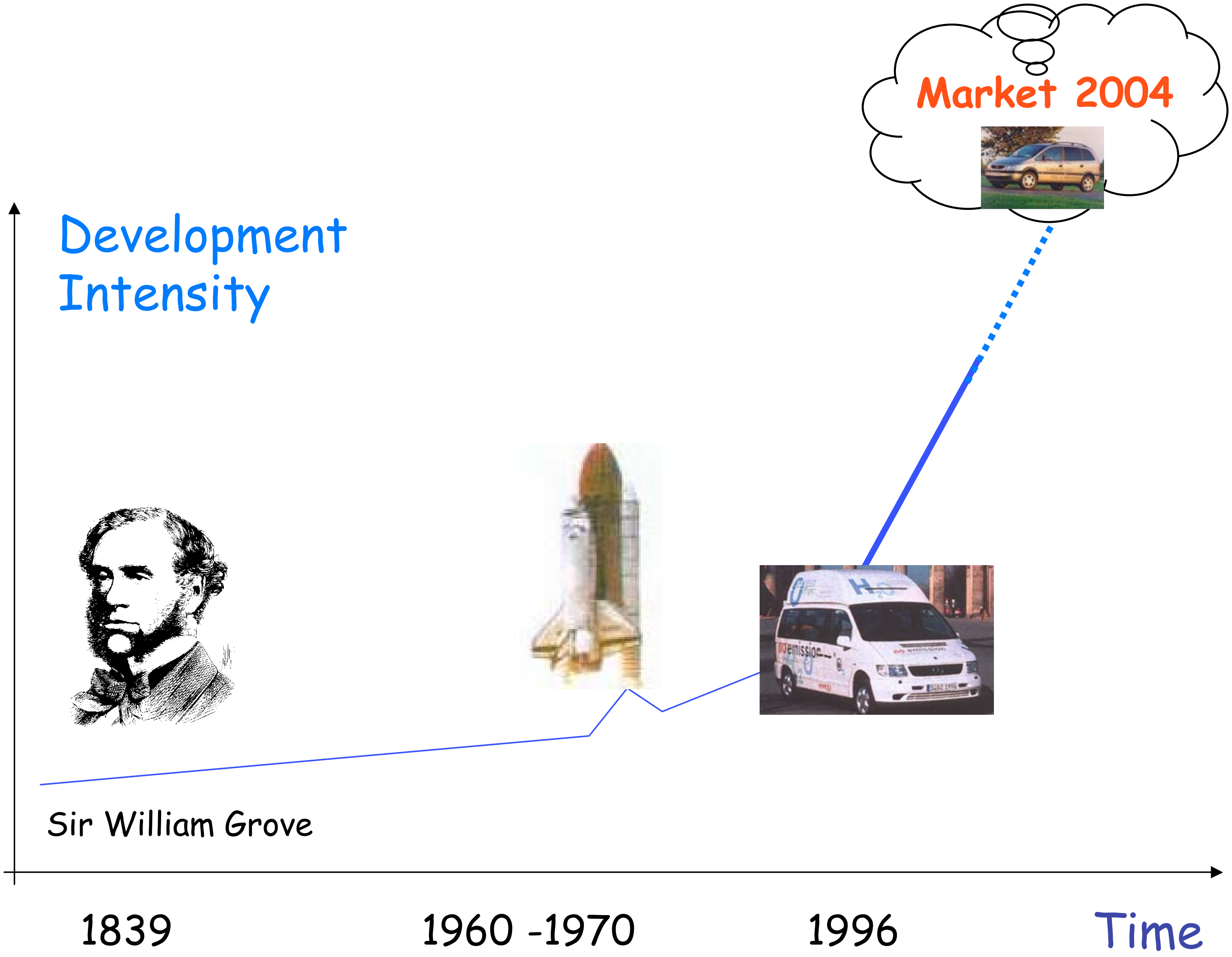
PEUGEOT / CITROËN
+ RENAULT

Source: Prof. Panik, DC


Development
Intensity
Sir William Grove
1839
Time


Development Intensity
Sir William Grove
1839
1960 -1970
Time


Development Intensity
!
Sir William Grove
1839
1960 -1970
1996
Time



Market 2004

Development Intensity

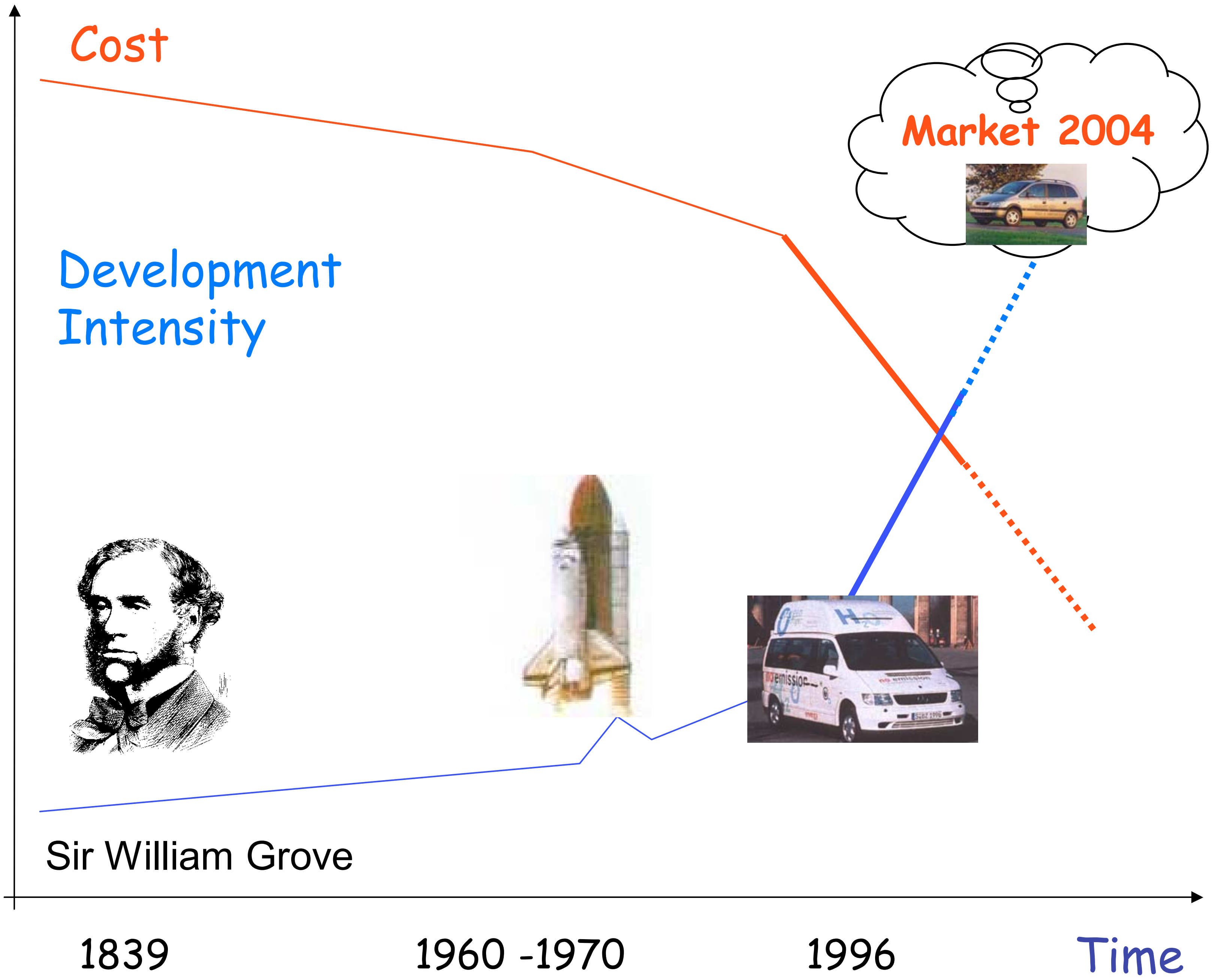
Sir William Grove

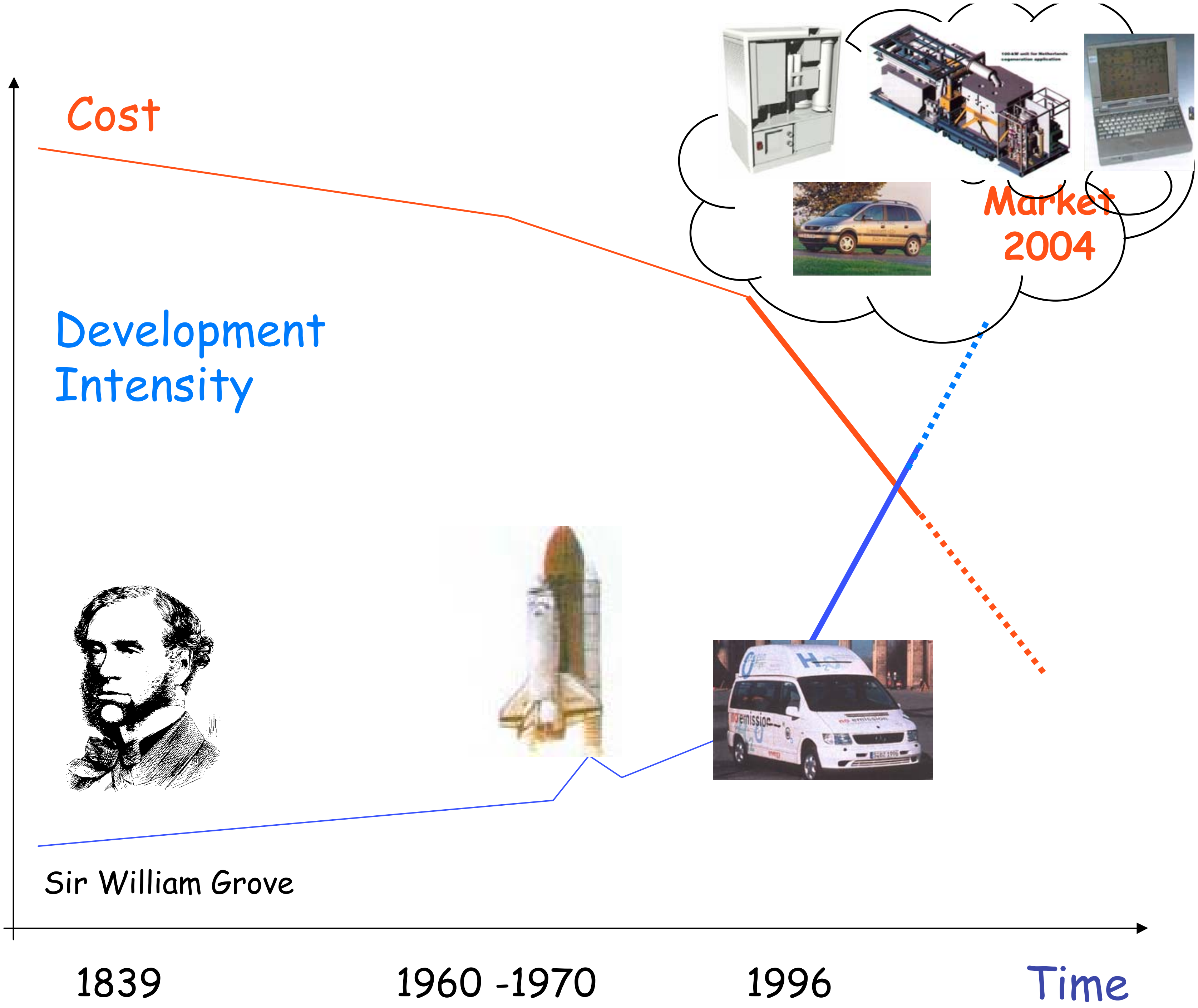
1839

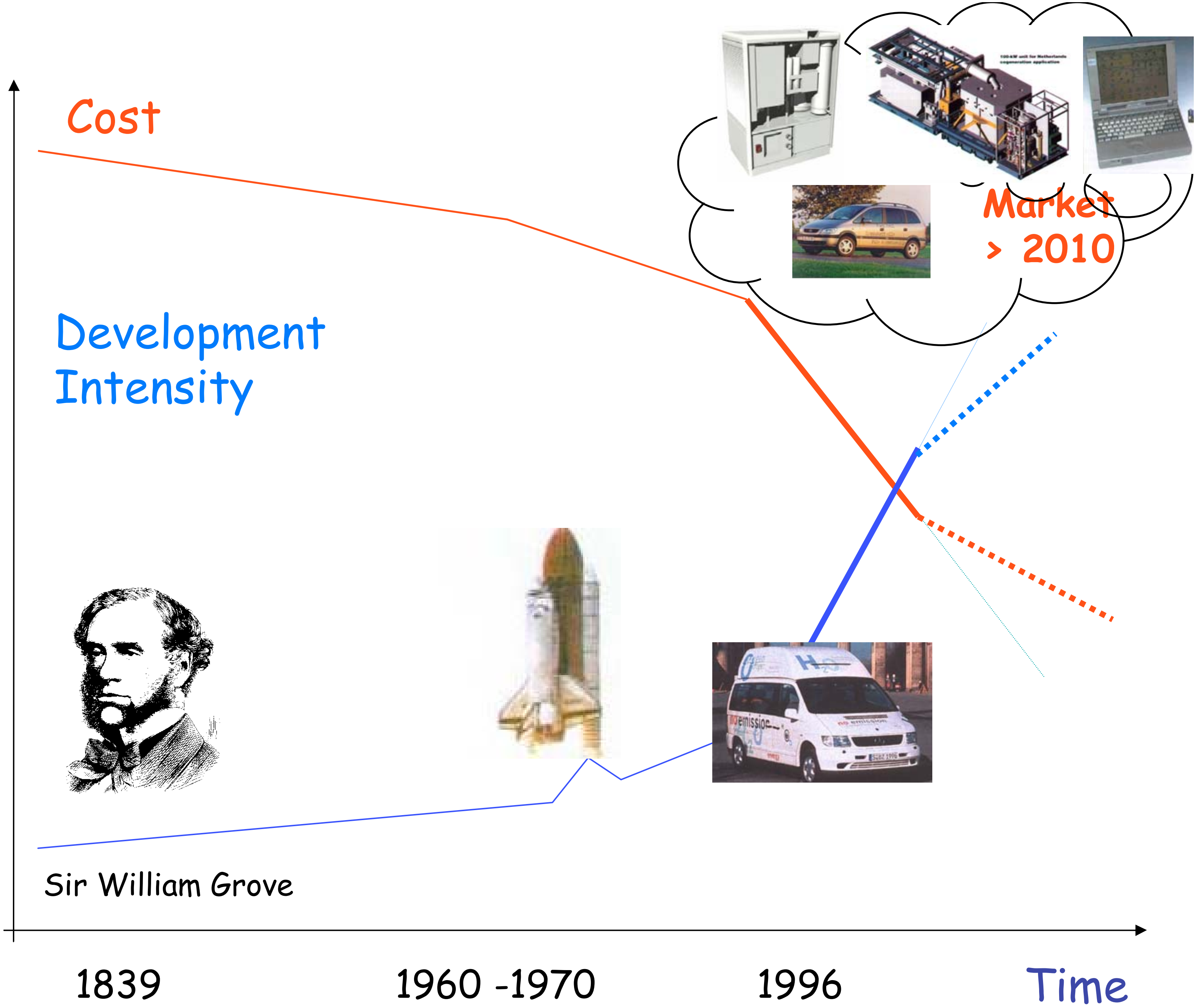
1960 -1970

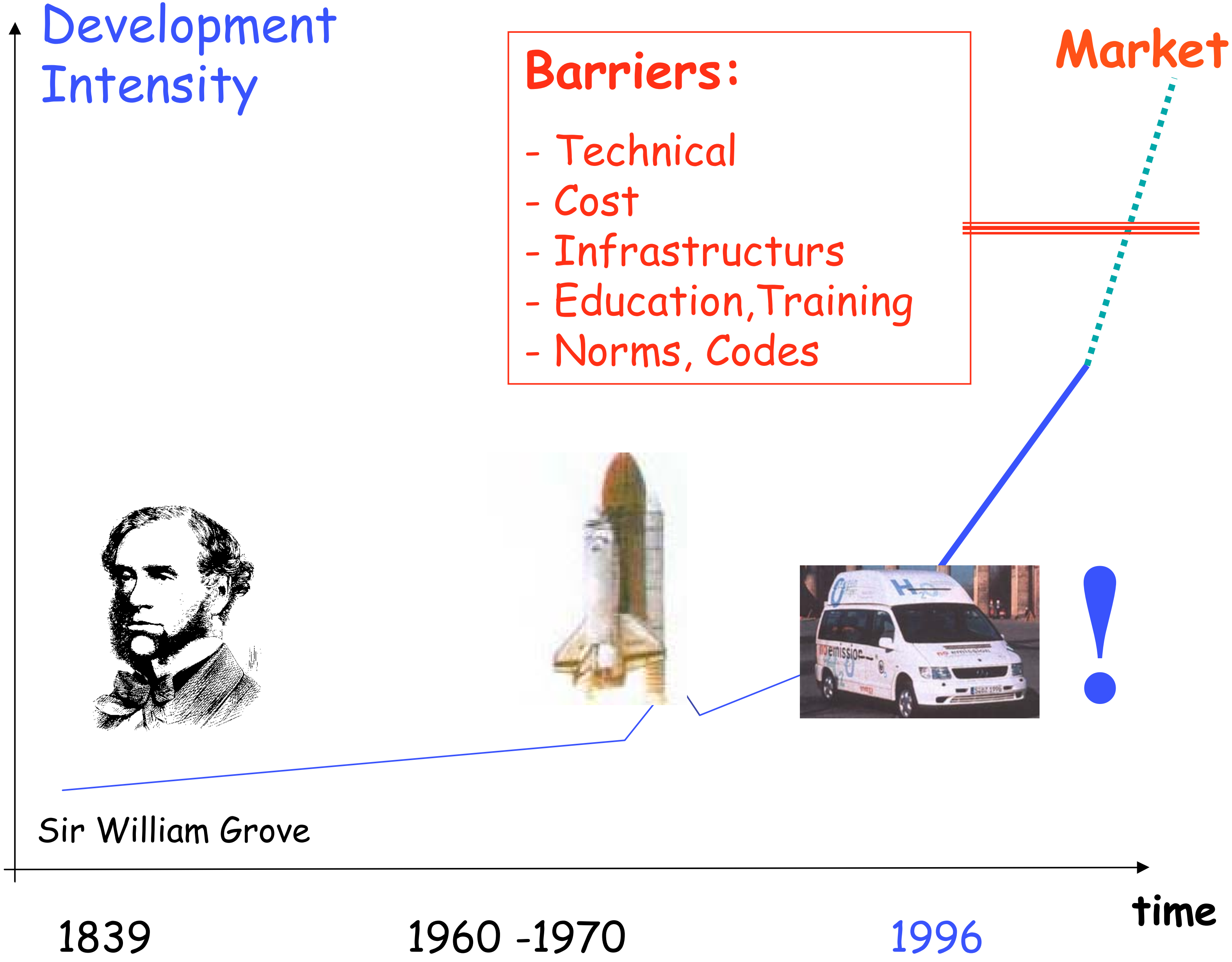
1996

Time


Cost
Market 2004
Development
Intensity
Sir William Grove
1839
1960 -1970
1996
Time


Cost
Development
Intensity
Market
2004
100-kW unit for Netherlands
cogeneration application
Sir William Grove
1839
1960 -1970
1996
Time


Cost
Development Intensity
Market
> 2010
Sir William Grove
1839
1960 -1970
1996
Time



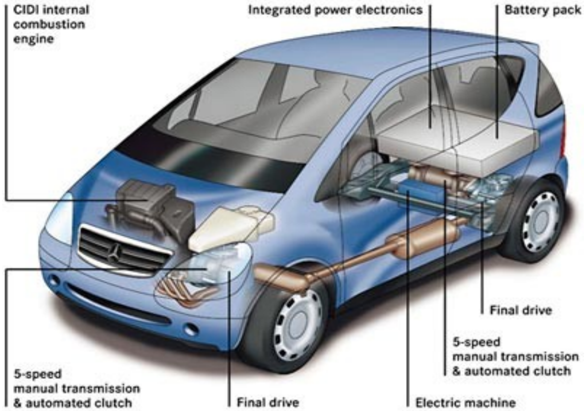
Barriers:

- Technical
- Cost
- Infrastructurs
- Education,Training
- Norms, Codes

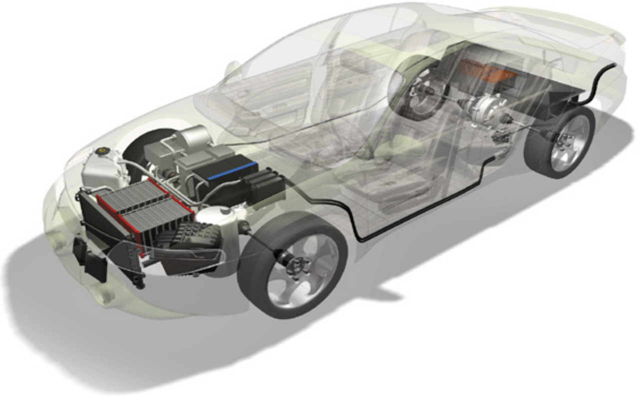

UN GIORNO LE MACCHINE ANDRANNO A ACQUA
E L'ACQUA COSTERÀ IL DOPPIO DELLA BENZINA
2004 GIULIANO

Ecologic car
Prospective

Electric car: prototypes
Zero emission



Hybrid car: in the market
Controlled emission



Hydrogen car: in the market by 2010 (prevision) Zero emission?

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