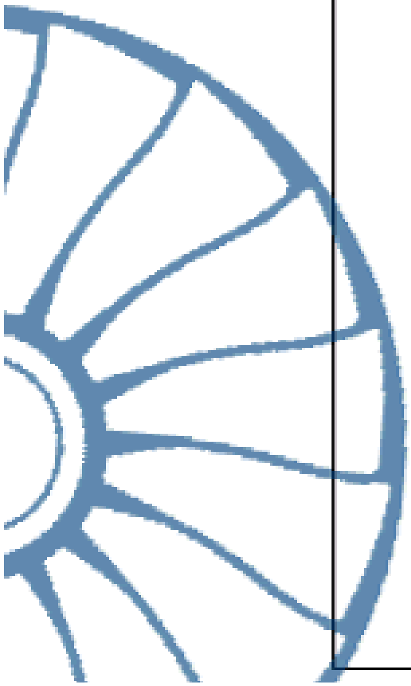

Master Degree in InnovativeTechnologies in Energy Efficient Buildings for Russian & Armenian Universities and Stakeholders

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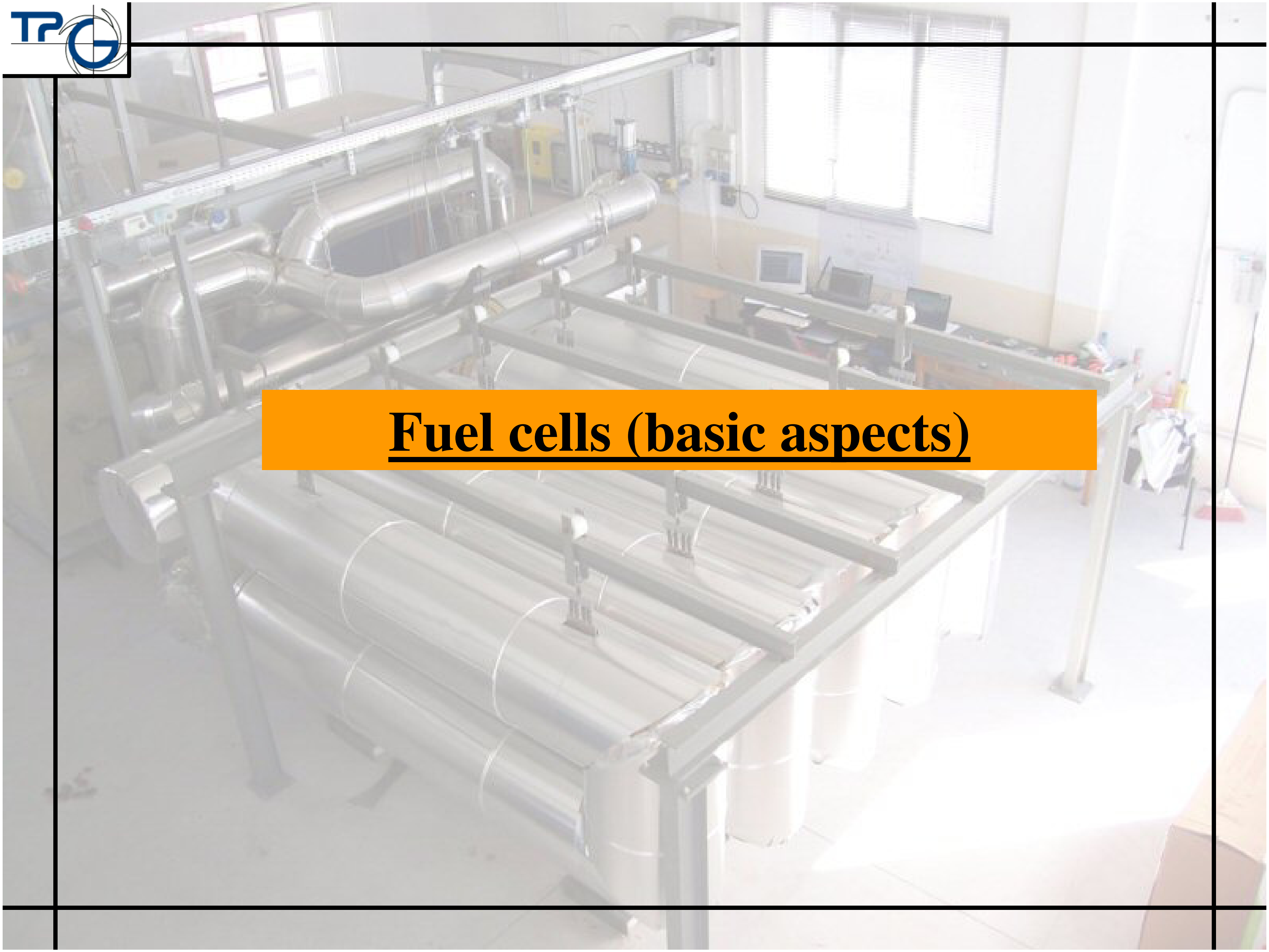
Co-funded by the
Erasmus+ Programme
of the European Union

MARUEEB

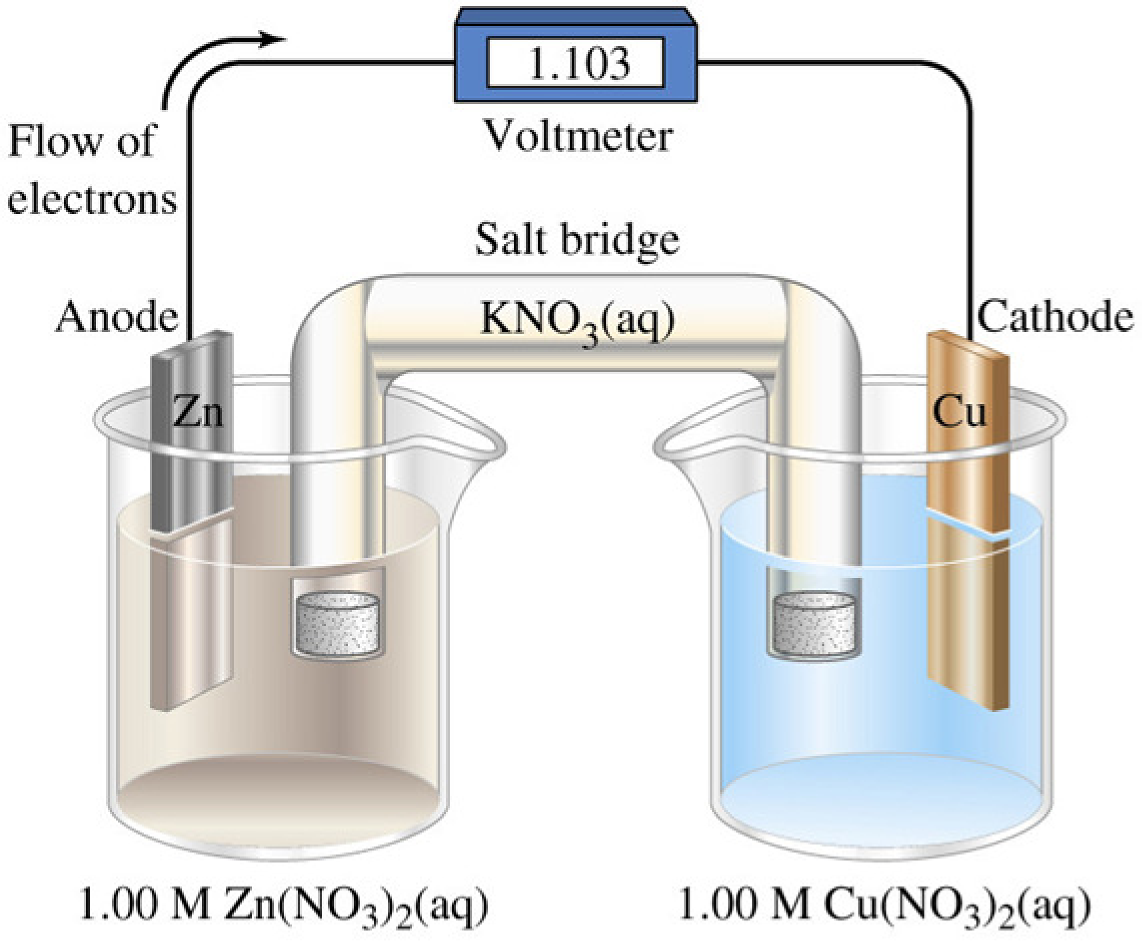
Fuel cells (basic aspects)



What is a fuel cell? (1/3)

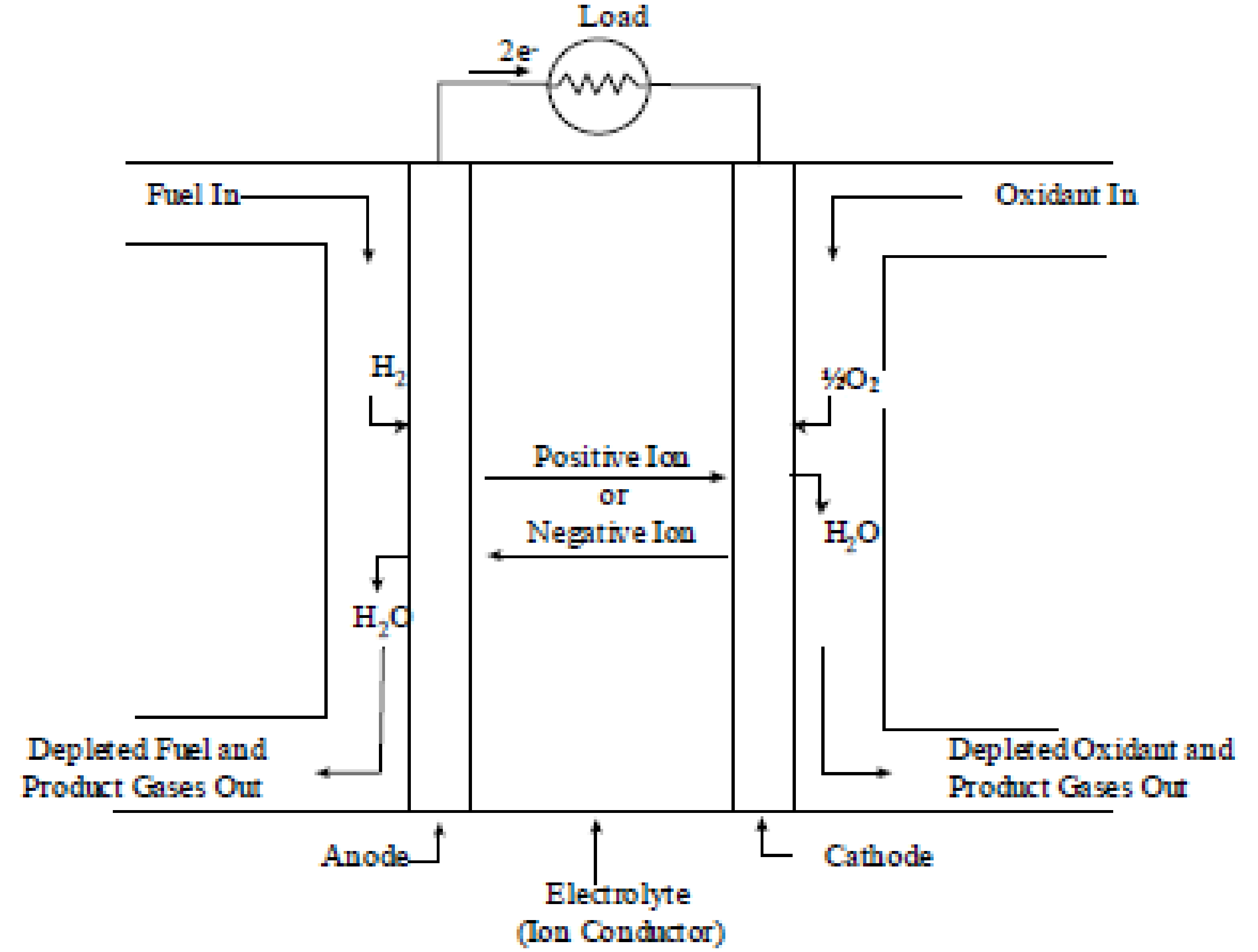
- Power generator based on electrochemical reactions
  - ✓Chemical energy => Electrical energy (no intermediate thermal energy).
  - ✓No Carnot cycle limitation => potential higher efficiency
  - ✓Clean fuels (hydrogen or hydrogen from CH_4 or other) => low pollution
  - ✓No moving parts => low noise
- Fuel cell – battery comparison
  - ✓Battery: electrodes are consumed during operations.
  - ✓Fuel cell: fuel and O_2 are consumed during operations.
- Fuel cell basic layout
  - ✓Anode-Electrolyte-Cathode.
  - ✓Anode side fed by fuel (H_2, other): negative electrode
  - ✓Cathode side fed by oxidant (from air): positive electrode
  - ✓Electrolyte conducts positive or negative ions (depending on cell type)
  - **✓No direct contact between Fuel and Oxidant!!!**

What is a fuel cell? (2/3)



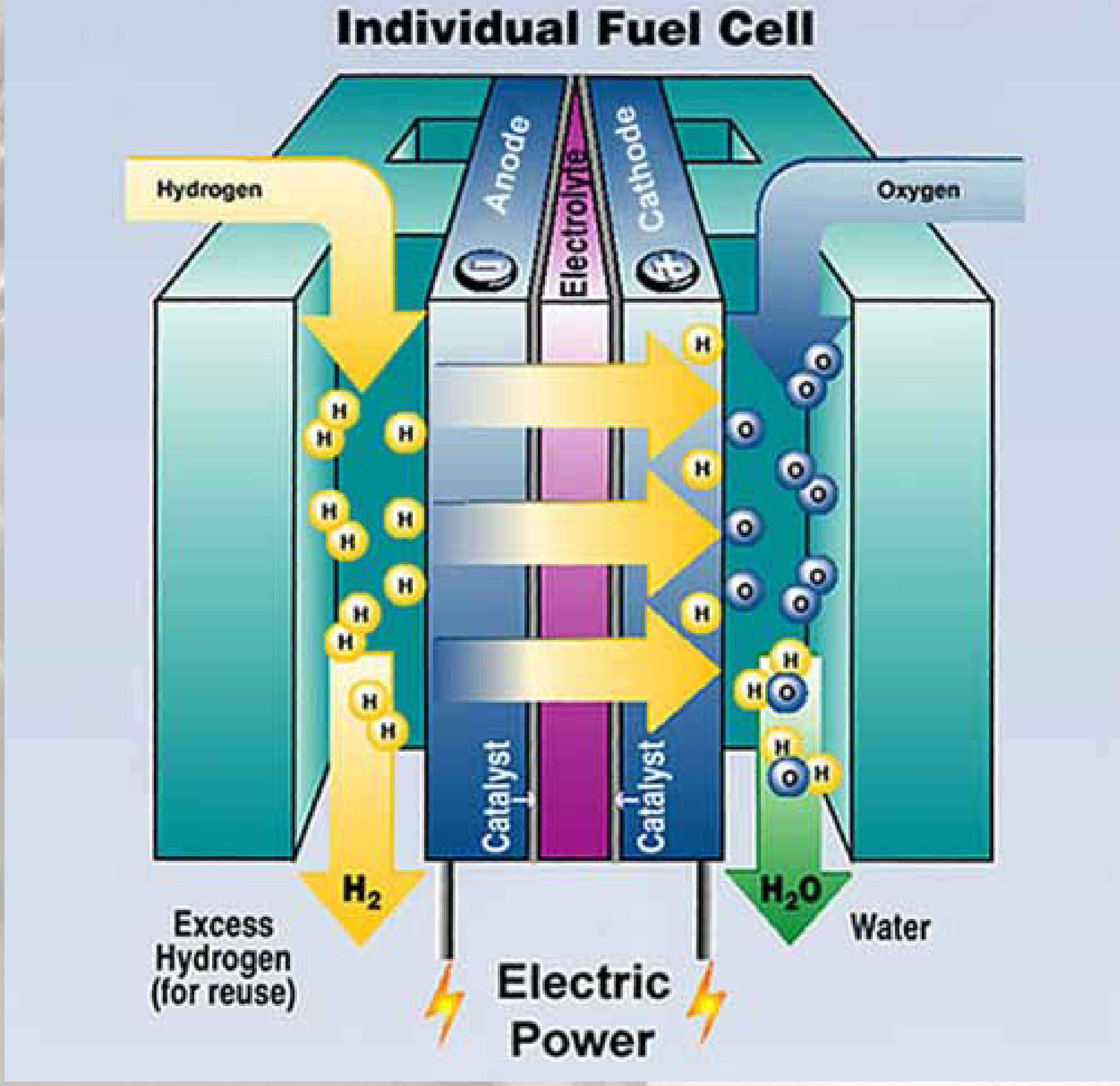
Battery: Anode and Catode are consumed

What is a fuel cell? (3/3)

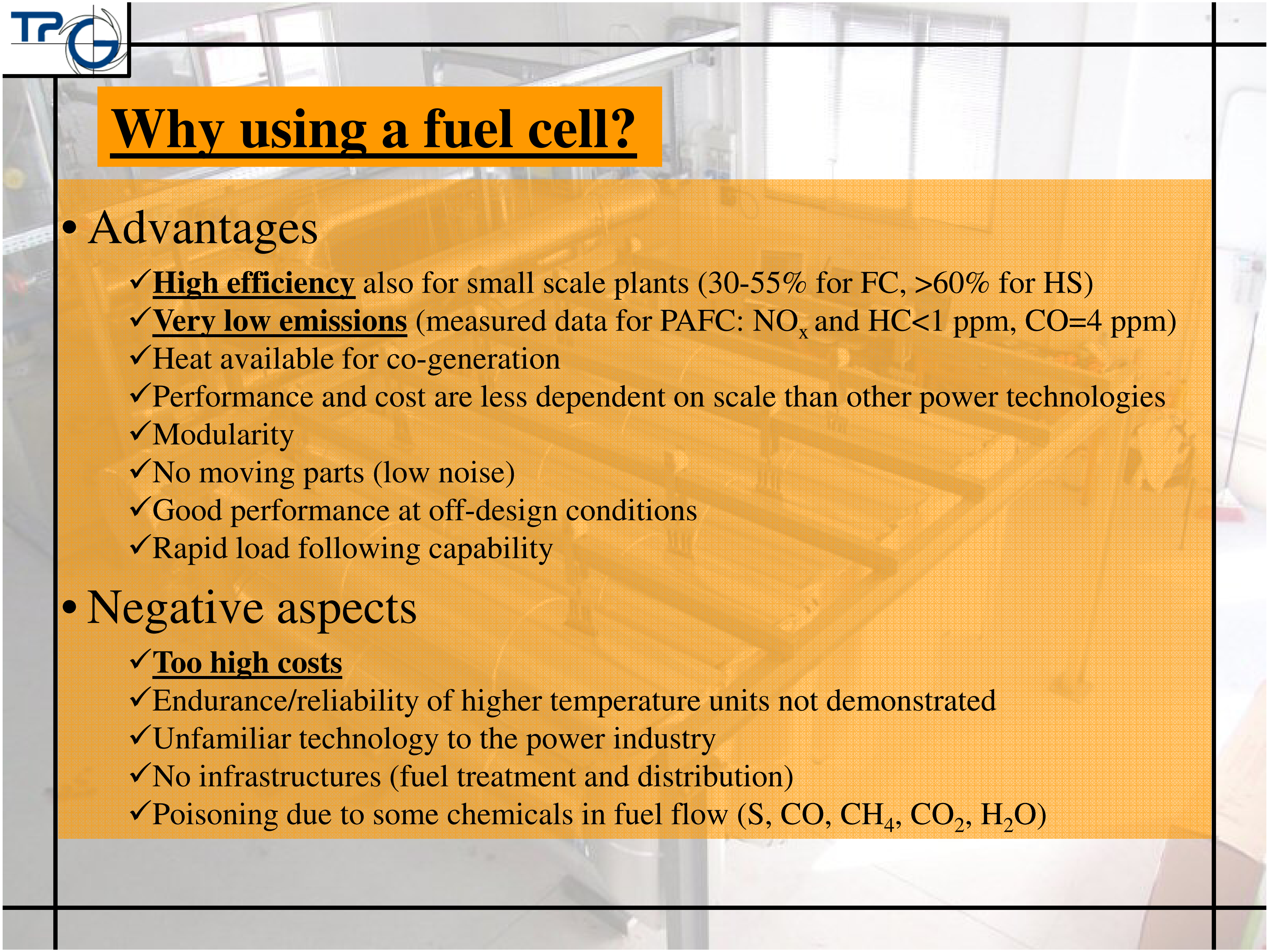


Fuel Cell: Fuel and Oxidant are consumed

How a fuel cell works?



Why using a fuel cell?



- Advantages
  - ✓**High efficiency** also for small scale plants (30-55% for FC, >60% for HS)
  - ✓**Very low emissions** (measured data for PAFC: NO_x and HC<1 ppm, CO=4 ppm)
  - ✓Heat available for co-generation
  - ✓Performance and cost are less dependent on scale than other power technologies
  - ✓Modularity
  - ✓No moving parts (low noise)
  - ✓Good performance at off-design conditions
  - ✓Rapid load following capability
- Negative aspects
  - ✓**Too high costs**
  - ✓Endurance/reliability of higher temperature units not demonstrated
  - ✓Unfamiliar technology to the power industry
  - ✓No infrastructures (fuel treatment and distribution)
  - ✓Poisoning due to some chemicals in fuel flow (S, CO, CH_4, CO_2, H_2O)

Fuel cell applications

✓Stationary electric power plant
✓Motive power for vehicles (open and closed environments)
✓Other applications: APU, auxiliary portable units

A brief history

✓1838: the Swiss Christian Friedrich Schönbein discovered the fuel cell principle
✓**1839: Sir William Robert Grove (Welsh) invented the first fuel cell**
✓1893: Friedrich Wilhelm Ostwald explained the working principle
✓1900-1920: fuel cell ready for marine propulsions (no applications)
✓1959: Francis Thomas Bacon successfully built a 5 kW alkali fuel cell
✓**1960-1970: alkali fuel cells used in the Apollo space program by NASA**
✓1970-1980: fuel cell technology development (PEM, PAFC, MCFC, SOFC)
✓1980-1990: pilot applications in military submarines
✓1993: Ballard Systems tested PEM cells in buses in Vancouver
✓**2000: Siemens-Westinghouse tested the first SOFC hybrid system**
✓2003: establishment of Rolls-Royce Fuel Cell Systems Ltd.
✓Today: several other manufacturers (FuelCell Energy, GenCell, IHI, MTU CFC, Nuvera, Siemens-Westinghouse, SOFC Power, TOPSOE, UTC Power, Voller, VTT)

Technology status (1/4)

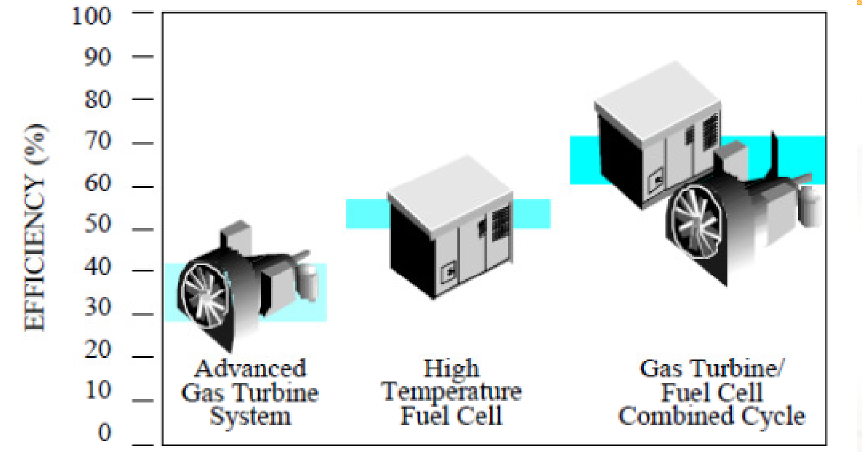
- Stationary electric power

✓UTC Fuel Cells (PC-25 unit): 200 kW PAFC natural gas power plants, one plant operated for 50000 hours, other 14 for 35000 hours, electrical efficiency = 40%, global (cogeneration) efficiency = 80%.

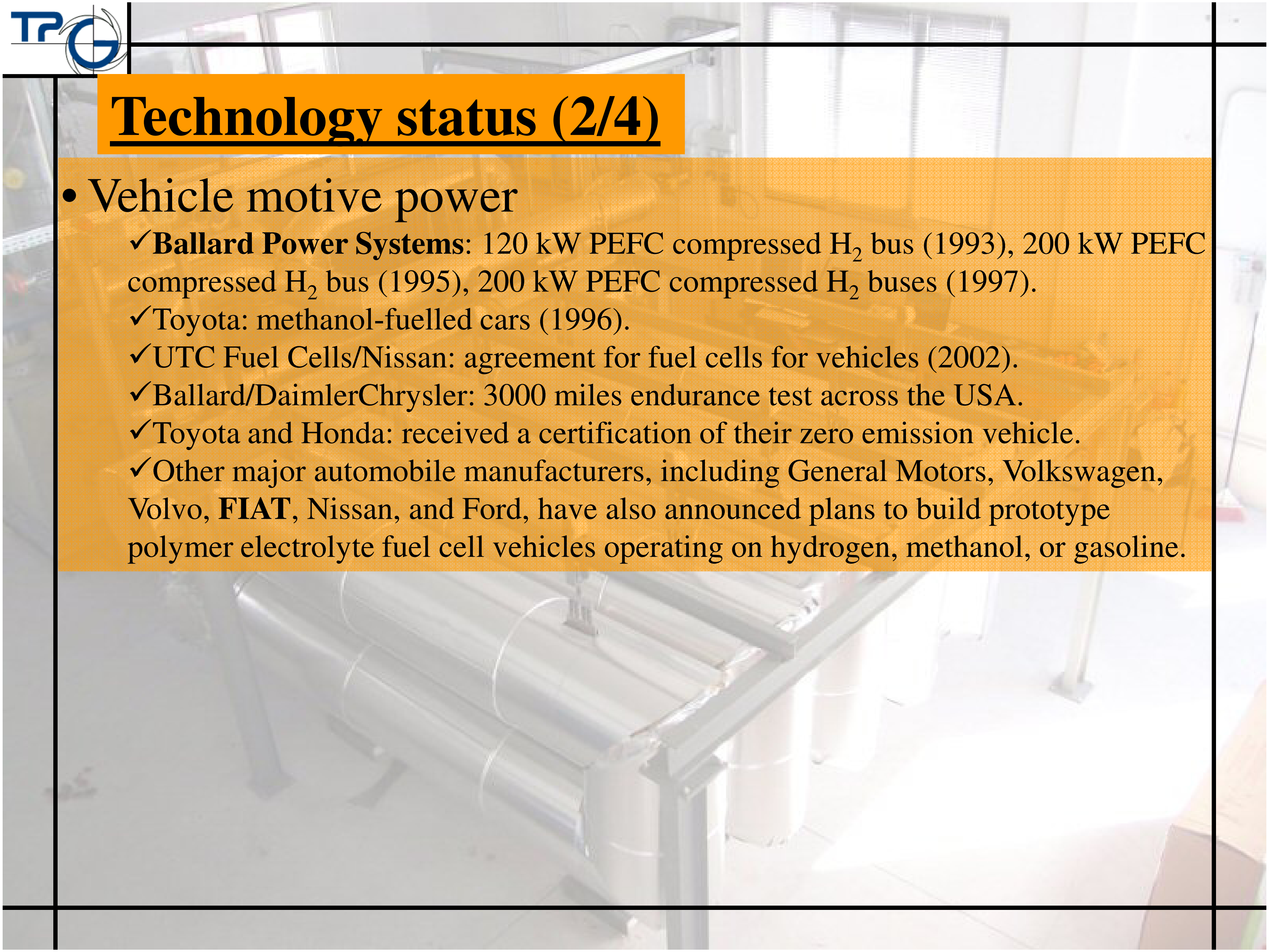
✓Ballard Generation Systems: 10 kW and 60 kW PEFC natural gas power plants, electrical efficiency = 40%; it launched the Nexa (1.2 kW) portable system.

✓FuelCell Energy: it reached a manufacturing capacity of 400 MW, it is developing a 300 kW MCFC natural gas power plant aiming to 57% of electric efficiency.

✓**Siemens Westinghouse Power Corporation**: 250 kW SOFC natural gas power plants (atmospheric pressure) in different sites, 200 kW SOFC/mGT hybrid system for 2000 hours at 53% of electrical efficiency.



Technology status (2/4)

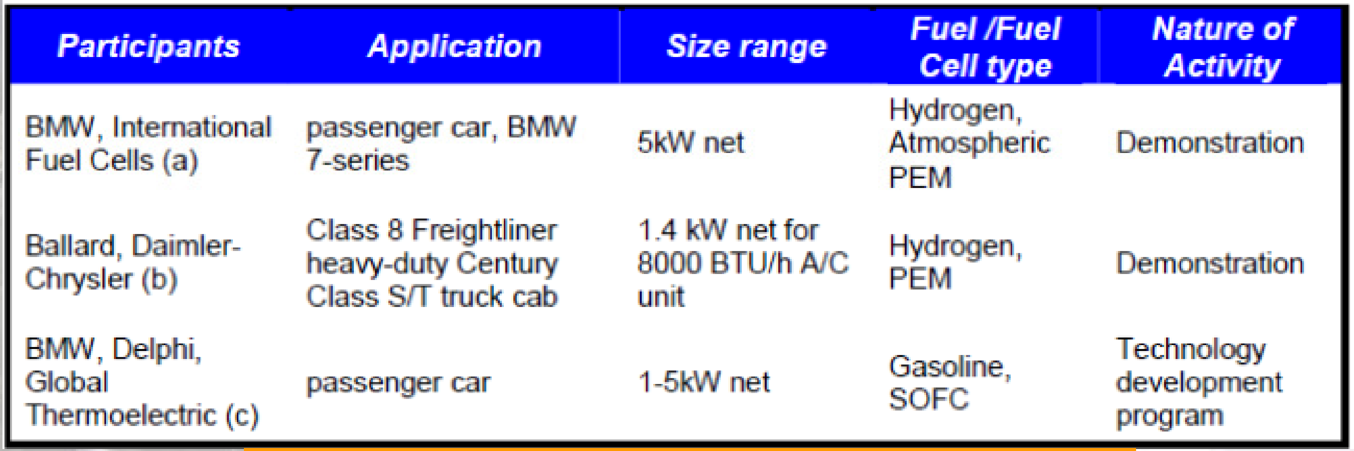


- Vehicle motive power
  - ✓**Ballard Power Systems**: 120 kW PEFC compressed H_2 bus (1993), 200 kW PEFC compressed H_2 bus (1995), 200 kW PEFC compressed H_2 buses (1997).
  - ✓Toyota: methanol-fuelled cars (1996).
  - ✓UTC Fuel Cells/Nissan: agreement for fuel cells for vehicles (2002).
  - ✓Ballard/DaimlerChrysler: 3000 miles endurance test across the USA.
  - ✓Toyota and Honda: received a certification of their zero emission vehicle.
  - ✓Other major automobile manufacturers, including General Motors, Volkswagen, Volvo, **FIAT**, Nissan, and Ford, have also announced plans to build prototype polymer electrolyte fuel cell vehicles operating on hydrogen, methanol, or gasoline.

Technology status (3/4)

- Auxiliary power systems (APU) (1/2)

✓Auxiliary power for vehicles (passenger cars, trucks, yachts, ships, airplanes, recreational vehicles).

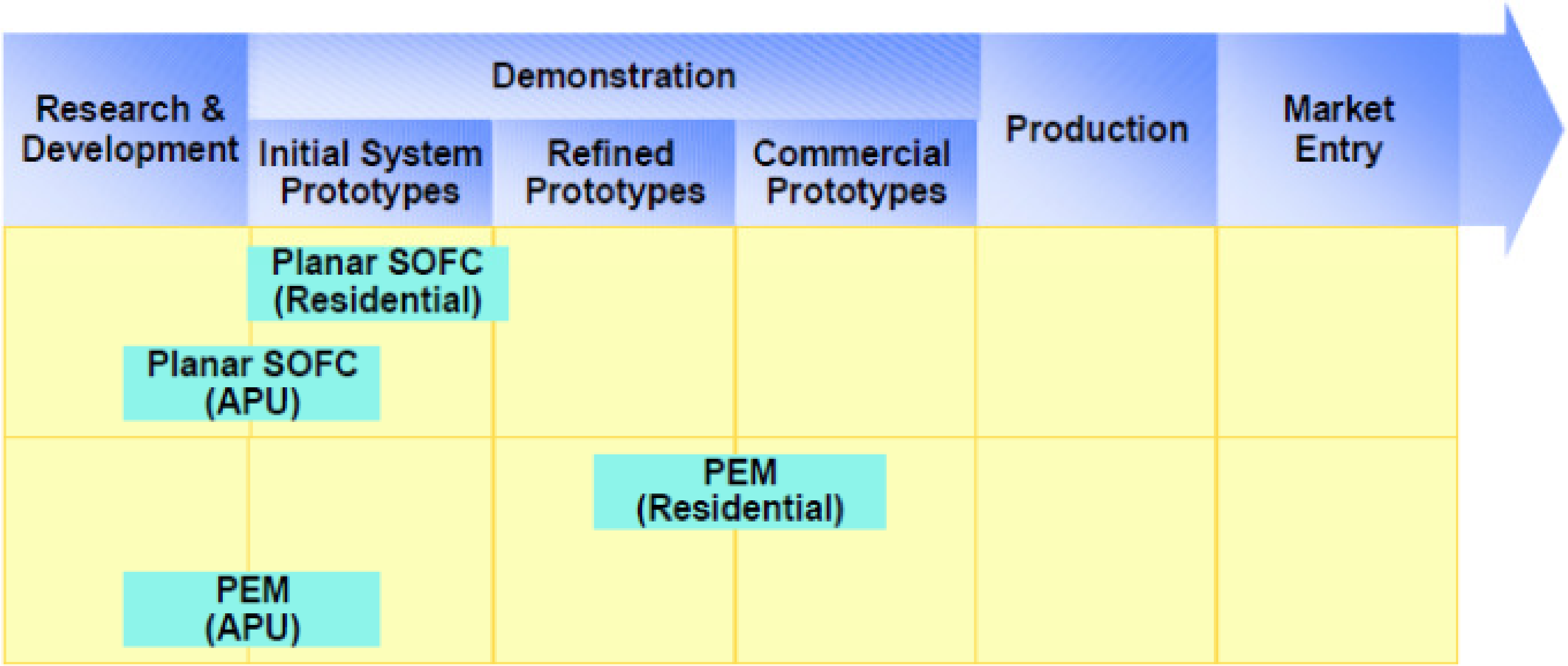


Participants	Application	Size range	Fuel /Fuel Cell type	Nature of Activity
BMW, International Fuel Cells (a)	passenger car, BMW 7-series	5kW net	Hydrogen, Atmospheric PEM	Demonstration
Ballard, Daimler-Chrysler (b)	Class 8 Freightliner heavy-duty Century Class S/T truck cab	1.4 kW net for 8000 BTU/h A/C unit	Hydrogen, PEM	Demonstration
BMW, Delphi, Global Thermoelectric (c)	passenger car	1-5kW net	Gasoline, SOFC	Technology development program

APU development examples

Technology status (4/4)

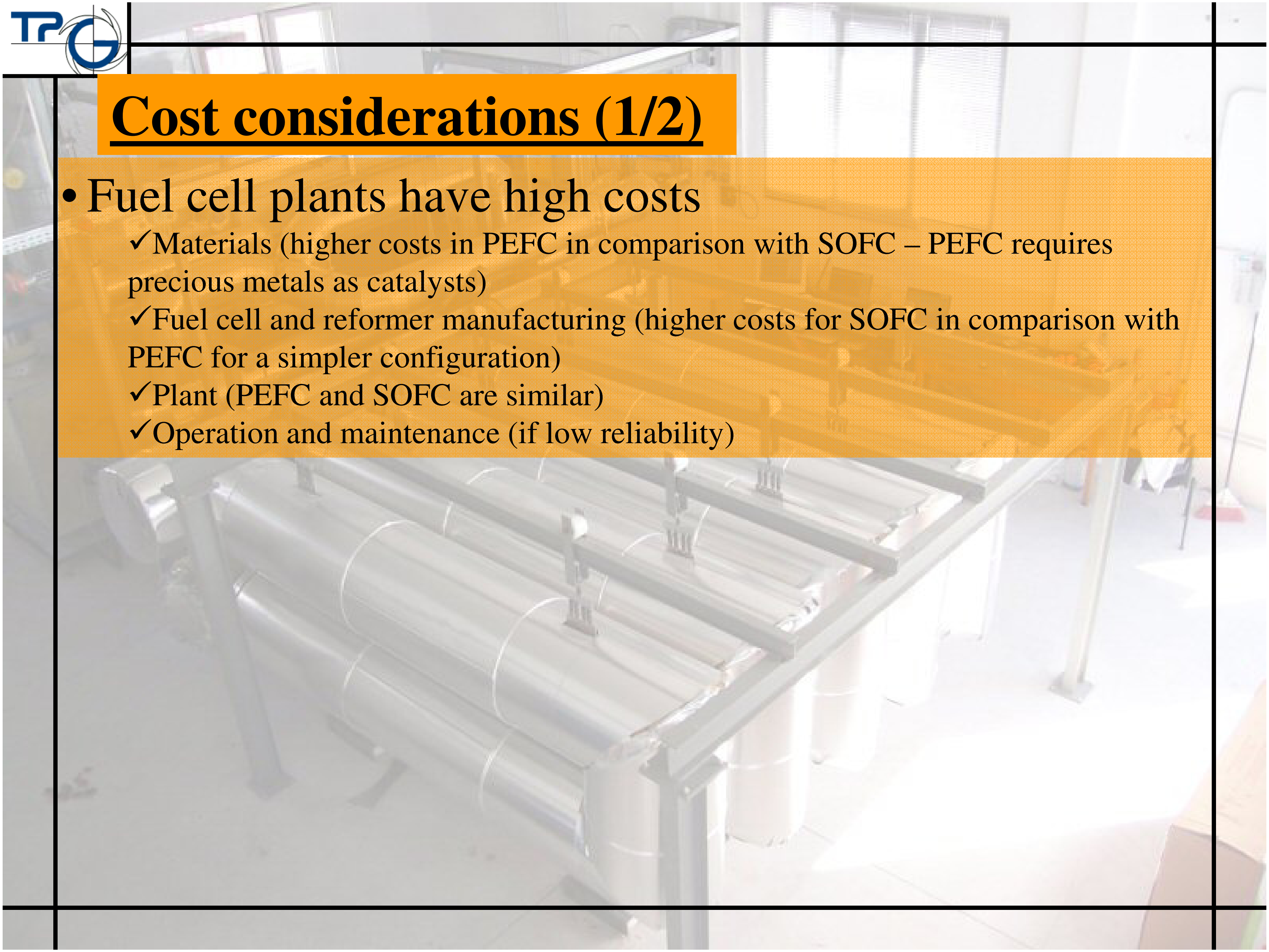
- Auxiliary power systems (APU) (2/2)



Research & Development	Demonstration			Production	Market Entry
	Initial System Prototypes	Refined Prototypes	Commercial Prototypes		
	Planar SOFC (Residential)				
Planar SOFC (APU)					
		PEM (Residential)			
PEM (APU)					

Fuel cell systems for APU: development status

Cost considerations (1/2)

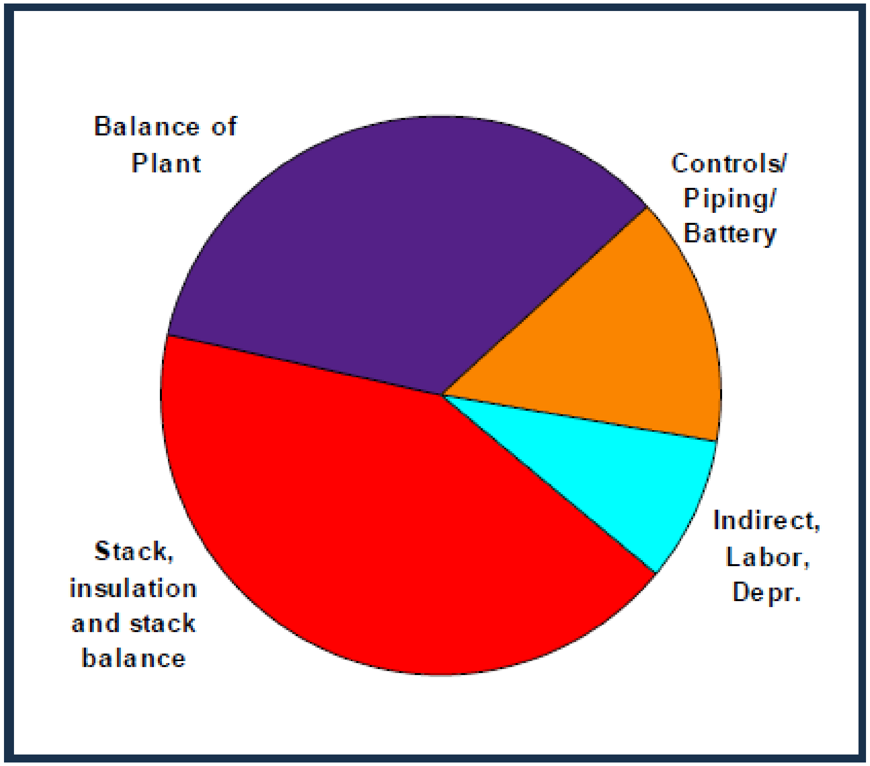


- Fuel cell plants have high costs
  - ✓Materials (higher costs in PEFC in comparison with SOFC – PEFC requires precious metals as catalysts)
  - ✓Fuel cell and reformer manufacturing (higher costs for SOFC in comparison with PEFC for a simpler configuration)
  - ✓Plant (PEFC and SOFC are similar)
  - ✓Operation and maintenance (if low reliability)

Cost considerations (2/2)

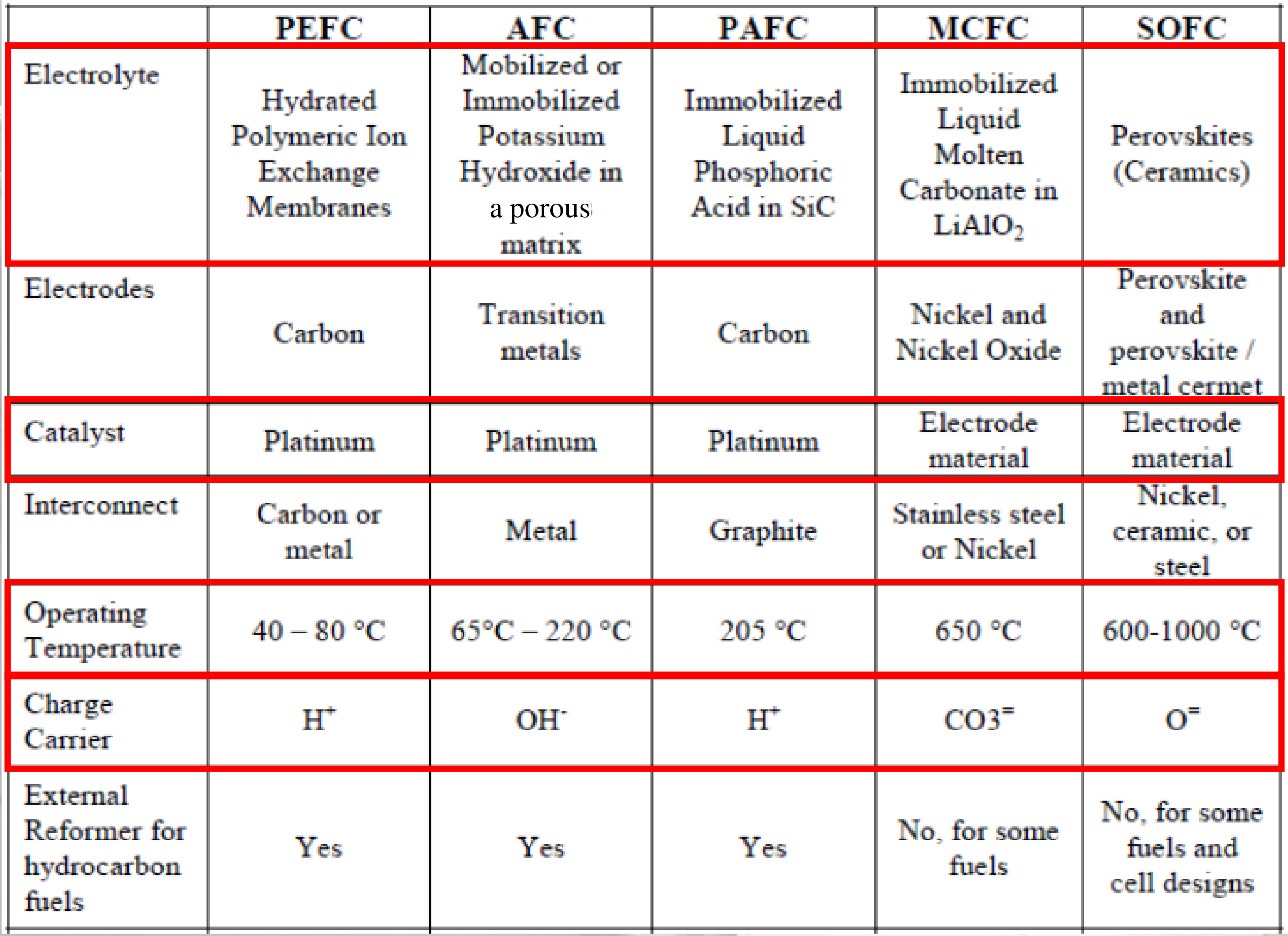
SOFC System
Cost Structure:

Manufacturing Costs:
$350-550/kW



- Cost details for a 5 kW APU SOFC system (gasoline fuelled)
- Analysis from U.S. DOE – NETL

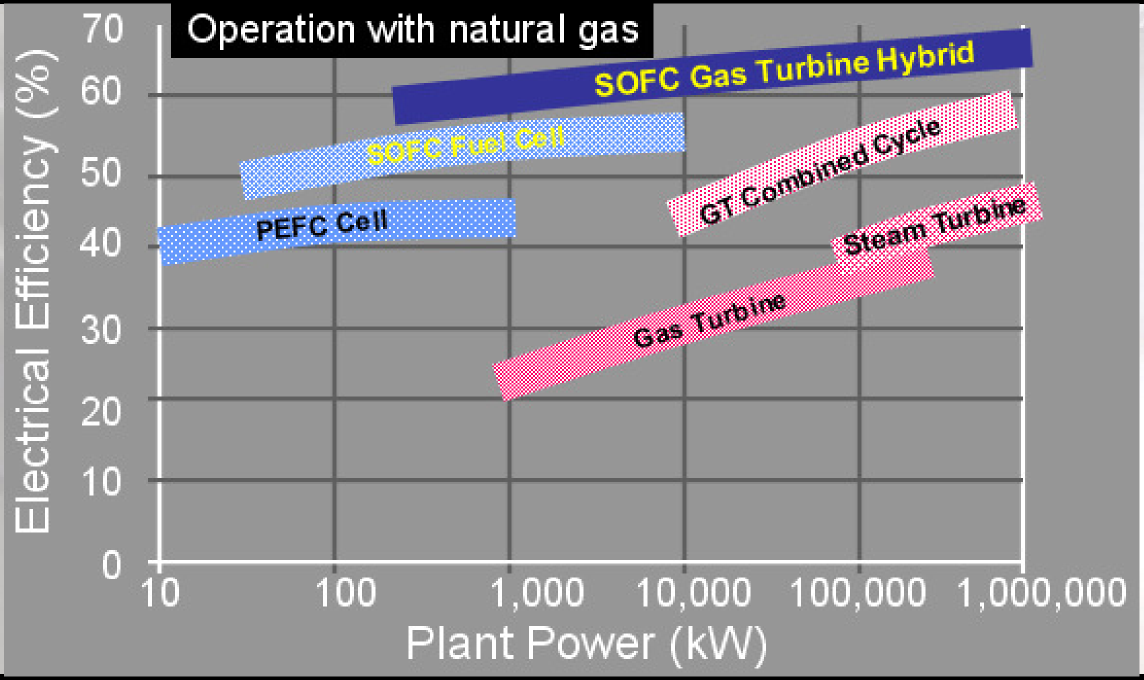
Fuel cell types (1/3)



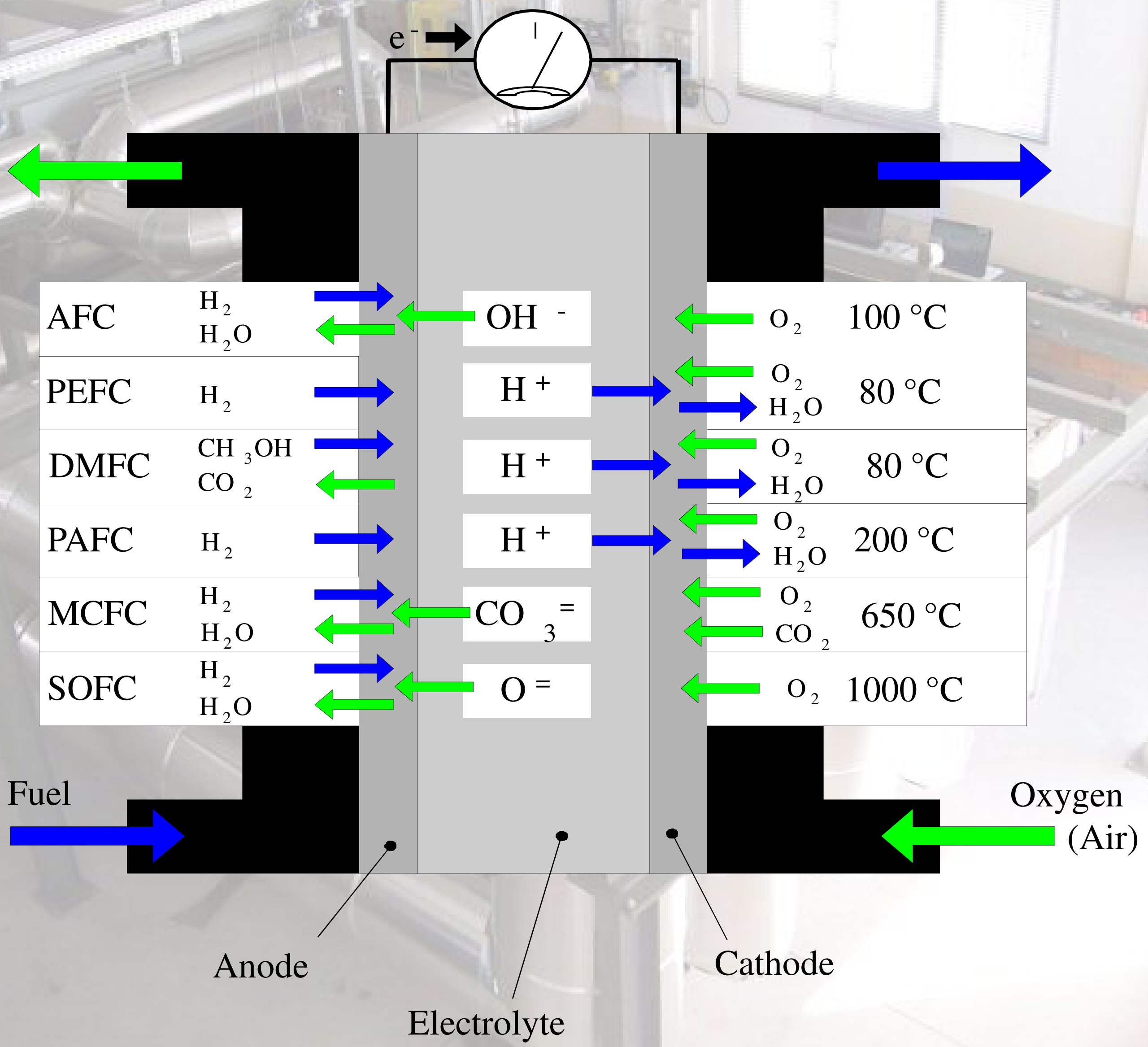
	PEFC	AFC	PAFC	MCFC	SOFC
Electrolyte	Hydrated Polymeric Ion Exchange Membranes	Mobilized or Immobilized Potassium Hydroxide in a porous matrix	Immobilized Liquid Phosphoric Acid in SiC	Immobilized Liquid Molten Carbonate in $LiAlO_2$	Perovskites (Ceramics)
Electrodes	Carbon	Transition metals	Carbon	Nickel and Nickel Oxide	Perovskite and perovskite / metal cermet
Catalyst	Platinum	Platinum	Platinum	Electrode material	Electrode material
Interconnect	Carbon or metal	Metal	Graphite	Stainless steel or Nickel	Nickel, ceramic, or steel
Operating Temperature	40 – 80 °C	65°C – 220 °C	205 °C	650 °C	600-1000 °C
Charge Carrier	H^+	OH^-	H^+	$CO3^{=}$	$O^{=}$
External Reformer for hydrocarbon fuels	Yes	Yes	Yes	No, for some fuels	No, for some fuels and cell designs

Fuel cell types (2/3)

	PEFC	AFC	PAFC	MCFC	SOFC
Electrical efficiency (only fuel cell)	35%-40%	40%-45%	35%-40%	50%-60%	45%-55%
Electrical efficiency (hybrid cycle)	No	No	No	Up to 63%	Up to 65%



Fuel cell types (3/3)



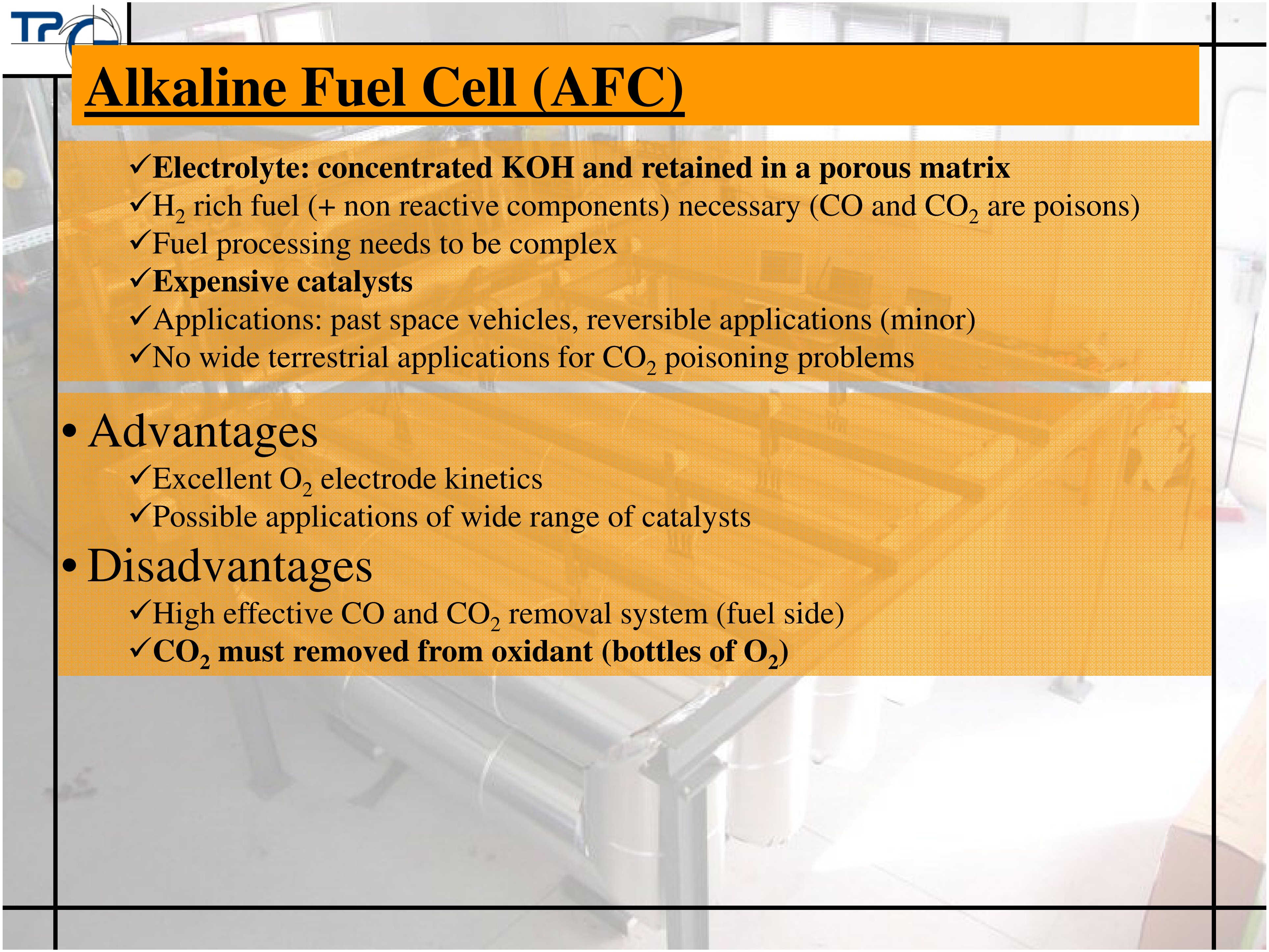
AFC	H_2 H_2O	OH^-	O_2	100 °C
PEFC	H_2	H^+	O_2 H_2O	80 °C
DMFC	CH_3OH CO_2	H^+	O_2 H_2O	80 °C
PAFC	H_2	H^+	O_2 H_2O	200 °C
MCFC	H_2 H_2O	$CO_3^=$	O_2 CO_2	650 °C
SOFC	H_2 H_2O	$O^=$	O_2	1000 °C

Polymer Electrolyte Fuel Cell (PEFC o PEM)

✓**Electrolyte: ion (H^+) exchange membrane (fluorinated sulfonic acid polymer)**
✓Membrane must be hydrated (water must not evaporate faster than it is produced)
✓H_2 rich fuel necessary **(CO is poison if >50 ppm)**
✓Fuel processing needs to be complex
✓**Expensive catalysts** (Pt in most cases)
✓Applications: vehicles, portable applications, stationary applications (minor)

- Advantages
  - ✓Solid electrolyte (strong resistance to gas crossover)
  - ✓Low temperature **(rapid start-up, no exotic materials)**
  - ✓No corrosive cell constituent
  - ✓High current density (specific power > 2 W/cm^2)
- Disadvantages
  - ✓Low temperature (low efficiency and difficult thermal management)
  - ✓No cogeneration
  - ✓Difficult water management **(hydration problems)**
  - ✓**Poisoning: CO, S, NH_3**
  - ✓Extensive fuel processing
  - ✓Hydrogen infrastructure

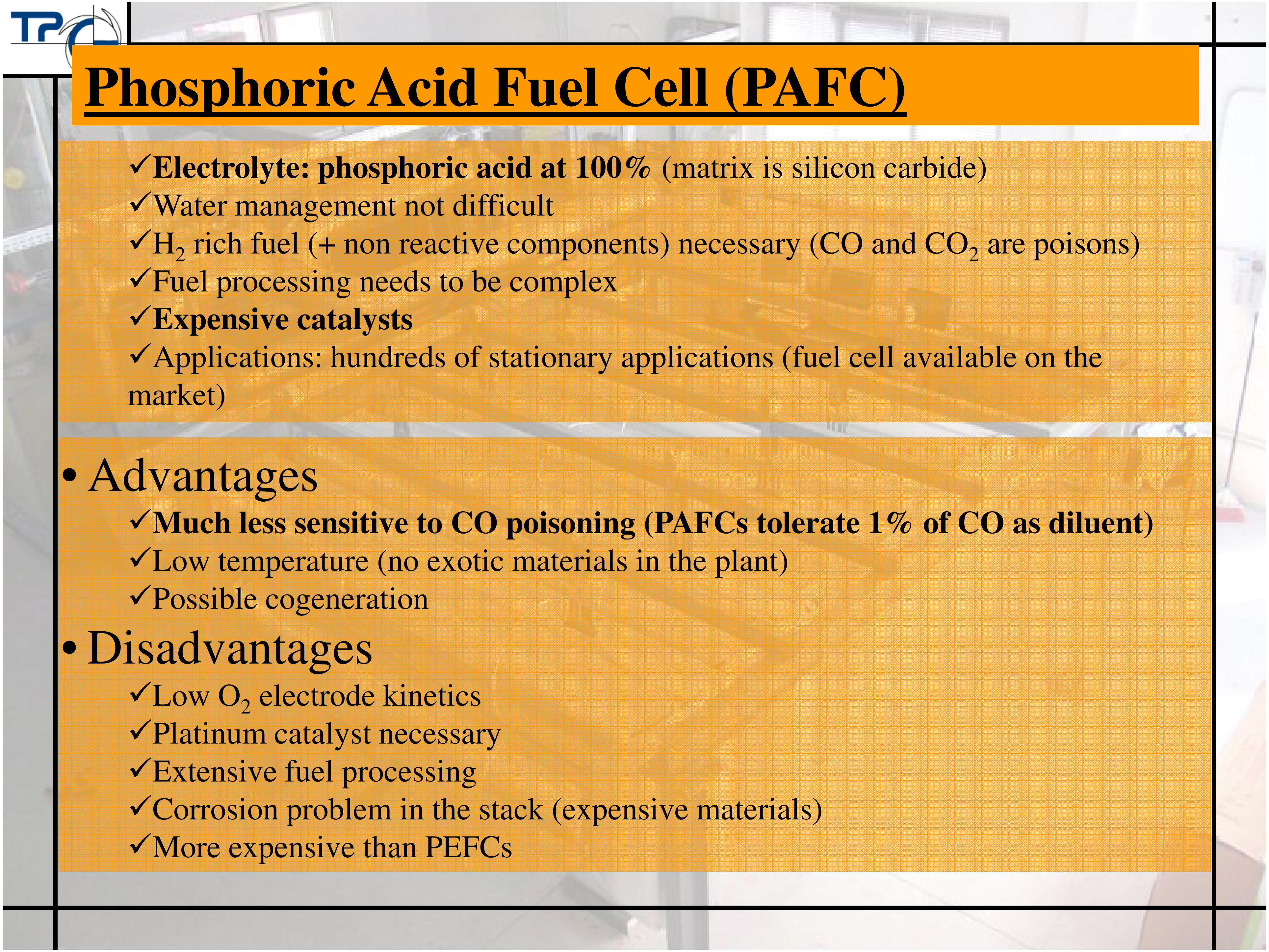
Alkaline Fuel Cell (AFC)



- ✓**Electrolyte: concentrated KOH and retained in a porous matrix**
- ✓H_2 rich fuel (+ non reactive components) necessary (CO and CO_2 are poisons)
- ✓Fuel processing needs to be complex
- ✓**Expensive catalysts**
- ✓Applications: past space vehicles, reversible applications (minor)
- ✓No wide terrestrial applications for CO_2 poisoning problems

- Advantages
  - ✓Excellent O_2 electrode kinetics
  - ✓Possible applications of wide range of catalysts
- Disadvantages
  - ✓High effective CO and CO_2 removal system (fuel side)
  - ✓**CO_2 must removed from oxidant (bottles of O_2)**

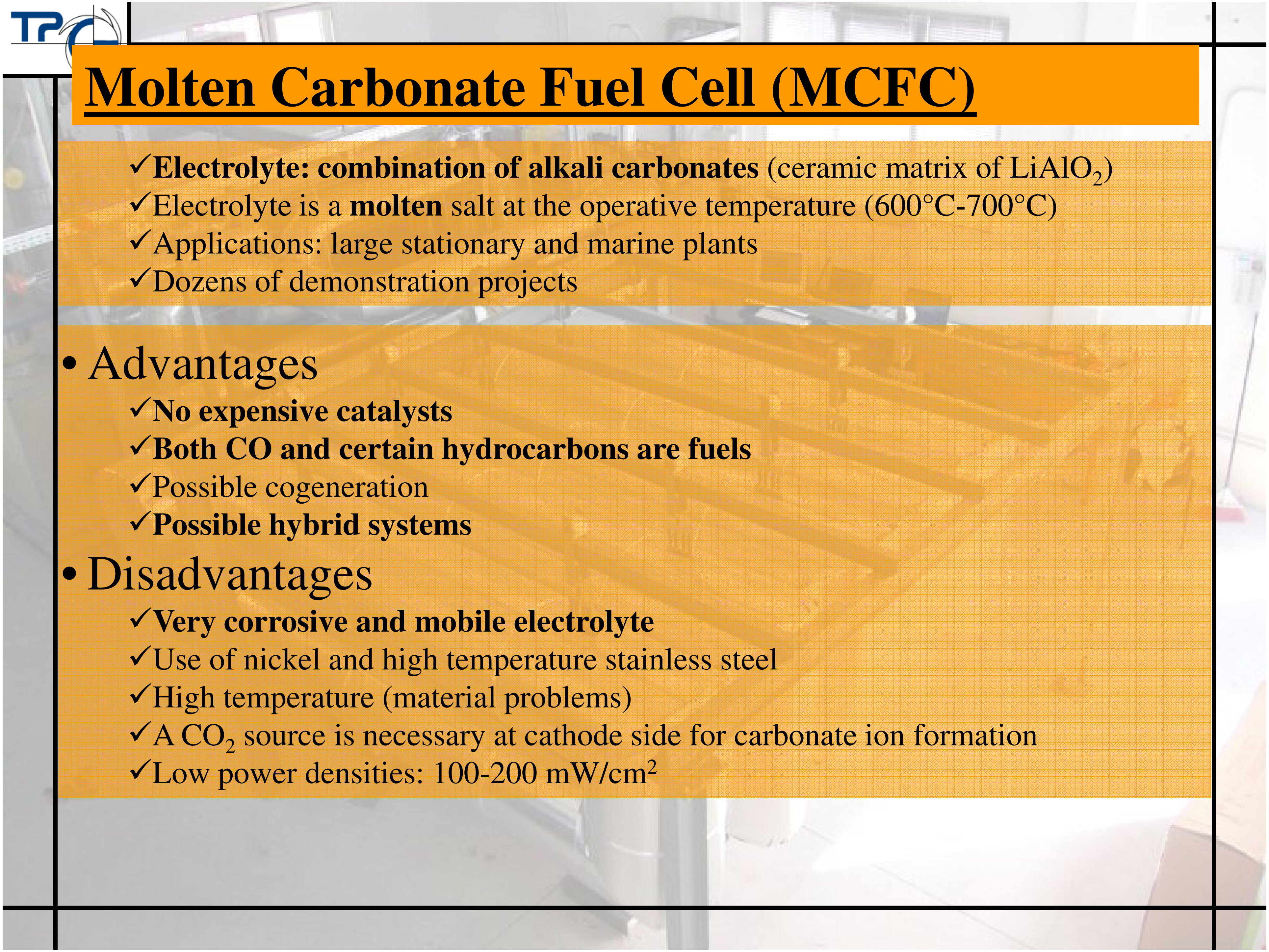
Phosphoric Acid Fuel Cell (PAFC)



✓**Electrolyte: phosphoric acid at 100%** (matrix is silicon carbide)
✓Water management not difficult
✓H_2 rich fuel (+ non reactive components) necessary (CO and CO_2 are poisons)
✓Fuel processing needs to be complex
✓**Expensive catalysts**
✓Applications: hundreds of stationary applications (fuel cell available on the market)

- Advantages
  - ✓**Much less sensitive to CO poisoning (PAFCs tolerate 1% of CO as diluent)**
  - ✓Low temperature (no exotic materials in the plant)
  - ✓Possible cogeneration
- Disadvantages
  - ✓Low O_2 electrode kinetics
  - ✓Platinum catalyst necessary
  - ✓Extensive fuel processing
  - ✓Corrosion problem in the stack (expensive materials)
  - ✓More expensive than PEFCs

Molten Carbonate Fuel Cell (MCFC)



✓**Electrolyte: combination of alkali carbonates** (ceramic matrix of $LiAlO_2$)
✓Electrolyte is a **molten** salt at the operative temperature (600°C-700°C)
✓Applications: large stationary and marine plants
✓Dozens of demonstration projects

- Advantages
  ✓**No expensive catalysts**
  ✓**Both CO and certain hydrocarbons are fuels**
  ✓Possible cogeneration
  ✓**Possible hybrid systems**
- Disadvantages
  ✓**Very corrosive and mobile electrolyte**
  ✓Use of nickel and high temperature stainless steel
  ✓High temperature (material problems)
  ✓A CO_2 source is necessary at cathode side for carbonate ion formation
  ✓Low power densities: 100-200 mW/cm^2

Solid Oxide Fuel Cell (SOFC)

✓Electrolyte: **solid non porous metal oxide** (usually Y_2O_3-stabilized ZrO_2)

✓Anode is Co-ZrO_2 or Ni-ZrO_2 cermet, and the cathode is Sr-doped $LaMnO_3$

✓Usually solid electrolyte at ~1000°C, recently thin-electrolyte cells (650-850°C)

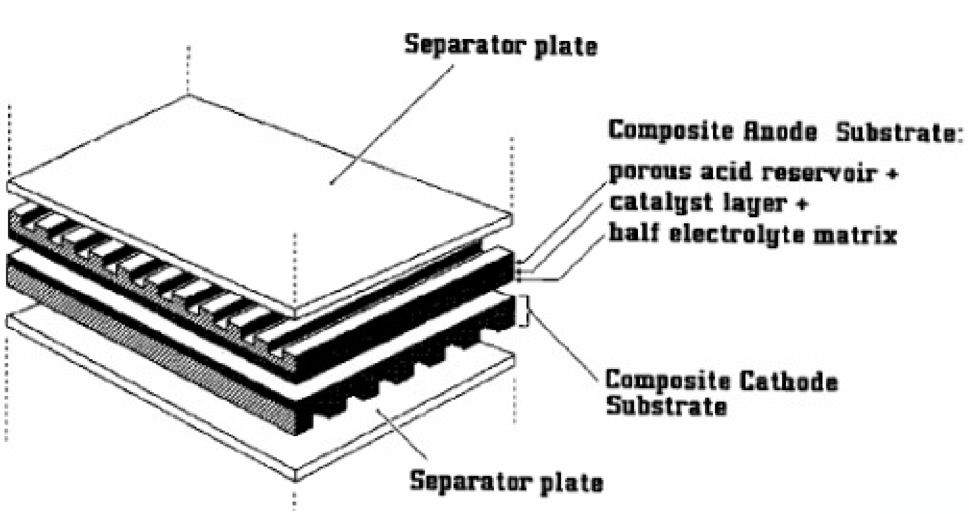
✓Applications: stationary generation, mobile power, auxiliary power for vehicles

✓High interest in the last ten years: research, investments, development

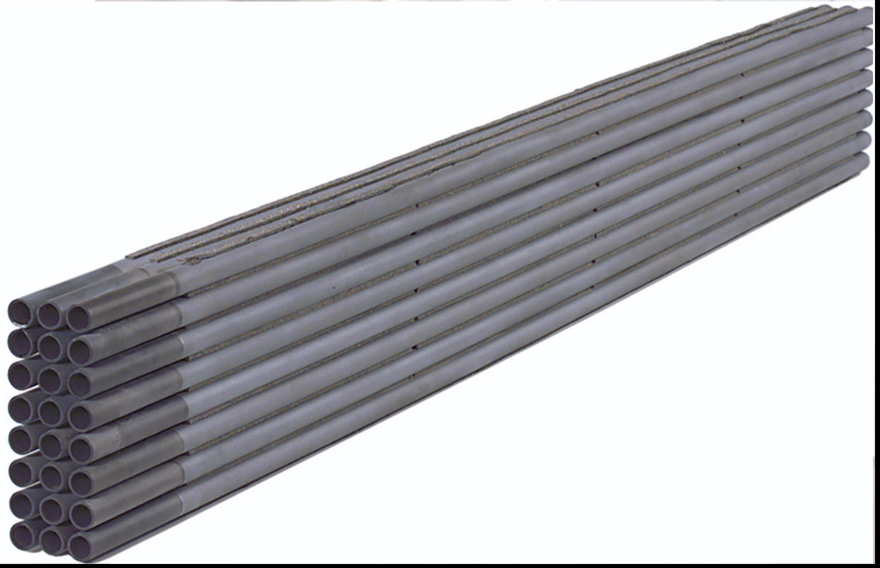
- Advantages
  - ✓**No expensive catalysts**
  - ✓No corrosion problems (solid electrolyte)
  - ✓No electrolyte movement
  - ✓Both CO and certain hydrocarbons are fuels
  - ✓Relatively low cost materials
  - ✓No requirement for CO_2 at the cathode side
  - ✓Power densities higher than PEFCs and MCFCs
  - ✓Possible cogeneration
  - ✓**Possible hybrid systems**
- Disadvantages
  - ✓Thermal expansion mismatches among materials (high temperature problem)
  - ✓Severe constraints on materials selection (high temperature problem)

Fuel cell stacking

- ✓Unit cells must be combined into a cell stack with modular components
- ✓Connecting multiple unit cells in series via electrically conductive interconnects



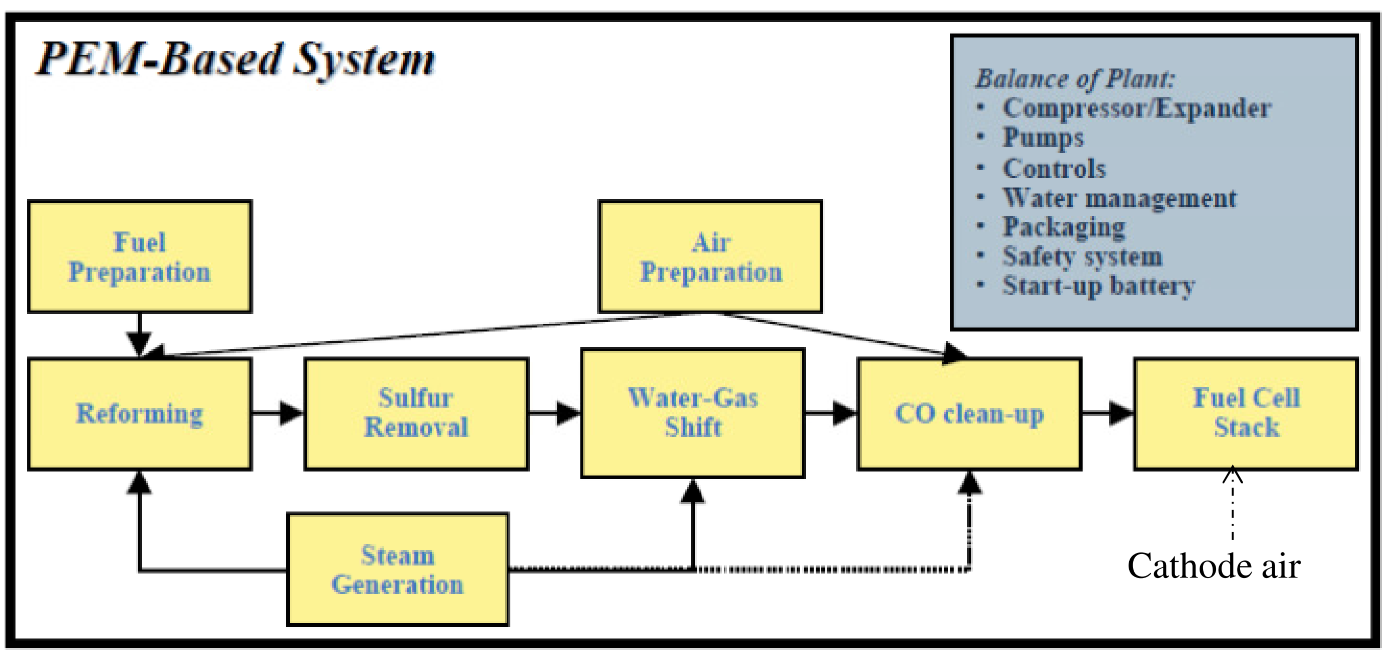
Planar-bipolar stacking: basic module



Stack with tubular cells

Fuel cell systems: examples (1/8)

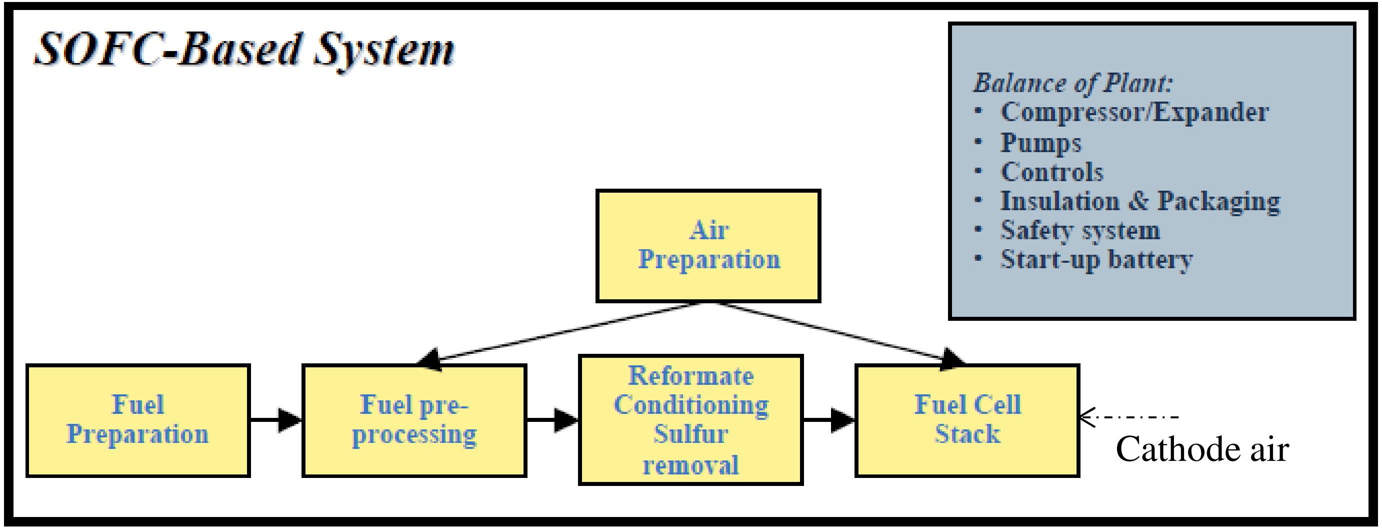
- ✓Fuel processing
- ✓Air supply
- ✓Thermal management system
- ✓Water management
- ✓Electric power management



PEFC (or PEM) system

Fuel cell systems: examples (2/8)

- ✓Fuel processing
- ✓Air supply
- ✓Thermal management system
- ✓Water management
- ✓Electric power management



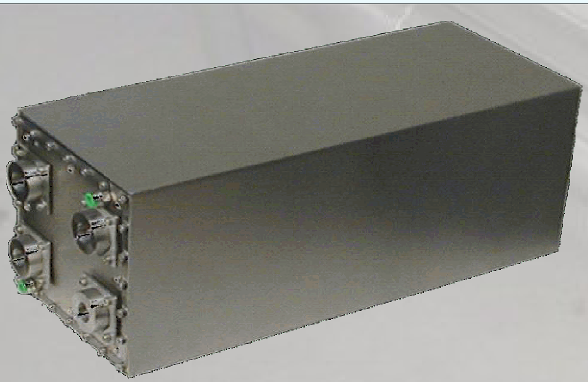
SOFC-Based System

Balance of Plant:
- Compressor/Expander
- Pumps
- Controls
- Insulation & Packaging
- Safety system
- Start-up battery

SOFC system

Fuel cell systems: examples (3/8)

Manufacturer	**ARCOTRONICS Fuel Cells**
Type	**P.E.M. (Polymer Electrolyte Membrane)**
Nominal power	**5 kW**
Cell number	**100**
V_0	**100 V**
$V_{nominal}$	**72 V**
$I_{nominal}$	**70 A**
H_2 consume	**0.83 Nm^3/kWh**
Nominal temperature	**70 °C**
Nominal pressure	**0,15 bar**
Dimensions (mm)	**250x250x550**



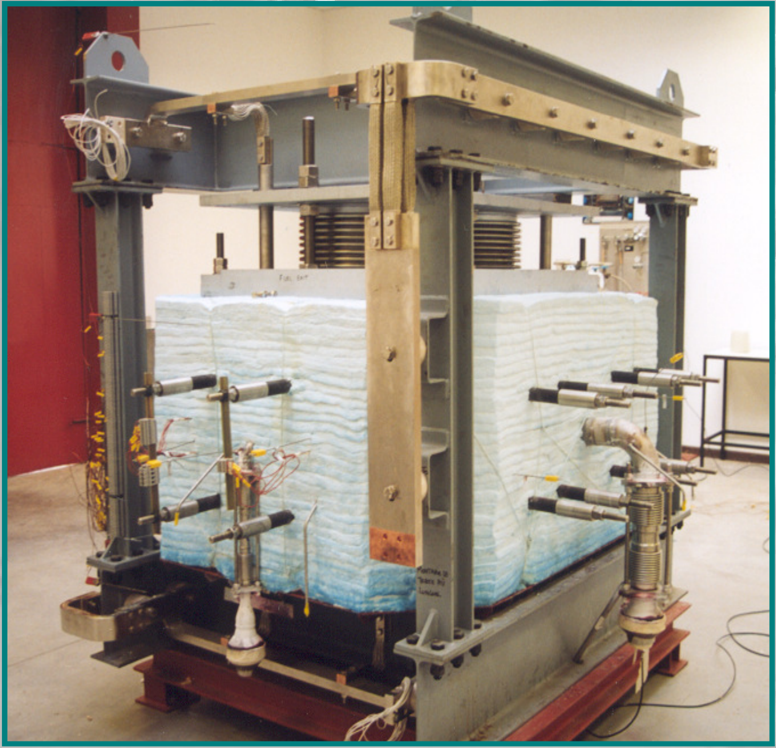
PEFC (or PEM) for vehicle applications

	Daily 65 Elettrical	**Daily 65 H_2**
Maximum speed	70 km/h	70 km/h
Maximum slope	25 %	25 %
Range	70-120 km	150-250 km
Total weight	6500 kg	6500 kg
Capacity	Up to 3910 kg	Up to 3600 kg
Battery capacity	34-64 kWh	34-42 kWh
Reduced gear	Yes	Yes
Maximum power	60 kW	60 kW

Fuel cell systems: examples (4/8)

MCFC for stationary applications

"STAD3" MCFC AFCo STACK



- Rectangular shape (1250×650 mm)
- External manifolds
- Cross Flow Configuration
- Cell number 15 *(1:10 "Series 500")*
- Cell area 0.81 m² *(the same as "Series 500" modules)*
- Operating pressure 3.5 bar

- No heater plates
- thicker matrices
- simplified soft rails
- modified axial load system
- improved bus bar configuration
- modified manifold tightening system

Fuel cell systems: examples (5/8)

SOFC for stationary applications

Tubular stack

Planar stack

Fuel cell systems: examples (6/8)

Completed SOFC Demonstration Program
EDB/ELSAM CHP100 SOFC Power System Installation

Westervort, The Netherlands; NUON [host utility] district heating booster station

PNG fuel; 16,610 hours; 110 kWe to grid; 46% Efficiency [net ac/LHV]; No Degradation

Fuel cell systems: examples (7/8)

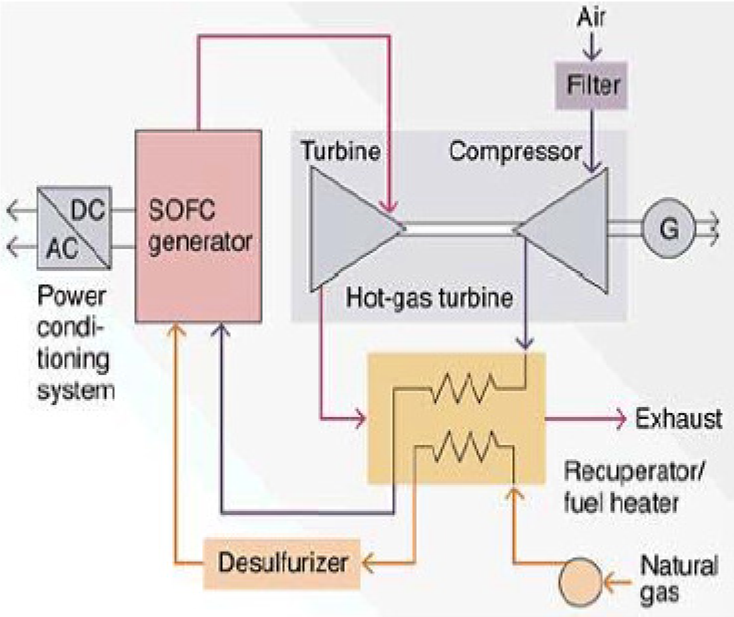
MTU - Fuel cells near to the market

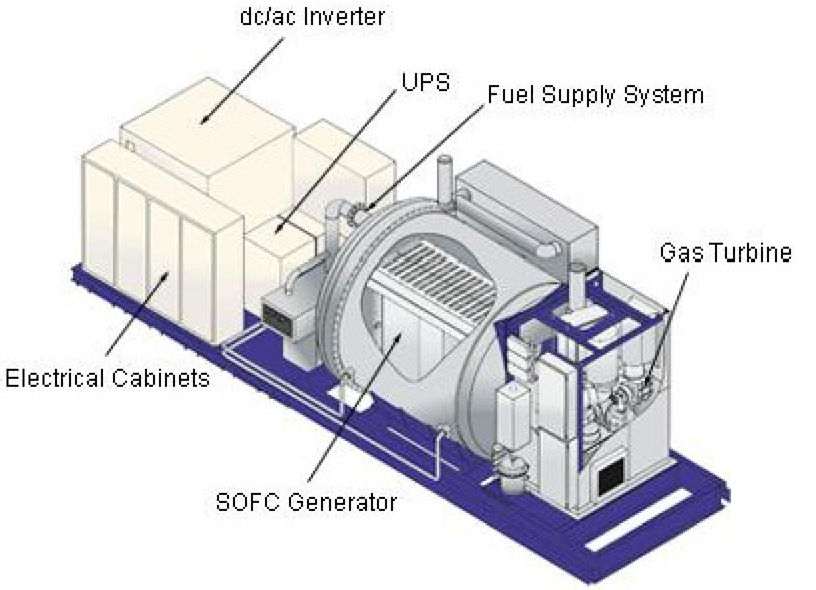
- Still too expensive for commercial production
- But used in particular demonstration cases

250 kW high-temperature fuel cells (MTU)
Produce electricity, steam, heat and cold...

Fuel cell systems: examples (8/8)

Siemens-Westinghouse hybrid system

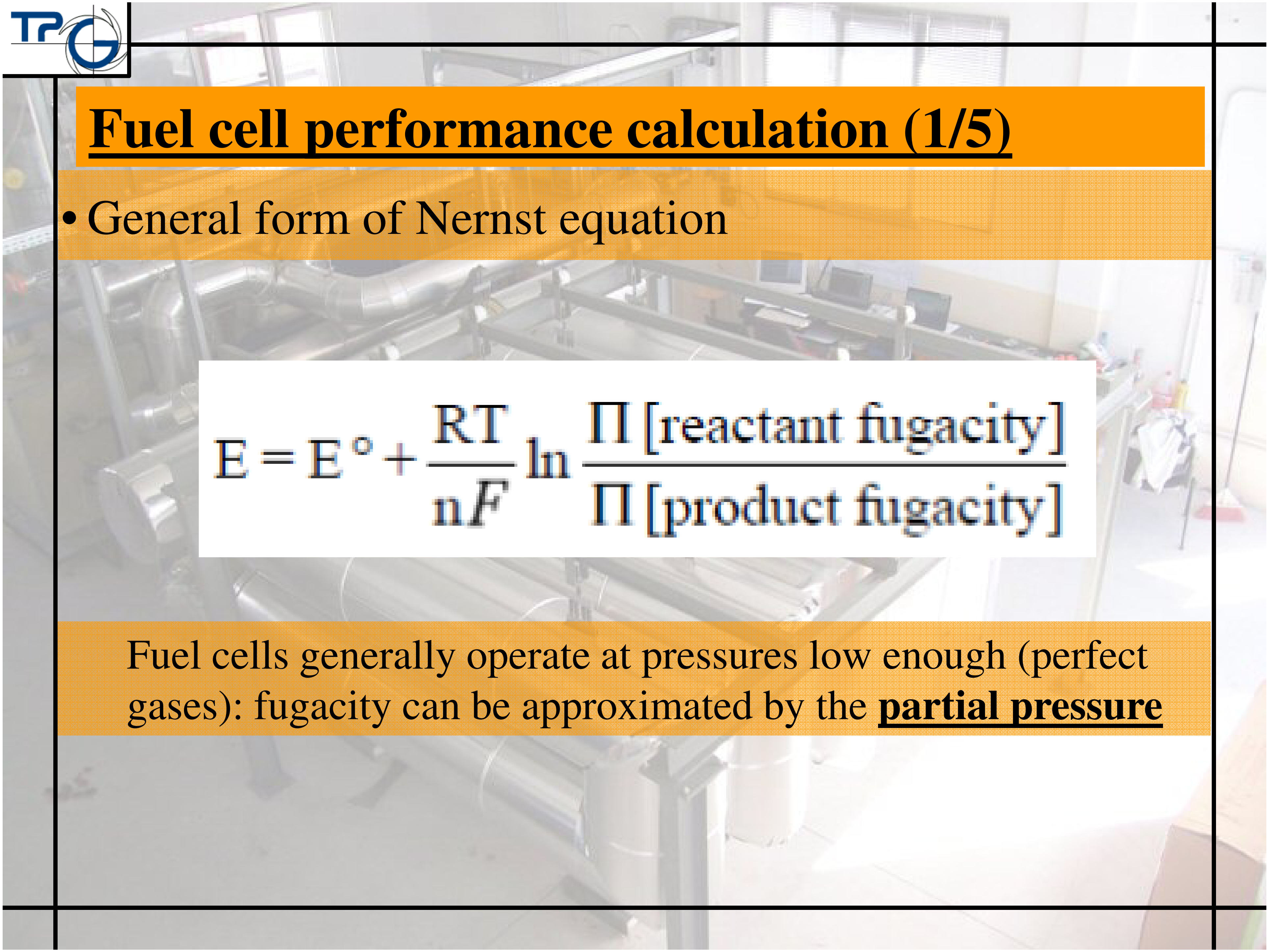




First SOFC hybrid system

- 53% electrical efficiency
- 217 kW
- 2000 hours

Too expensive!!!



Fuel cell performance calculation (1/5)

- General form of Nernst equation

$$E = E^{\circ} + \frac{RT}{nF} \ln \frac{\Pi\,[\text{reactant fugacity}]}{\Pi\,[\text{product fugacity}]}$$

Fuel cells generally operate at pressures low enough (perfect gases): fugacity can be approximated by the **partial pressure**

Fuel cell performance calculation (2/5)

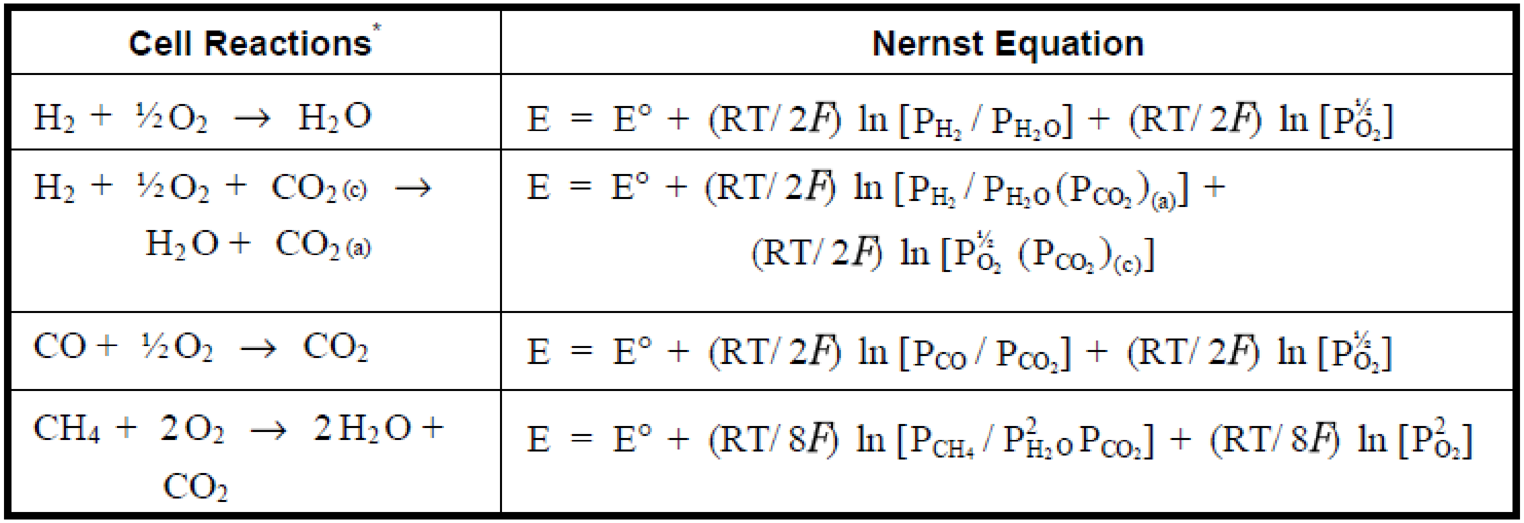
- Electrochemical reactions in fuel cells

Fuel Cell	**Anode Reaction**	**Cathode Reaction**
Polymer Electrolyte and Phosphoric Acid	$H_2 \rightarrow 2H^+ + 2e^-$	$\frac{1}{2} O_2 + 2H^+ + 2e^- \rightarrow H_2O$
Alkaline	$H_2 + 2(OH)^- \rightarrow 2H_2O + 2e^-$	$\frac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2(OH)^-$
Molten Carbonate	$H_2 + CO_3^= \rightarrow H_2O + CO_2 + 2e^-$ $CO + CO_3^= \rightarrow 2CO_2 + 2e^-$	$\frac{1}{2} O_2 + CO_2 + 2e^- \rightarrow CO_3^=$
Solid Oxide	$H_2 + O^= \rightarrow H_2O + 2e^-$ $CO + O^= \rightarrow CO_2 + 2e^-$ $CH_4 + 4O^= \rightarrow 2H_2O + CO_2 + 8e^-$	$\frac{1}{2} O_2 + 2e^- \rightarrow O^=$

- The cell potential increases with an increase in the partial pressure (concentration) of reactants and a decrease in the partial pressure of products
- For example, for the hydrogen reaction, the ideal cell potential at a given temperature can be increased by operating at higher reactant pressures

Fuel cell performance calculation (3/5)

- Fuel cell reactions and Nernst voltage



Cell Reactions*	Nernst Equation
$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$	$E = E^\circ + (RT/2F)\ln[P_{H_2}/P_{H_2O}] + (RT/2F)\ln[P_{O_2}^{1/2}]$
$H_2 + \frac{1}{2}O_2 + CO_{2(c)} \rightarrow H_2O + CO_{2(a)}$	$E = E^\circ + (RT/2F)\ln[P_{H_2}/P_{H_2O}(P_{CO_2})_{(a)}] + (RT/2F)\ln[P_{O_2}^{1/2}(P_{CO_2})_{(c)}]$
$CO + \frac{1}{2}O_2 \rightarrow CO_2$	$E = E^\circ + (RT/2F)\ln[P_{CO}/P_{CO_2}] + (RT/2F)\ln[P_{O_2}^{1/2}]$
$CH_4 + 2O_2 \rightarrow 2H_2O + CO_2$	$E = E^\circ + (RT/8F)\ln[P_{CH_4}/P_{H_2O}^2 P_{CO_2}] + (RT/8F)\ln[P_{O_2}^2]$

- E° at 298 K for $H_2+1/2*O_2$: 1.229 V (liquid water product) or 1.18 V (steam product)
- The difference is Gibbs free energy change of vaporization

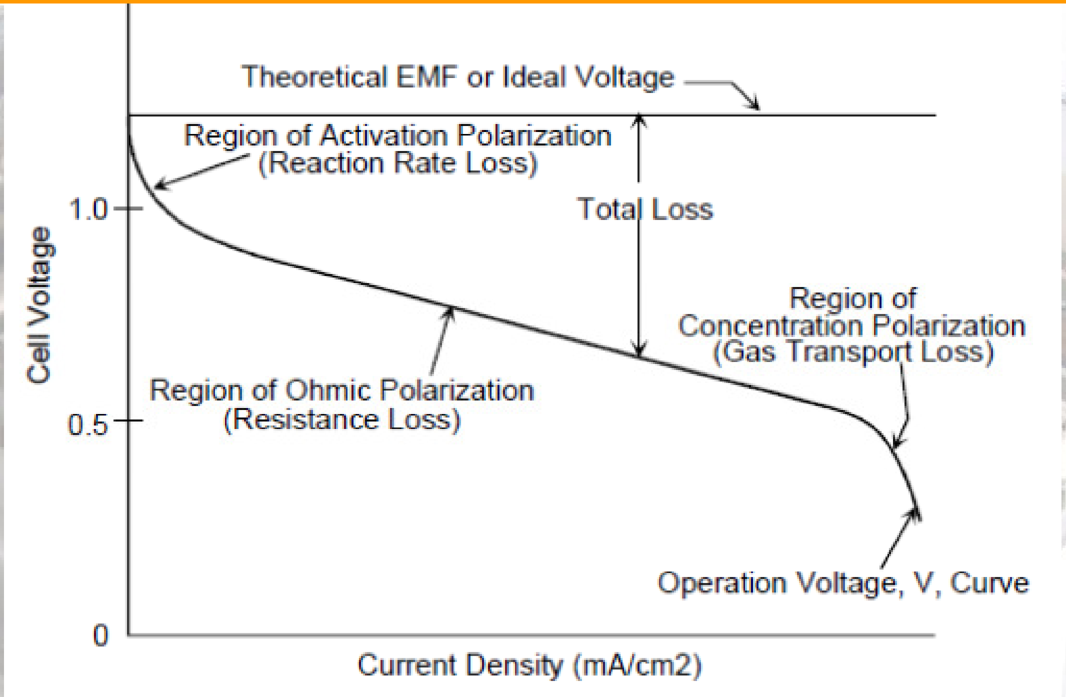
Fuel cell performance calculation (4/5)

The actual cell potential is decreased from its ideal potential because of several types of irreversible losses (often they are named polarization, overpotential or overvoltage)

- Types of losses

  - **Activation-related losses**. These come from the activation energy of the electrochemical reactions at the electrodes. These losses depend on the reactions, the electro-catalyst material and microstructure, reactant activities, and weakly on current density.
  - **Ohmic losses**. Ohmic losses are caused by ionic resistance in the electrolyte and electrodes, electronic resistance in the electrodes, current collectors and interconnects, and contact resistances. These losses are proportional to the current density, depend on materials selection, stack geometry and temperature.
  - **Mass-transport-related losses (or concentration-related losses)**. These come from finite mass transport limitation rates of the reactants and depend strongly on the current density, reactant activity, and electrode structure.

Fuel cell performance calculation (5/5)



•Activation and concentration polarization data presented are generally only valid for that particular cell and operating geometry.

•A mathematical model will generally be required to interpret activation and concentration polarization data and translate it into data useful for stack engineers.

•Detailed reactant concentration information (including utilization) is essential for interpretation of activation and concentration polarization data.

•Several cell data presented and published.