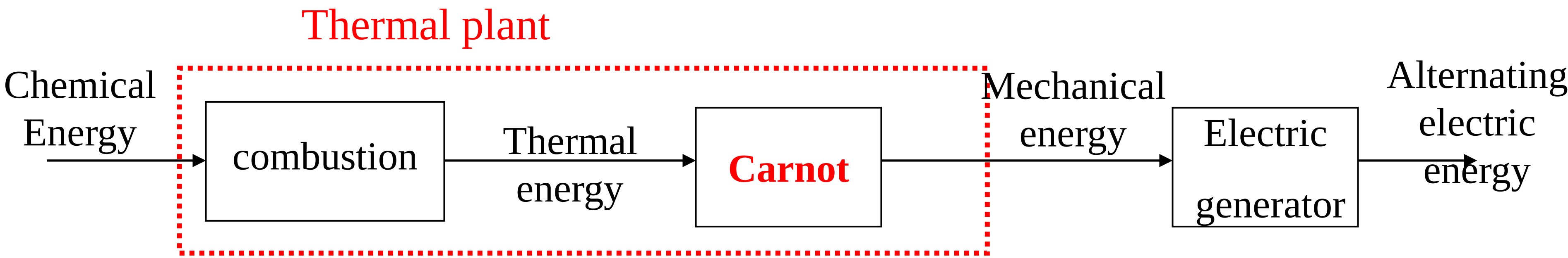
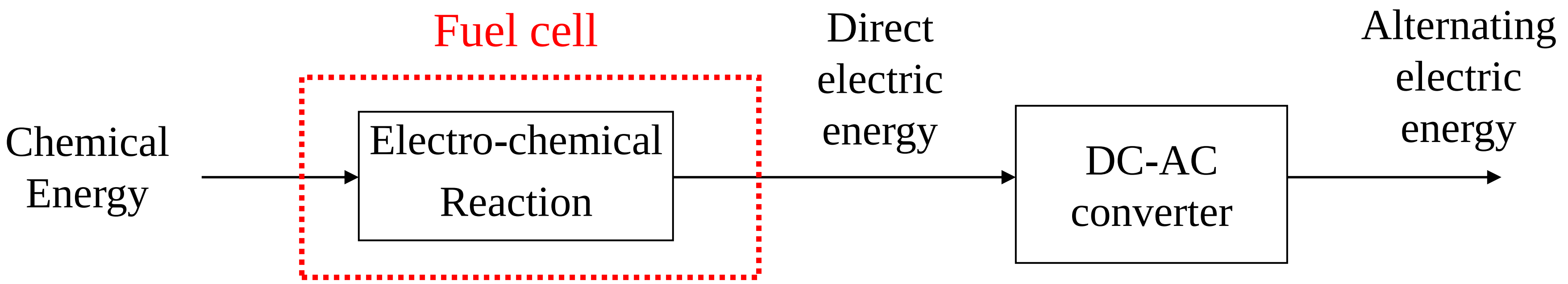
Hydrogen use as energy vector

FUEL CELLS

Electro-chemical systems
vs
thermal systems





- High Heating Value

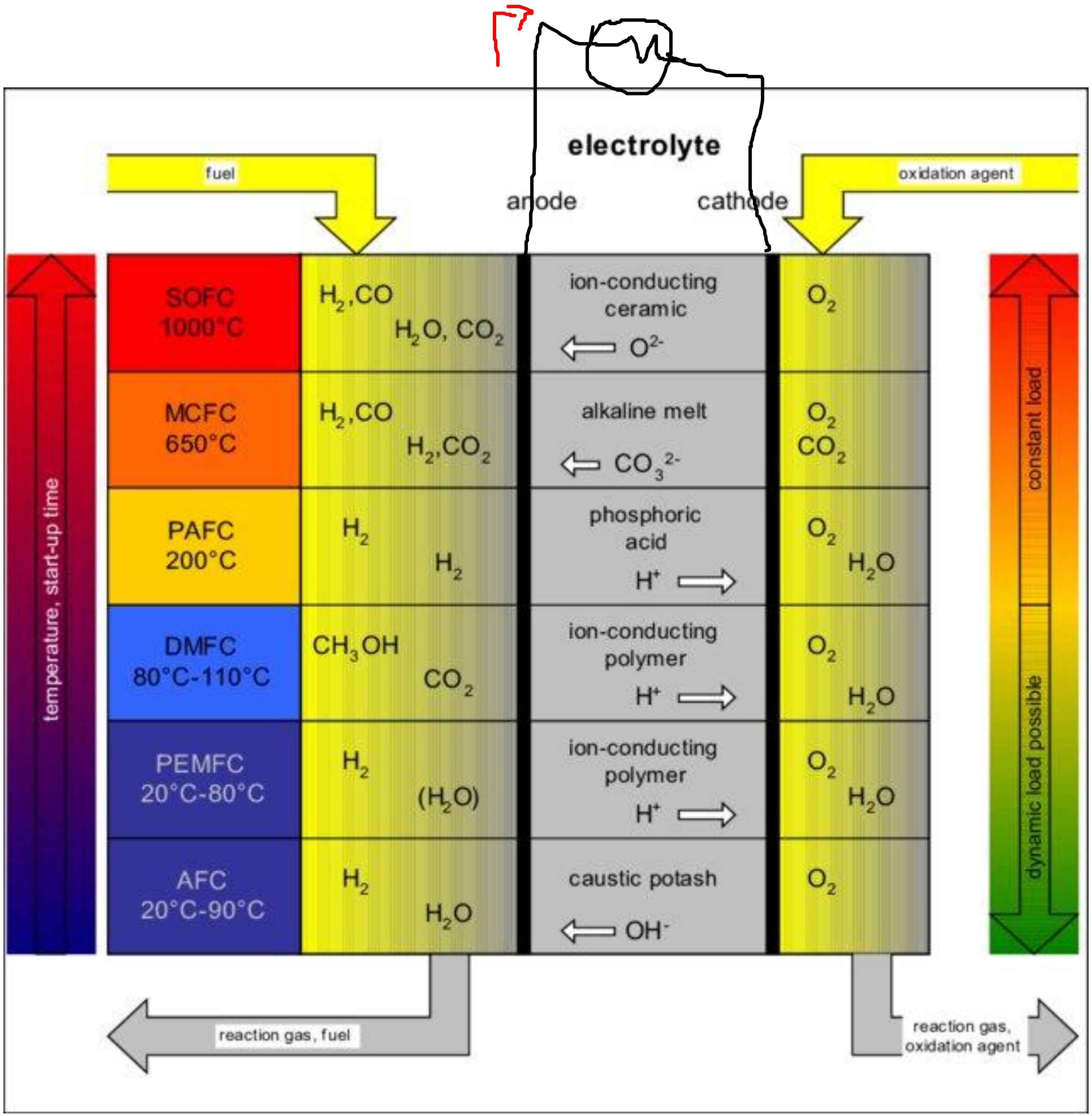
$$HHV= H_{react}(T_0, p_0)-H_{prod}(T_0, p_0)$$

- Max extractable work

$$W_{max}=H_{react}(T_0, p_0)-H_{prod}(T_0, p_0)-T_0(S_{reac}(T_0, p_0)-S_{prod}(T_0, p_0))$$

Comparison between Heating values and maximum extractable work

Fuel	HHV [kJ/mol]	LHV [kJ/mol]	W_{max} [kJ/mol]	$\eta = W_{max}/$ HHV [%]	$\eta = W_{max}/$ LV [%]
Hydrogen	295.9	241.8	237.2	82.9	98.1
Methane	890.4	802.3	818.0	91.87	101.96
Propane	2220.0	2044.0	2108.4	94.96	103.15
Methanol	726.6	638.5	702.5	96.68	110.02


electrolyte
fuel
oxidation agent
anode
cathode
SOFC
1000°C
H_2,CO
H_2O, CO_2
ion-conducting ceramic
O^{2-}
O_2
MCFC
650°C
H_2,CO
H_2,CO_2
alkaline melt
CO_3^{2-}
O_2
CO_2
PAFC
200°C
H_2
H_2
phosphoric acid
H^+
O_2
H_2O
DMFC
80°C-110°C
CH_3OH
CO_2
ion-conducting polymer
H^+
O_2
H_2O
PEMFC
20°C-80°C
H_2
(H_2O)
ion-conducting polymer
H^+
O_2
H_2O
AFC
20°C-90°C
H_2
H_2O
caustic potash
OH^-
O_2
temperature, start-up time
constant load
dynamic load possible
reaction gas, fuel
reaction gas, oxidation agent

Reactions

- AFC
- PEMFC
- PAFC
- MCFC
- SOFC

Anode: $H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$

Cathode: $H_2O + \frac{1}{2} O_2 + 2e^- \rightarrow 2OH^-$

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

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

Anode: $H_2 + CO_3^{2-} \rightarrow H_2O + 2e^- + CO_2$

Cathode: $CO_2 + \frac{1}{2} O_2 + 2e^- \rightarrow CO_3^{2-}$

Anode: $H_2 + O^{2-} \rightarrow 2H_2O + 2e^-$

Cathode: $\frac{1}{2} O_2 + 2e^- \rightarrow O_2^{2-}$

Reactions

- DMFC

Anode: $CH_3OH + H_20 \rightarrow 6H^+ + 6e^- + CO_2$

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

FC classification

- On the basis of the electrolyte
  - Liquid
  - Electrolytic solutions
  - Molten salts
  - Ionic solid

For a cell

- W_{el}=Wmax=-nFE_{rev}

N = Number of electrons for a reaction

F= Faraday constant =96485 Coulomb/mol of electrons

E_{rev} = reversible potential of the cell

Cell efficiency

$$\eta_{cella} = \frac{E_{el}}{E_{in}} = \eta_{rev} \cdot \eta_V \cdot U_f \propto V_C \cdot U_f$$

$$\eta_{rev} = \frac{V_{rev}}{V_{LHV}}$$

Reversible voltage eq. di *Nernst* →

$$V_{rev} = V^0 + \frac{RT}{nF} \ln \frac{\prod (p_{part.rea.})^r}{\prod (p_{part.prod.})^p}$$

F = *Faraday constant*

LHV = *241.8 kJ/mol* (H_2)

n = *2 moles of elett./mole fuel* (H_2)

$$V_{LHV} = \frac{LHV}{nF} \cong 1.25V$$

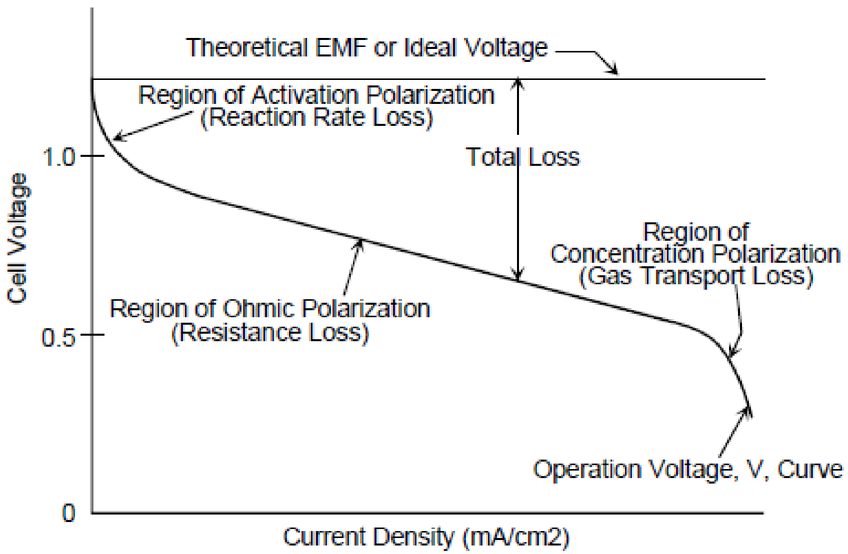
$$\eta_V = \frac{V_C}{V_{rev}}$$

Cell voltage

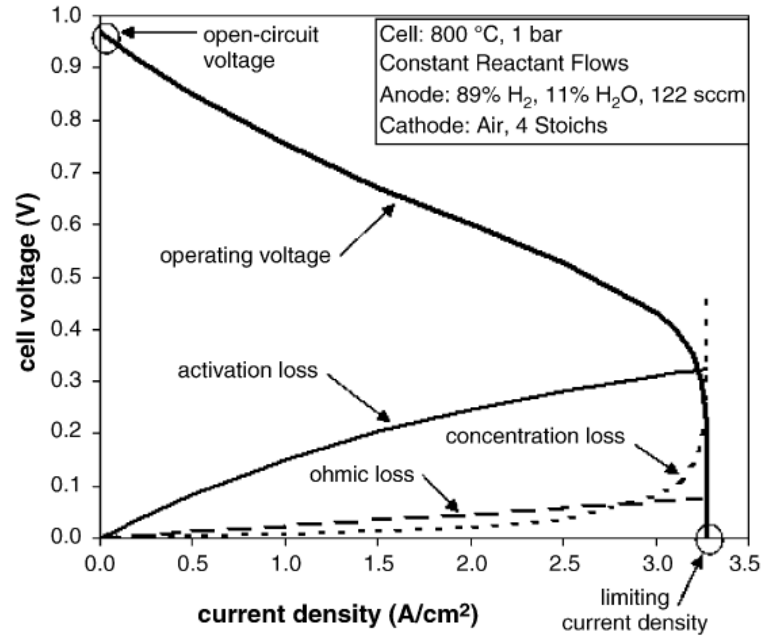
Losses:
1. activation
2. Ohmic
3. concentration

$$U_f = \frac{m_{H_{2,consumed}}}{m_{H_{2,in}}}$$

Fuel utilization coefficient

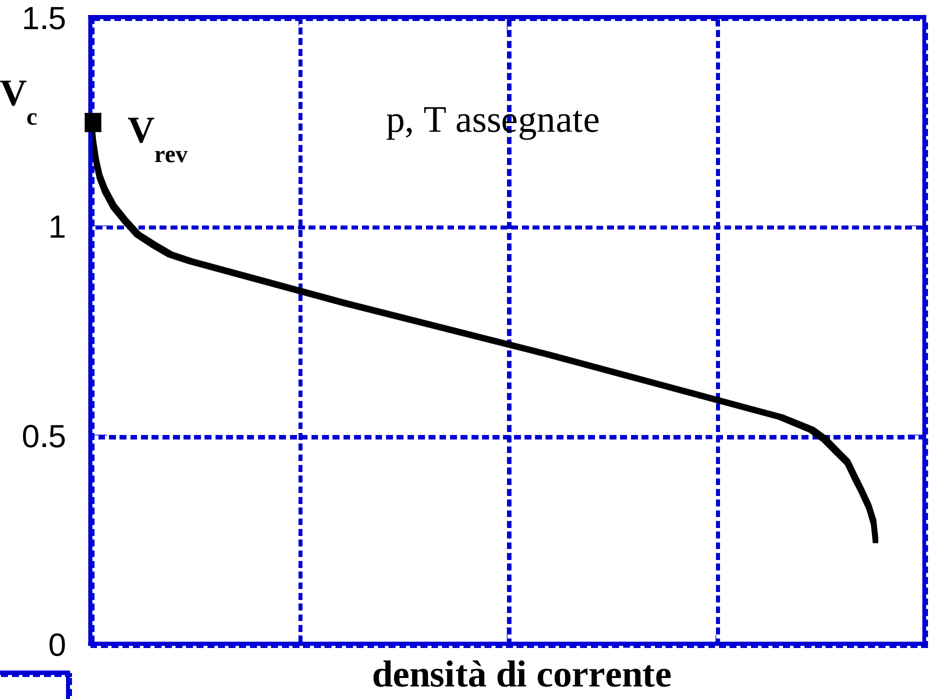


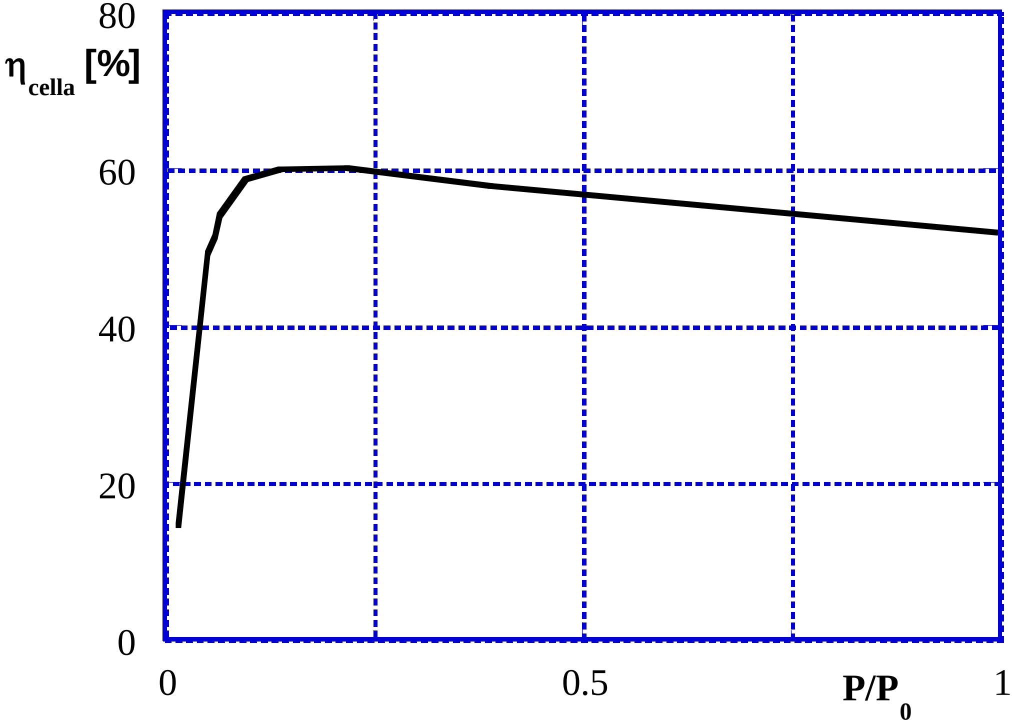
Theoretical EMF or Ideal Voltage
Region of Activation Polarization (Reaction Rate Loss)
Total Loss
Region of Concentration Polarization (Gas Transport Loss)
Region of Ohmic Polarization (Resistance Loss)
Operation Voltage, V, Curve
Cell Voltage
1.0
0.5
0
Current Density (mA/cm2)



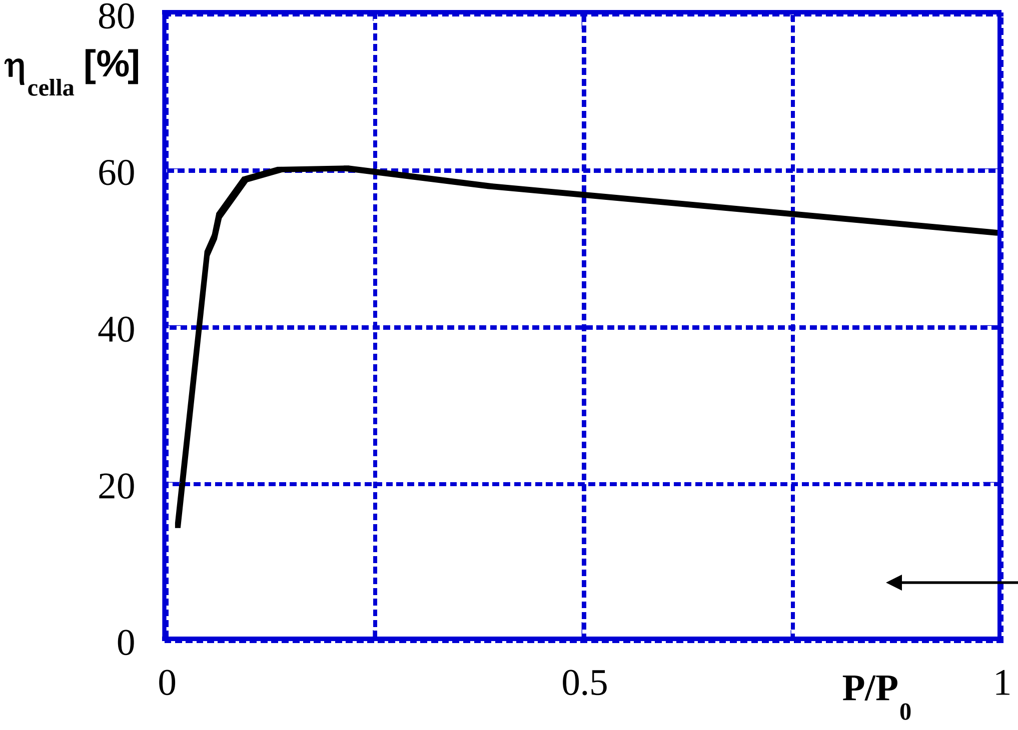
open-circuit voltage
Cell: 800 °C, 1 bar
Constant Reactant Flows
Anode: 89% H_2, 11% H_2O, 122 sccm
Cathode: Air, 4 Stoichs
operating voltage
activation loss
concentration loss
ohmic loss
cell voltage (V)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
current density (A/cm²)
limiting current density

Cell voltage

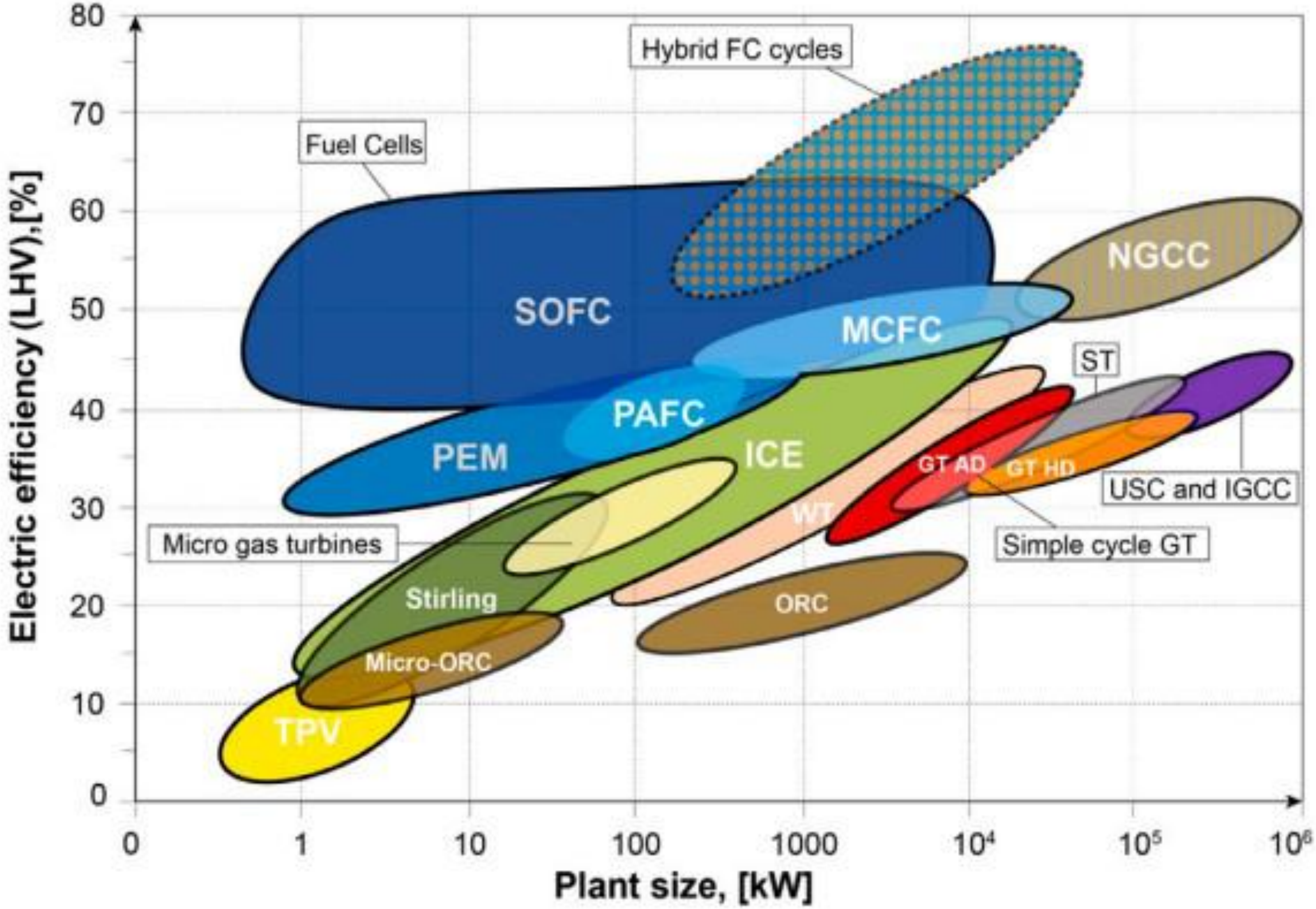




Cell efficiency



FC electric efficiency


Hybrid FC cycles
Fuel Cells
SOFC
MCFC
NGCC
PAFC
PEM
ICE
ST
GT AD
GT HD
USC and IGCC
WT
Simple cycle GT
Micro gas turbines
Stirling
ORC
Micro-ORC
TPV
Electric efficiency (LHV),[%]
Plant size, [kW]
0
10
20
30
40
50
60
70
80
0
1
10
100
1000
10^4
10^5
10^6

Characteristics	PEMFCs	DMFCs	SOFCs	AFCs	PAFCs	MCFCs
Operating temperature (°C)	60–110	70–130	500–1000	60–250	150–210	500–700
System efficiency (%)	40–55	40	40–60	60–70	40–50	50–60
Combined heat and power efficiency (%)	70–90	80	<90	>80	>85	>80
Stack power (kW)	1–100	0.001–100	0.5–2.000	1–100	100–400	300–3.000,000
Energy density (kW hr/m^3)	112.2–770	29.9–274	172–462.09	—	—	25–40
Power density (kW/m^3)	3.8–6.5	~0.6	4.20–19.25	~1	0.8–1.9	1.5–2.6
Lifespan (hr)	2.000–3.000	1.000–4500	1.000	8.000	>50,000	7.000–8.000
Cell voltage (V)	1.1	0.2–0.4	0.8–1.0	1.0	1.1	0.7–1.0
Nominal current density (A/cm^2)	0.5–1	0.15–0.3	—	0.1–0.3	0.15	0.14–0.16
Electrolyte	Polymer membrane	—	Yttria-stabilized zirconia (YSZ)	KOH	Phosphoric acid (H_3PO_4)	Molten carbonate
Fuel type	Hydrogen	Methanol	Hydrogen, natural gas biogas coal gas	Hydrogen ammonia	Hydrogen methanol	Natural gas biogas coal gas
Startup time	<1 min	—	60 min	<1 min	—	10 min
Advantages	(1) Small size (2) Lightweight (3) Quick startup time and load response (4) Low temperature	(1) Low cost of fuel methanol, low operational temperature, and pressure (2) High power density	(1) High efficiency (2) Fuel flexibility. (3) Solid electrolyte (4) Suitable for CHP (5) Hybrid/gas turbine cycle	(1) A wider range of stable materials allows components to be priced lower (2) Low temperature (3) Quick startup	(1) Suitable for CHP (2) Increased tolerance to fuel impurities	(1) Fuel variety (2) High efficiency
Disadvantages	(1) Sensitivity to low temperature, humidity, salinity, and fuel impurities	(1) Low reaction kinetics (2) Methanol is very toxic and highly flammable	(1) High temperature (2) Long startup time (3) Limited number of shutdowns (4) Intensive heat	(1) Sensitive to CO_2 in fuel and air (2) Electrolyte management (aqueous) (3) Electrolyte conductivity (polymer)	(1) Expensive catalysts (2) Long startup time (3) Sulfur sensitivity	(1) Slow response time (2) Highly corrosive (3) Low power density
Applications	(1) Transportation, portable power, unmanned aerial vehicles (UAVs)	(1) Transportation, portable power, unmanned aerial vehicles (UAVs)	(1) UAVs, transportation, power plant (2) Auxiliary power units	(1) Transport, military, auxiliary power units, aerospace (2) Off-grid telecom	(1) Building (2) Utilities (3) Distributed generation	(1) Distributed generation, Utilities

FCs's competitors

	MCI	**TG**	**MTG**	**FC**
Size	50kW - 5MW	500kW - 25MW	25 - 150 kW	3kW - 10MW
Electric efficiency	30-45 %	23-35 %	20-30 %	30-50 %
Fuel	Natural gas, diesel, biogas, syngas	Natural gas, liquid fuels,	Natural gas, propane	Hydrogen, (natural gas, methanol)
NO_X emissions	>1.4 g/kWh	0.3-0.5 g/kWh	0.2-0.65 g/kWh	< 0.02 g/kWh
SO_X emissions	3.6-5.4 g/kWh	3.6-7.3 g/kWh	5-5.9 g/kWh	< 0.01 g/kWh
CO_2 emissions	420-640 g/kWh	450-850 g/kWh	590-720 g/kWh	330-510 g/kWh
Exhaust gas temperature	400-600°C	450-550°C	200-300°C	80-1000°C

MAIN ADVANTAGES OF FUEL CELLS

- High efficiency at partial load
- Low emissions (CO_2, NO_x, SO_x)
- Rapid load variability
- Absence of moving parts (low noise-no vibrations)
- Modularity
- High efficiency
- Possibility of CHP

- H_2 must be pure
- Low energy density
- EE is produced as DC