Giornata della ricerca chimica
L’innovazione al servizio dell’energia

Immagazzinamento e trasporto dell'energia: l'approccio P2X

Prof. Antonella Glisenti

Dipartimento di Scienze Chimiche Università di Padova

28 settembre 2023 c/o Auditorium Federchimica Via Giovanni da Procida, 11 - Milano

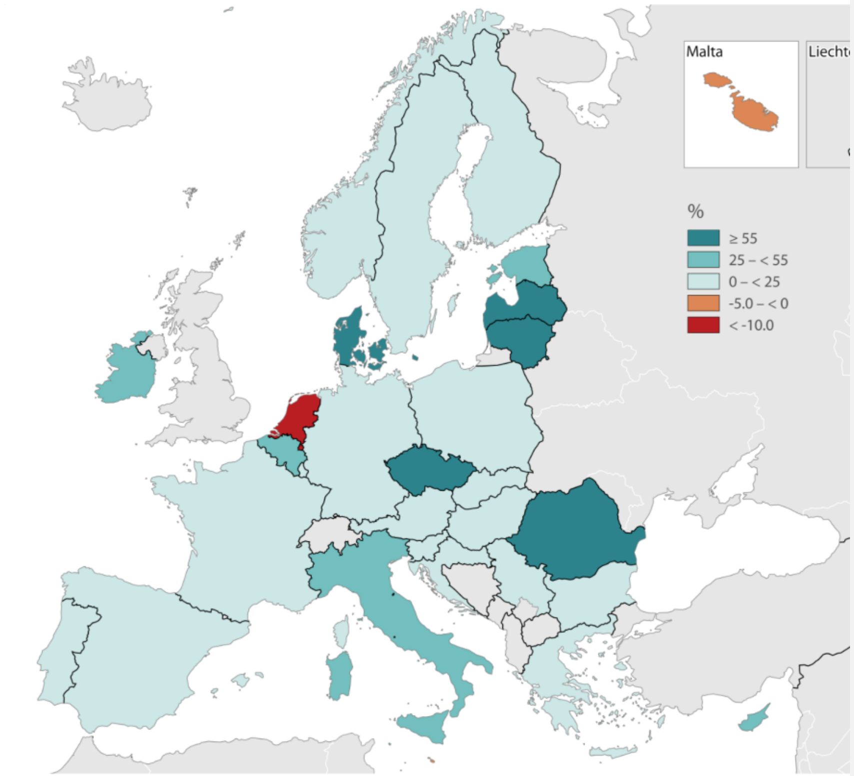
IMPACT

28/09/2023

INCREMENTO COSTI per uso DOMESTICO

Change in electricity prices for households consumers, 2nd half of 2022

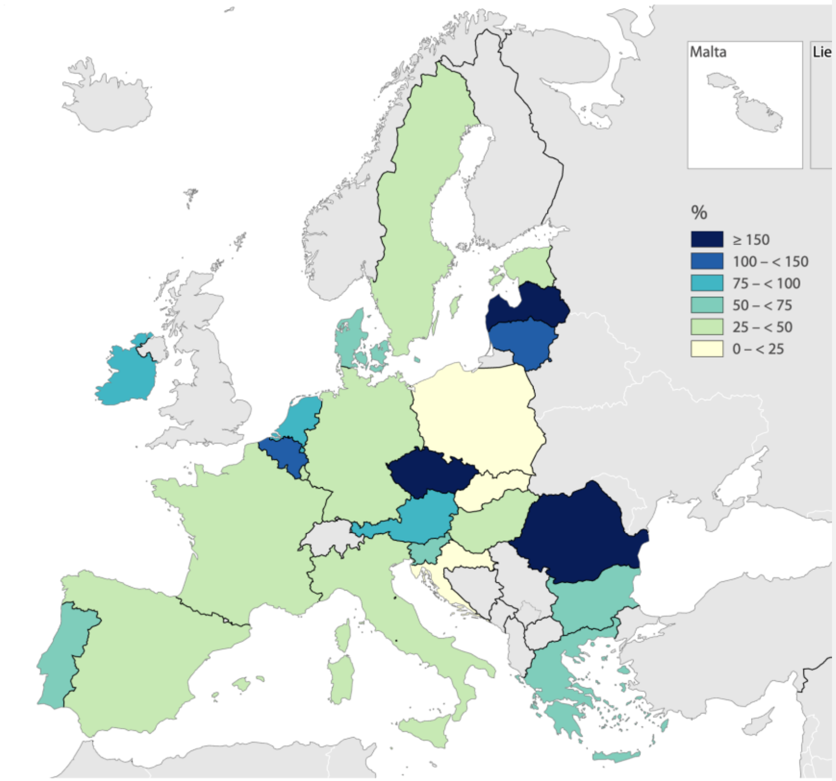
(compared with 2nd half of 2021, based on prices in national currency; in %)


Malta
Liechte
%
≥ 55
25 – < 55
0 – < 25
-5.0 – < 0
< -10.0

Administrative boundaries: © EuroGeographics © U
Cartography: Eurostat – IMAGE, 04/2023

Change in natural gas prices for households consumers, 2nd half of 2022

(compared with the 2nd half of 2021, based on prices in national currency; in %)


Malta
Lie
%
≥ 150
100 – < 150
75 – < 100
50 – < 75
25 – < 50
0 – < 25

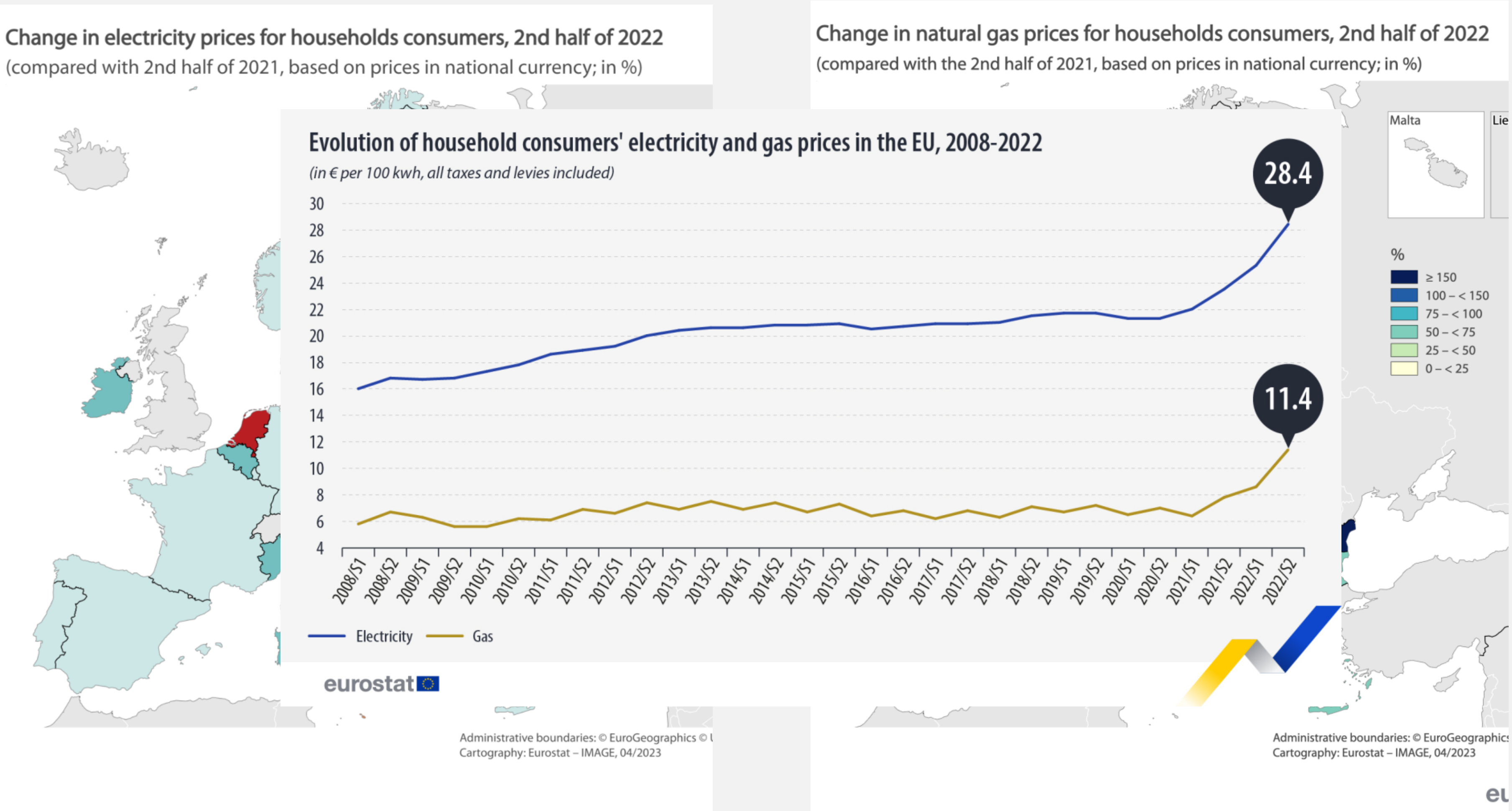
Administrative boundaries: © EuroGeographics
Cartography: Eurostat – IMAGE, 04/2023

eu

IMPACT

28/09/2023

INCREMENTO COSTI per uso DOMESTICO



Change in electricity prices for households consumers, 2nd half of 2022

(compared with 2nd half of 2021, based on prices in national currency; in %)

Change in natural gas prices for households consumers, 2nd half of 2022

(compared with the 2nd half of 2021, based on prices in national currency; in %)

Evolution of household consumers' electricity and gas prices in the EU, 2008-2022

(in € per 100 kwh, all taxes and levies included)

28.4
11.4
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2008/S1
2008/S2
2009/S1
2009/S2
2010/S1
2010/S2
2011/S1
2011/S2
2012/S1
2012/S2
2013/S1
2013/S2
2014/S1
2014/S2
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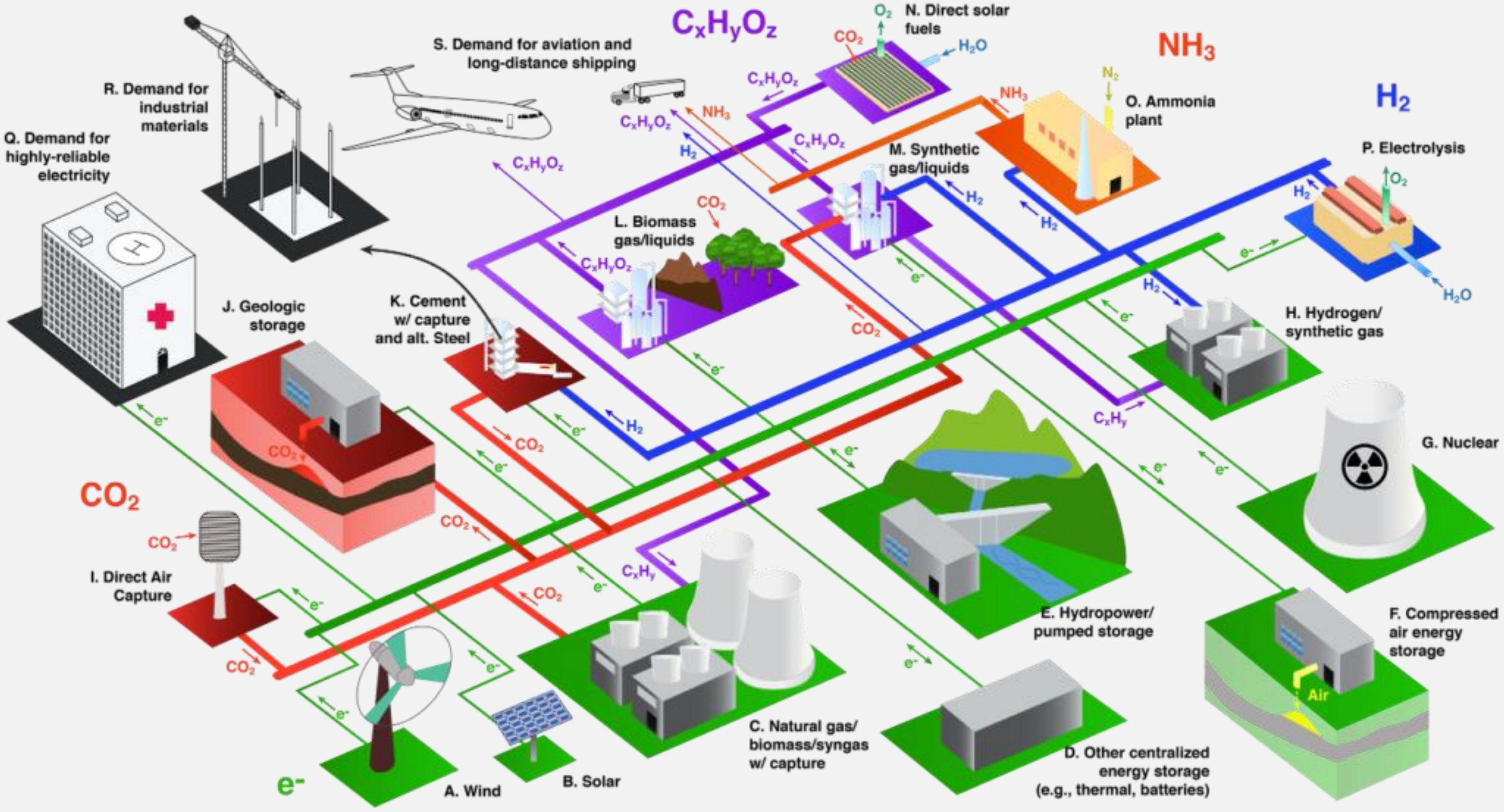
2018/S1
2018/S2
2019/S1
2019/S2
2020/S1
2020/S2
2021/S1
2021/S2
2022/S1
2022/S2
Electricity
Gas
eurostat
Malta
Lie
%
≥ 150
100 – < 150
75 – < 100
50 – < 75
25 – < 50
0 – < 25
eu

Administrative boundaries: © EuroGeographics © U
Cartography: Eurostat – IMAGE, 04/2023

Administrative boundaries: © EuroGeographics
Cartography: Eurostat – IMAGE, 04/2023

INTEGRAZIONE DI SERVIZI E RISORSE


$C_xH_yO_z$
NH_3
H_2
CO_2
e-
S. Demand for aviation and long-distance shipping
R. Demand for industrial materials
Q. Demand for highly-reliable electricity
N. Direct solar fuels
O. Ammonia plant
P. Electrolysis
M. Synthetic gas/liquids
L. Biomass gas/liquids
K. Cement w/ capture and alt. Steel
J. Geologic storage
H. Hydrogen/ synthetic gas
G. Nuclear
I. Direct Air Capture
E. Hydropower/ pumped storage
F. Compressed air energy storage
Air
C. Natural gas/ biomass/syngas w/ capture
D. Other centralized energy storage (e.g., thermal, batteries)
A. Wind
B. Solar
O_2
H_2O
N_2
C_xH_y

SISTEMA INTEGRATO DI SERVIZI (SENZA CO_2 A-S) CONVERSIONE E TRASPORTO DI ENERGIA; PRODUZIONE E TRASPORTO DI IDROGENO, PRODUZIONE E TRASPORTO DI IDROCARBURI, PRODUZIONE E TRASPORTO DI AMMONIACA, UTENTI FINALI DI ENERGIA E MATERIALI

Davis et al Science 29 (2018) 6396

ELETTROCHIMICA ED ELETTROLIZZATORI

ENERGIA CHIMICA ⟷ **ENERGIA ELETTRICA**

ELETTROCHIMICA: È la branca della chimica che studia l'impiego delle reazioni chimiche spontanee per produrre elettricità e l'impiego dell'elettricità per provocare reazioni non spontanee.

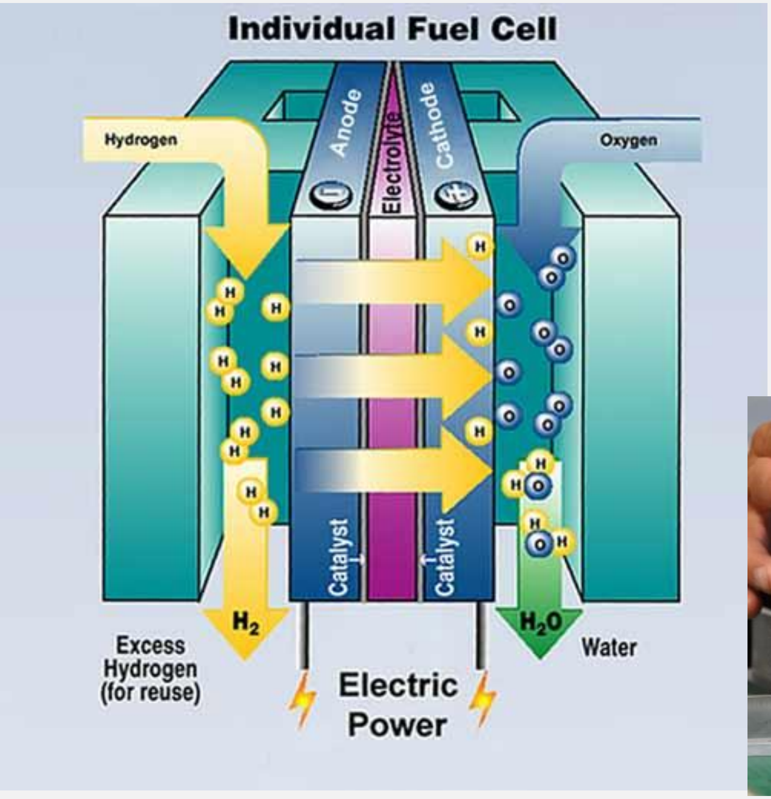
1. Celle galvaniche o pile

Processo ossidoriduttivo SPONTANEO - trasformazione di energia chimica in energia elettrica

2. Celle elettrolitiche o ELETTROLIZZATORI

Processo ossidoriduttivo NON SPONTANEO - trasformazione di energia elettrica in energia chimica

CELLE A COMBUSTIBILE (o Fuel Cells)


Individual Fuel Cell
Hydrogen
Anode
Electrolyte
Cathode
Oxygen
Catalyst
Catalyst
H_2
H_2O
Excess Hydrogen (for reuse)
Electric Power
Water

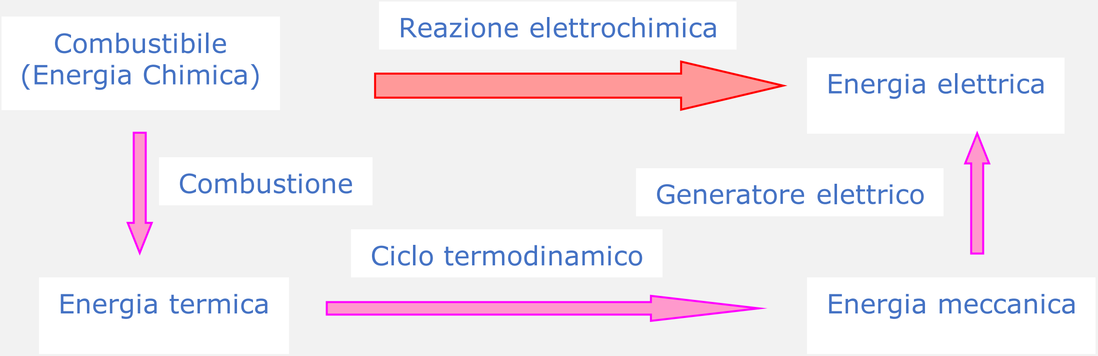
Simili alle Batterie

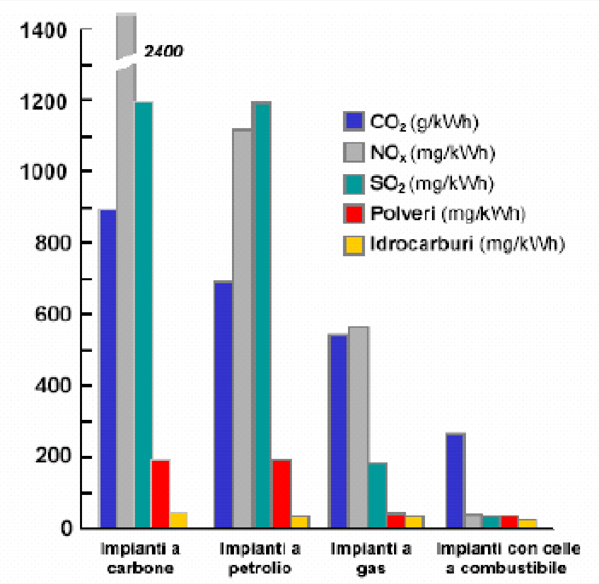
… ma…

NON SI ESAURISCONO

CELLE A COMBUSTIBILE: PERCHE'?

CELLE A COMBUSTIBILE: DISPOSITIVI ELETTROCHIMICI CAPACI DI CONVERTIRE L'ENERGIA CHIMICA DI COMBUSTIBILI IN ENERGIA ELETTRICA DIRETTAMENTE


Combustibile (Energia Chimica)
Reazione elettrochimica
Energia elettrica
Combustione
Generatore elettrico
Ciclo termodinamico
Energia termica
Energia meccanica



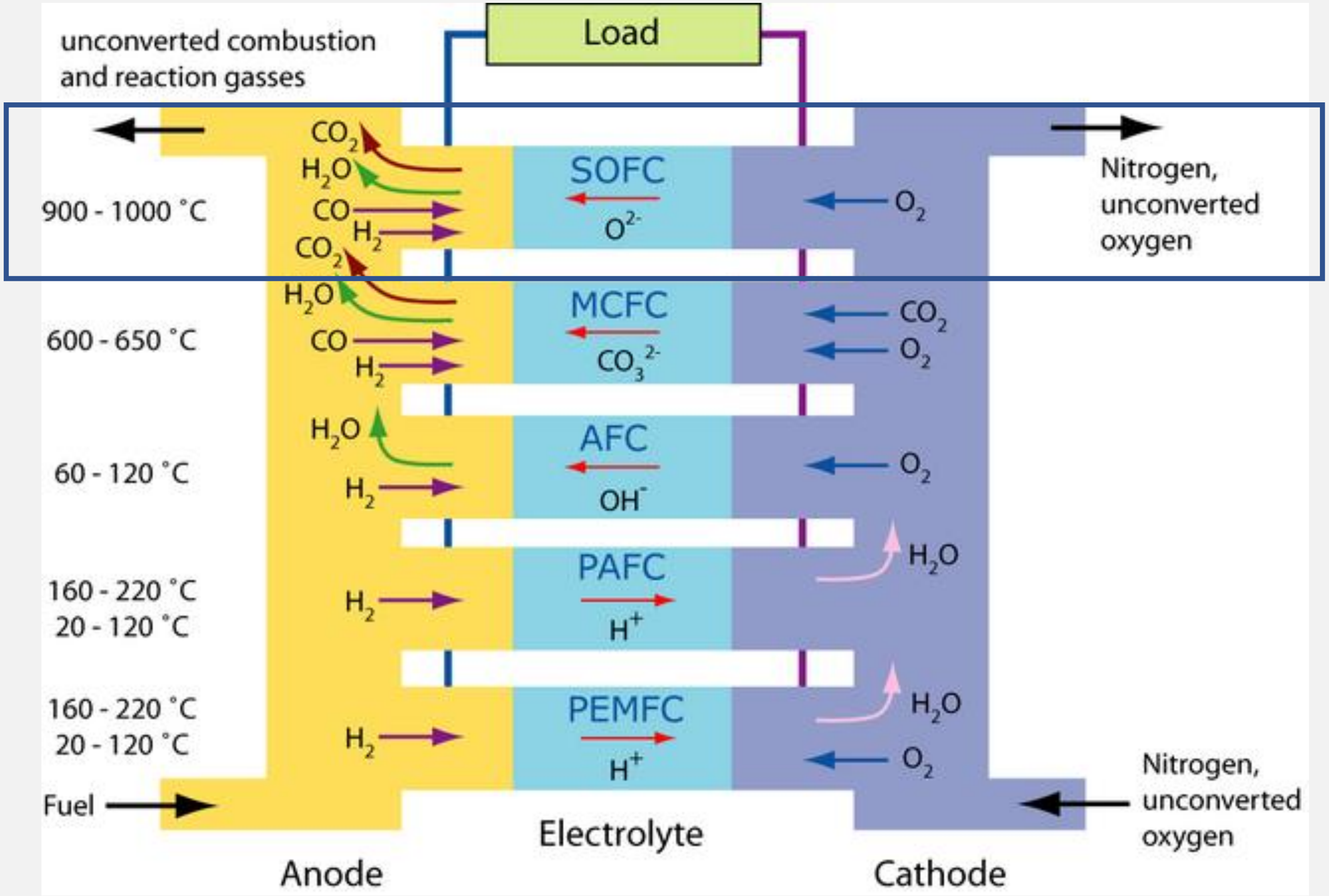
ESSENDO DISPOSITIVI ELETTROCHIMICI LA LORO EFFICIENZA NON E' LIMITATA DAL CICLO DI CARNOT

ESSENDO EVITATO IL PROCESSO DI COMBUSTIONE LE CELLE A COMBUSTIBILE SONO ASSAI MENO INQUINANTI

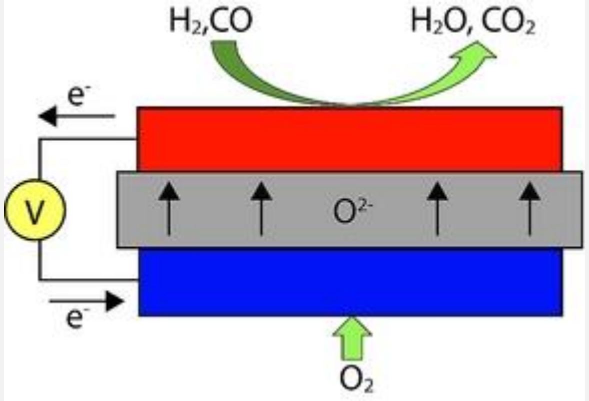
CELLE A COMBUSTIBILE: come funzionano?

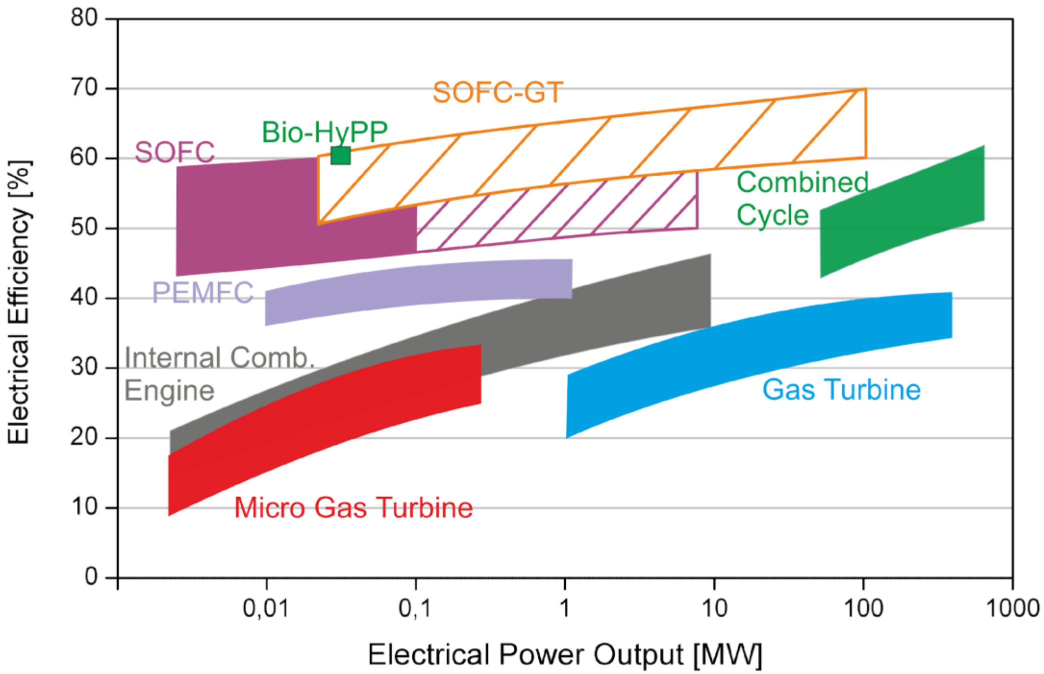
$H_2 + ½ O_2 \rightarrow H_2O$ + ENERGIA

La reazione che dà più energia


Load
unconverted combustion and reaction gasses
900 - 1000 °C
CO_2
H_2O
CO
H_2
SOFC
O^{2-}
O_2
Nitrogen, unconverted oxygen
600 - 650 °C
CO_2
H_2O
CO
H_2
MCFC
CO_3^{2-}
CO_2
O_2
60 - 120 °C
H_2O
H_2
AFC
OH^-
O_2
160 - 220 °C
20 - 120 °C
H_2
PAFC
H^+
H_2O
160 - 220 °C
20 - 120 °C
H_2
PEMFC
H^+
H_2O
O_2
Fuel
Nitrogen, unconverted oxygen
Anode
Electrolyte
Cathode

CELLE A COMBUSTIBILE AD OSSIDO SOLIDO





Cella a combustibile più efficiente (70%)

Le CELLE A COMBUSTIBILE AD OSSIDO SOLIDO (SOFCs) operano ad alta temperatura e dunque:

5

NON RICHIEDONO METALLI NOBILI

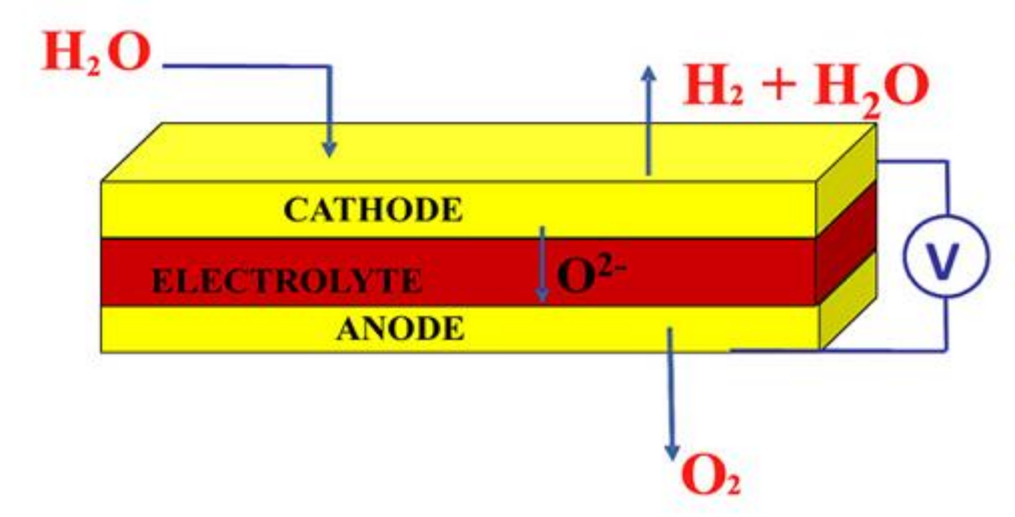
POSSONO OPERARE CON TUTTI I COMBUSTIBILI

ELETTROLIZZATORI AD ALTA TEMPERATURA

$$H_2O + 2e^- \rightarrow H_2(g) + O^{2-} \quad \text{(cathode)}$$

$$O^{2-} \rightarrow 1/2O_2(g) + 2e^- \quad \text{(anode)}$$

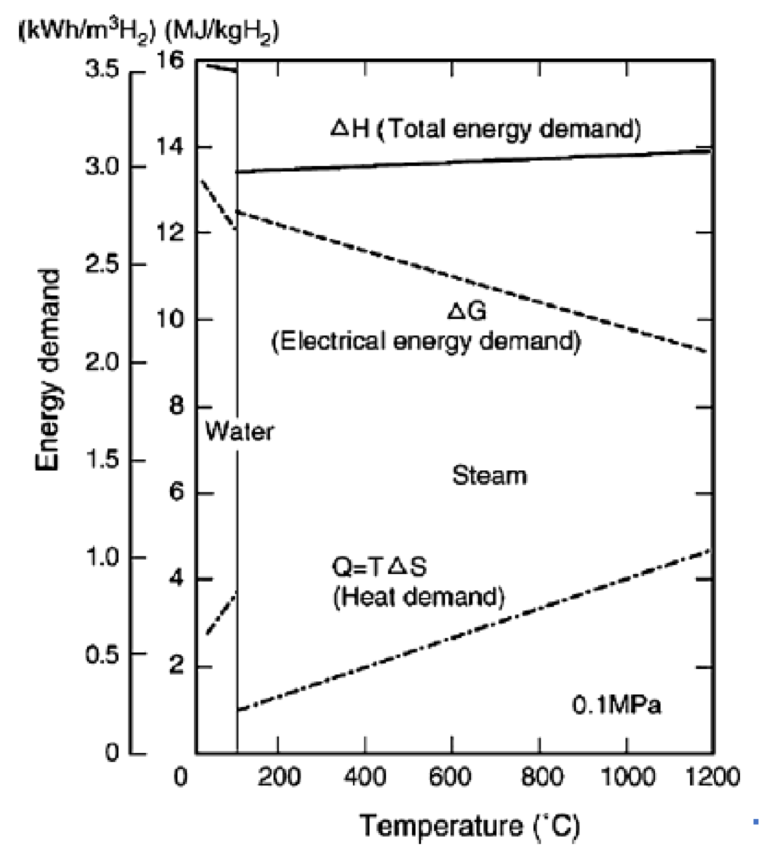
$$H_2O \rightarrow H_2 + 1/2O_2$$


H₂O
H₂ + H₂O
CATHODE
ELECTROLYTE
O²⁻
ANODE
V
O₂

Cella a Combustibile ad ossido solido operante in modalità elettrolizzatore

ALTA TEMPERATURA: perché?

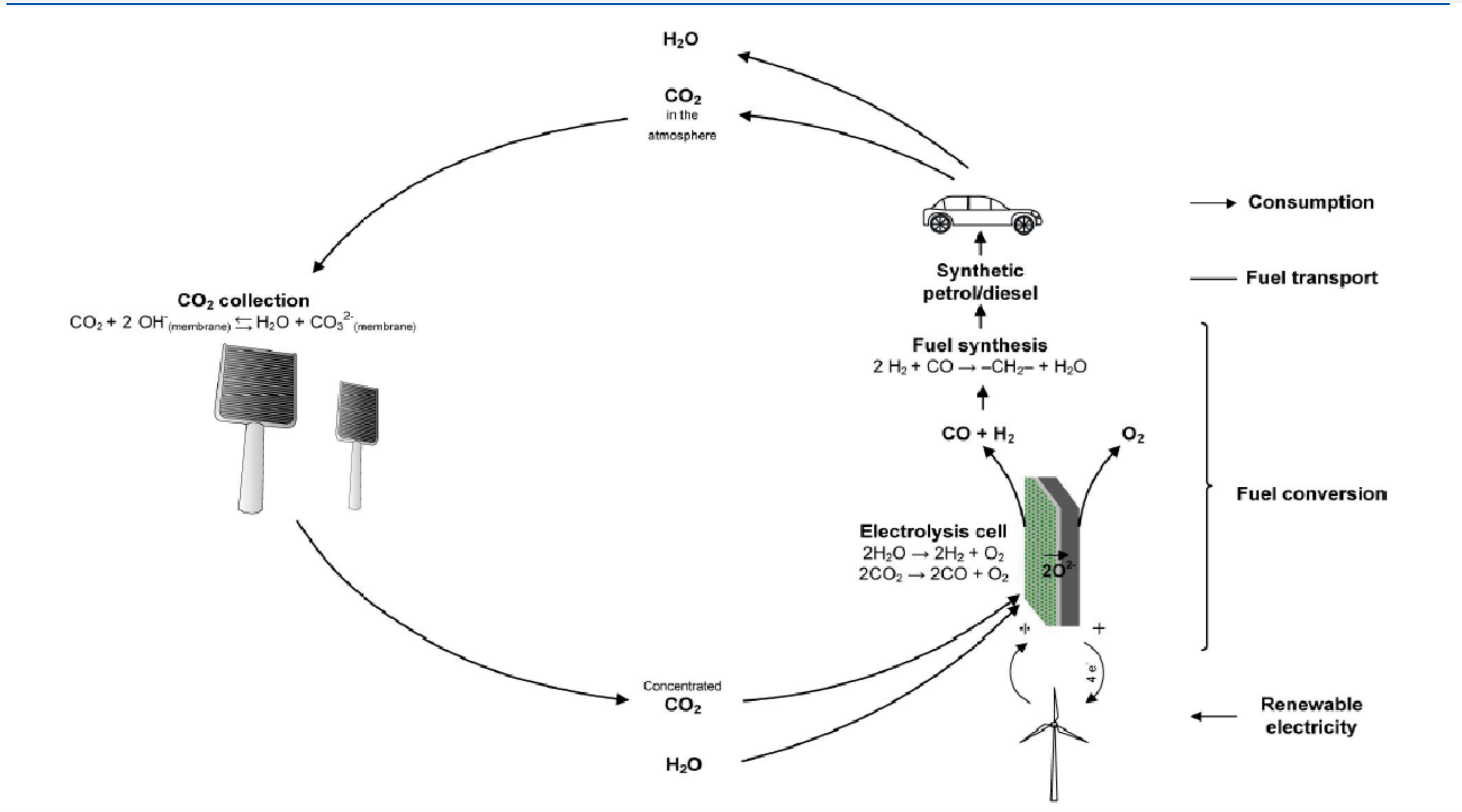
La decomposizione dell’acqua in idrogeno ed Ossigeno richiede energia; l’energia elettrica può essere inferiore se si opera a maggiore temperatura



25°C and 1 atm.
Energia elettrica richiesta
(ΔG) = 474 kJ/mol
Voltaggio teorico (U^{θ}) = 1.23 V

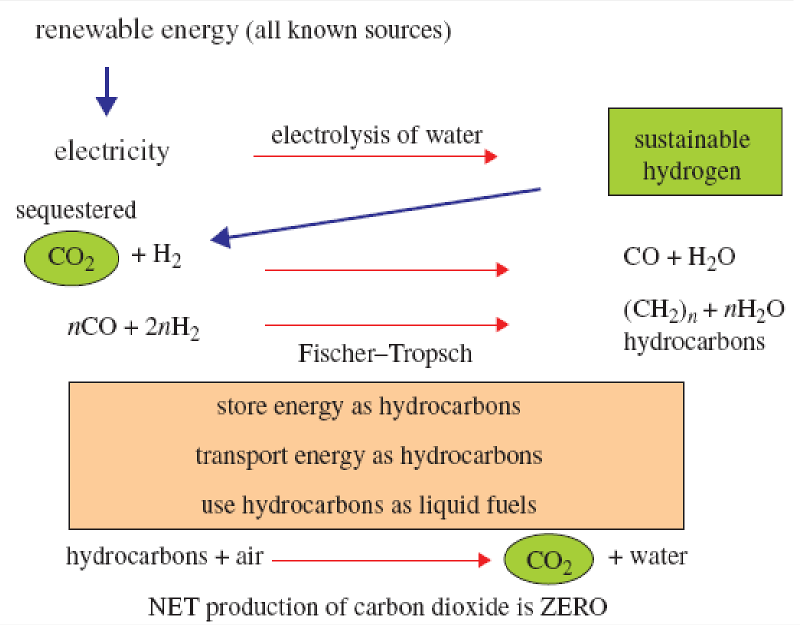
At 900°C and 1 atm.
Energia elettrica richiesta
(ΔG) = 366 kJ/mol
Voltaggio teorico
(U^{θ}) = 0,95 V

ELETTROLIZZATORI AD ALTA TEMPERATURA: non solo acqua/idrogeno


H_2O
CO_2 in the atmosphere
Consumption
Fuel transport
Synthetic petrol/diesel
Fuel synthesis
$2 H_2 + CO \rightarrow -CH_2- + H_2O$
$CO + H_2$
O_2
Fuel conversion
Electrolysis cell
$2H_2O \rightarrow 2H_2 + O_2$
$2CO_2 \rightarrow 2CO + O_2$
$2O^{2-}$
+
$4e^-$
Renewable electricity
CO_2 collection
$CO_2 + 2\ OH^-_{(membrane)} \leftrightarrows H_2O + CO_3^{2-}{}_{(membrane)}$
Concentrated CO_2
H_2O

Ciclo energetico 0-anidride carbonica basato su Elettrolizzatori ad Ossido Solido

ANIDRIDE CARBONICA: da gas serra a risorsa



renewable energy (all known sources)

electricity

electrolysis of water

sustainable hydrogen

sequestered

$CO_2 + H_2$ → $CO + H_2O$

$nCO + 2nH_2$ → $(CH_2)_n + nH_2O$ hydrocarbons

Fischer–Tropsch

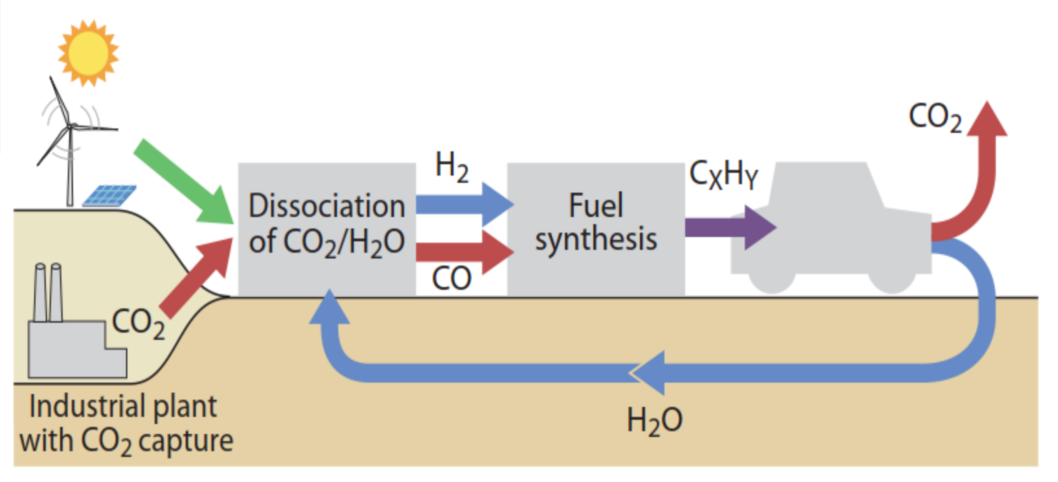
store energy as hydrocarbons

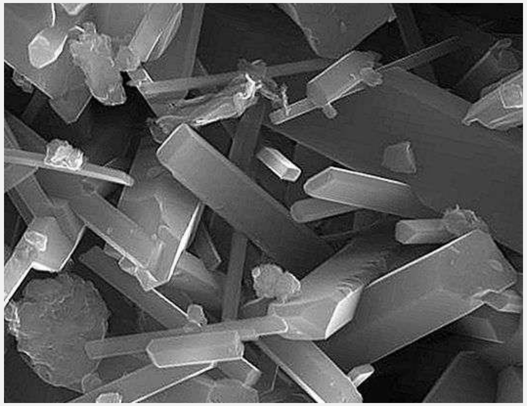
transport energy as hydrocarbons

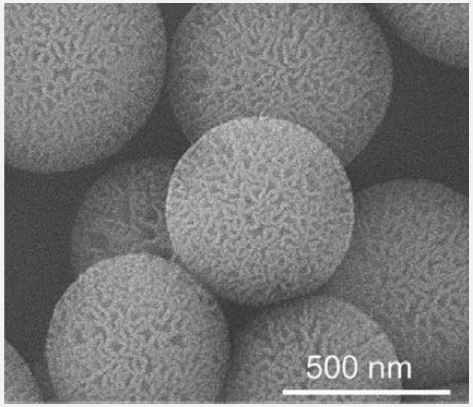
use hydrocarbons as liquid fuels

hydrocarbons + air → CO_2 + water

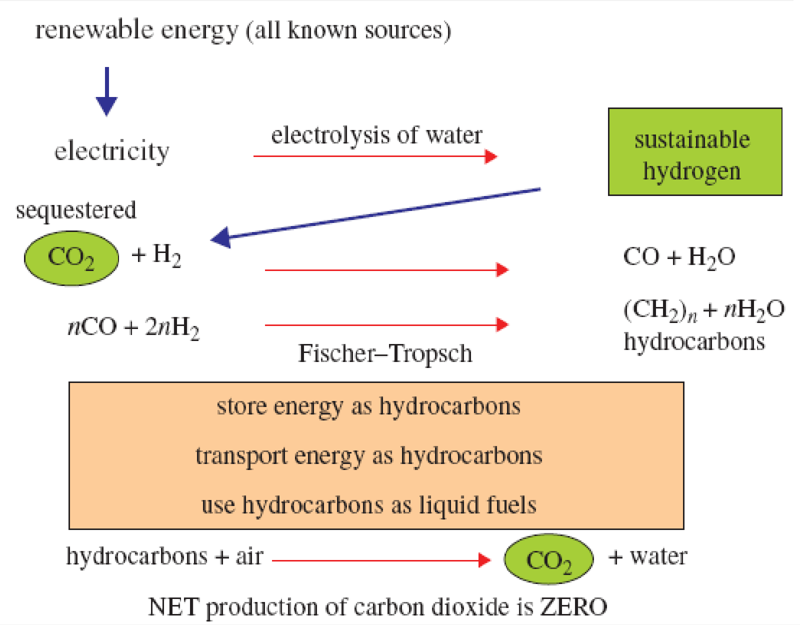
NET production of carbon dioxide is ZERO


CO_2
H_2
Dissociation of CO_2/H_2O
Fuel synthesis
C_XH_Y
CO
CO_2
Industrial plant with CO_2 capture
H_2O





ANIDRIDE CARBONICA: da gas serra a risorsa



renewable energy (all known sources)

electricity $\xrightarrow{\text{electrolysis of water}}$ sustainable hydrogen

sequestered $CO_2 + H_2 \rightarrow CO + H_2O$

$nCO + 2nH_2 \xrightarrow[\text{Fischer–Tropsch}]{} (CH_2)_n + nH_2O$ hydrocarbons

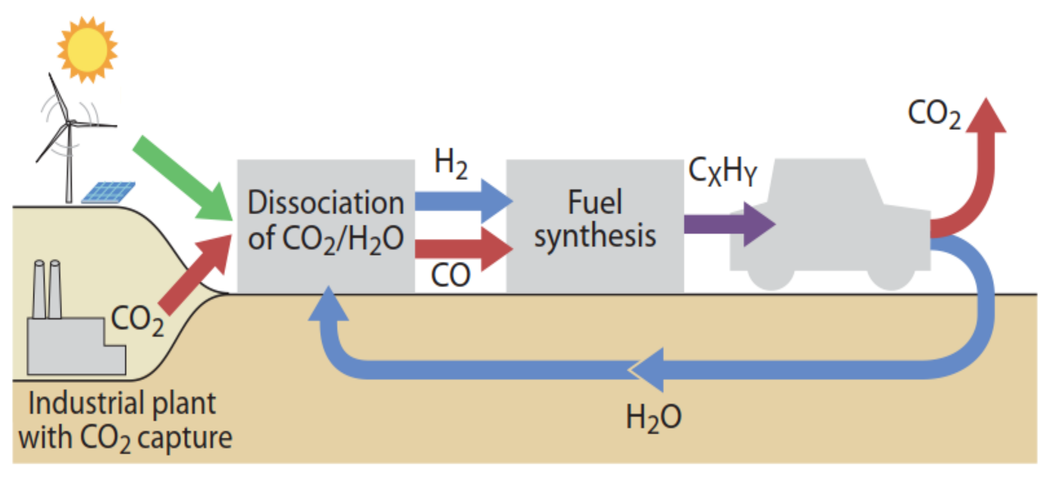
store energy as hydrocarbons

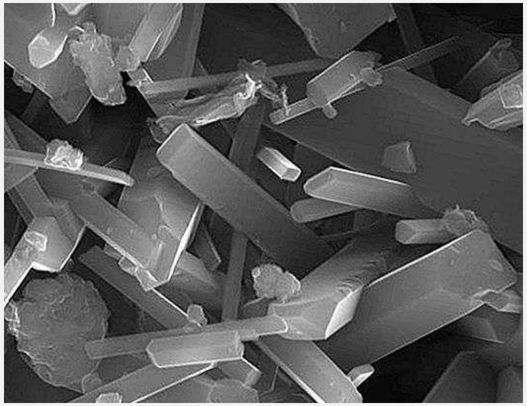
transport energy as hydrocarbons

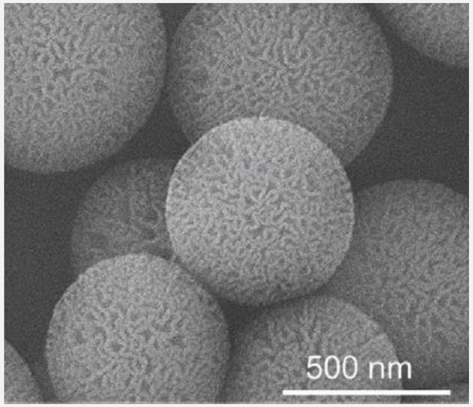
use hydrocarbons as liquid fuels

hydrocarbons + air $\rightarrow CO_2$ + water

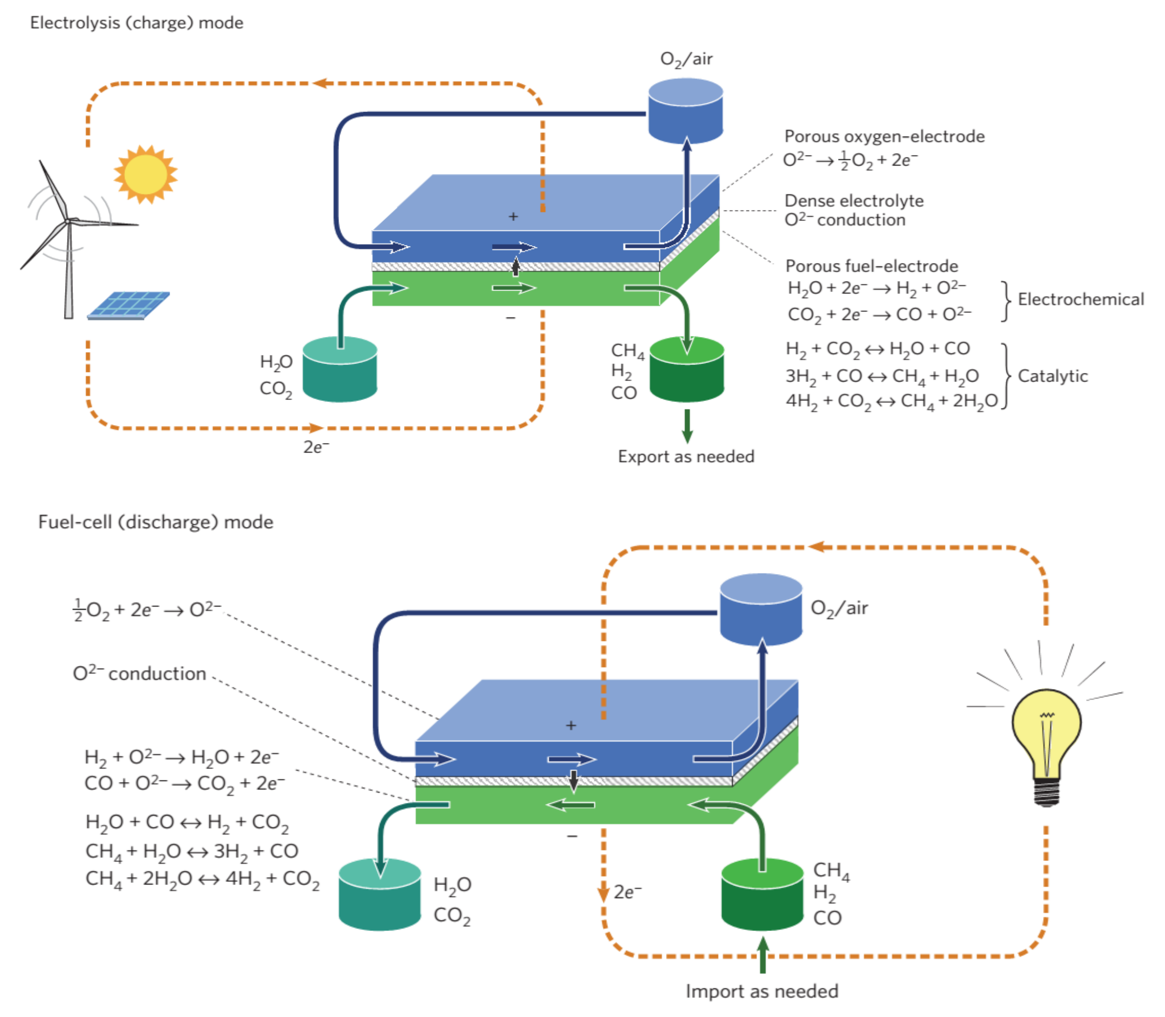
NET production of carbon dioxide is ZERO


CO_2
H_2
C_XH_Y
Dissociation of CO_2/H_2O
Fuel synthesis
CO
CO_2
Industrial plant with CO_2 capture
H_2O



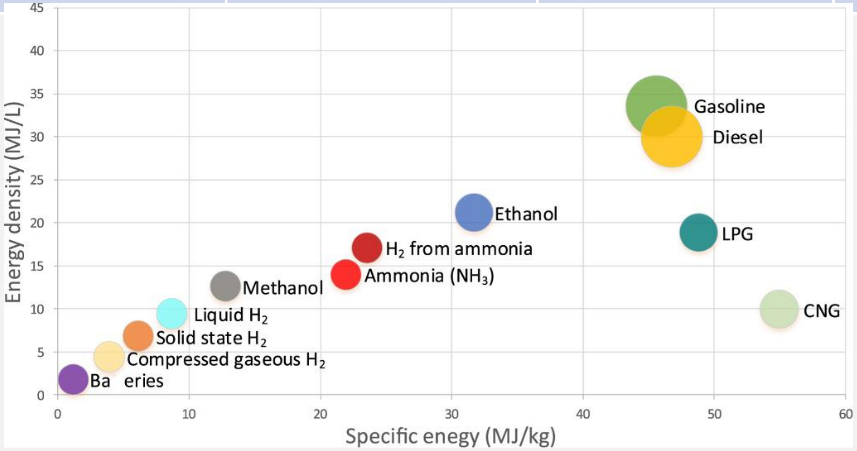


ELETTROLIZZATORI AD OSSIDO SOLIDO per L'IMMAGAZZINAMENTO DI ENERGIA

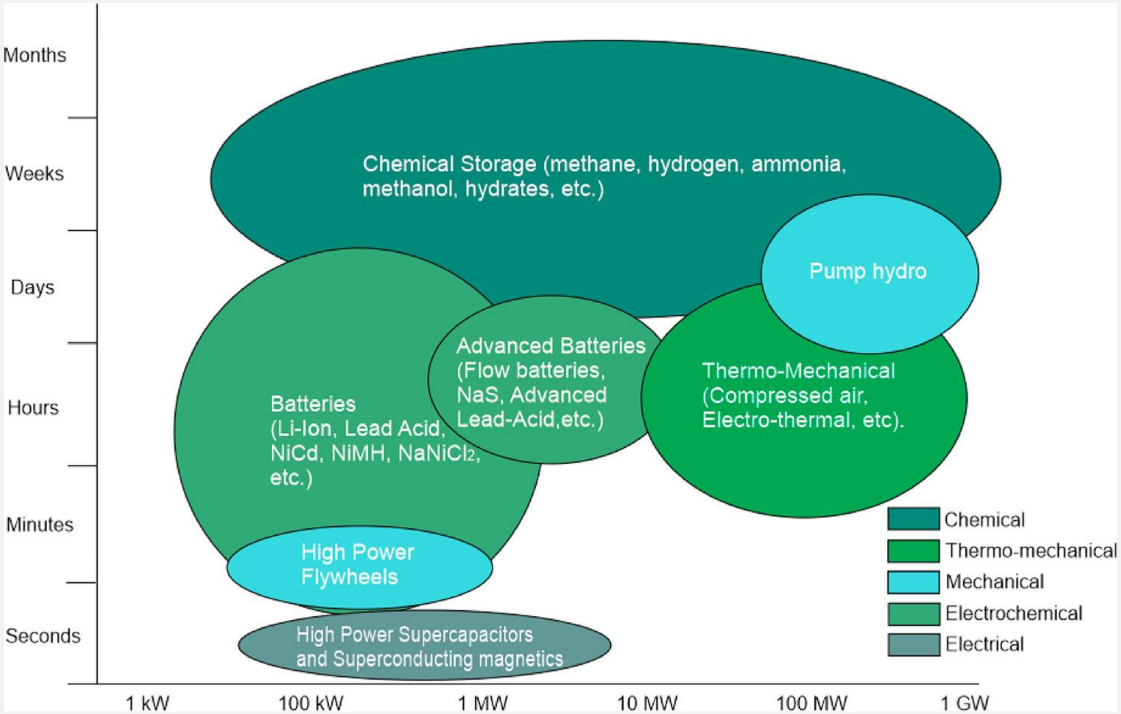

Electrolysis (charge) mode
O_2/air
Porous oxygen-electrode
$O^{2-} \rightarrow \frac{1}{2}O_2 + 2e^-$
Dense electrolyte
O^{2-} conduction
Porous fuel-electrode
$H_2O + 2e^- \rightarrow H_2 + O^{2-}$
$CO_2 + 2e^- \rightarrow CO + O^{2-}$
Electrochemical
$H_2 + CO_2 \leftrightarrow H_2O + CO$
$3H_2 + CO \leftrightarrow CH_4 + H_2O$
$4H_2 + CO_2 \leftrightarrow CH_4 + 2H_2O$
Catalytic
+
–
H_2O
CO_2
CH_4
H_2
CO
$2e^-$
Export as needed
Fuel-cell (discharge) mode
$\frac{1}{2}O_2 + 2e^- \rightarrow O^{2-}$
O^{2-} conduction
$H_2 + O^{2-} \rightarrow H_2O + 2e^-$
$CO + O^{2-} \rightarrow CO_2 + 2e^-$
$H_2O + CO \leftrightarrow H_2 + CO_2$
$CH_4 + H_2O \leftrightarrow 3H_2 + CO$
$CH_4 + 2H_2O \leftrightarrow 4H_2 + CO_2$
O_2/air
+
–
H_2O
CO_2
$2e^-$
CH_4
H_2
CO
Import as needed

INFIAMMABILITA’ e DENSITA’ ENERGETICA

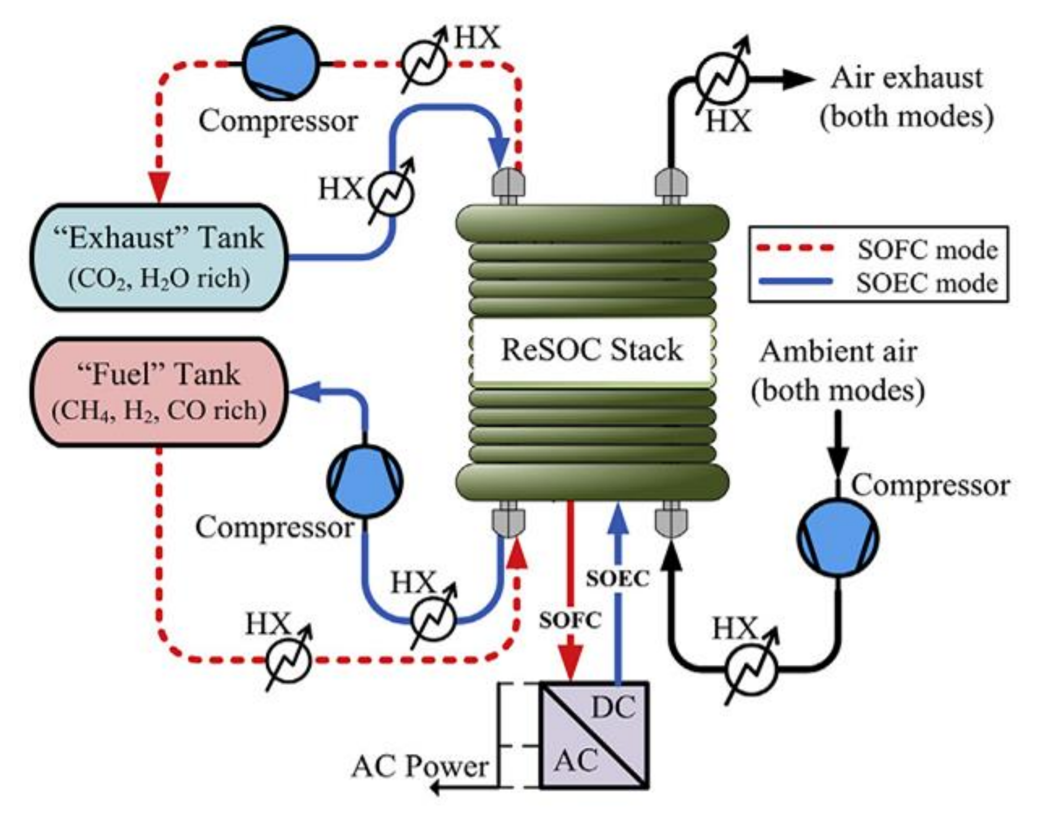
Combustibile	Limite Inferiore Infiammabilità (% vol)	Limite Superiore Infiammabilità (% vol)	Densità gravimetrica di energia (MJ/kg)	Densità volumetrica energia (MJ/L)
Benzina	1.0	6.5	43.1-46.5	32.1-34.6
Gasolio	0.6	6.5	42.8-47.5	35.8-38.3
Idrogeno	4.0	75.6	119.9-141.9	8.5-10.1
Ammoniaca	15.0	18.0	18.6-22.5	12.7-15.3
Metano	5.0	15.0	50.0-55.5	0.0378 (1atm) 10 (200 atm)



STOCCAGGIO DI ENERGIA: la variabile "tempo"



CELLE AD OSSIDO SOLIDO REVERSIBILI: ReSOC


HX
Compressor
HX
"Exhaust" Tank
(CO_2, H_2O rich)
"Fuel" Tank
(CH_4, H_2, CO rich)
Compressor
HX
HX
ReSOC Stack
HX
Air exhaust
(both modes)
SOFC mode
SOEC mode
Ambient air
(both modes)
Compressor
SOEC
SOFC
HX
DC
AC
AC Power

SCHEMA SEMPLIFICATO DI UN SISTEMA PER L'IMMAGAZZINAMENTO DI ENERGIA BASATO SU CELLE AD OSSIDO SOLIDO REVERSIBILI

C.H. Wendel et al. Design and techno-economic analysis of high efficiency reversible solid oxide cell systems for distributed energy storage Applied Energy 172 (2016) 118–131

ReSOCs: COSTI ED EFFICIENZA

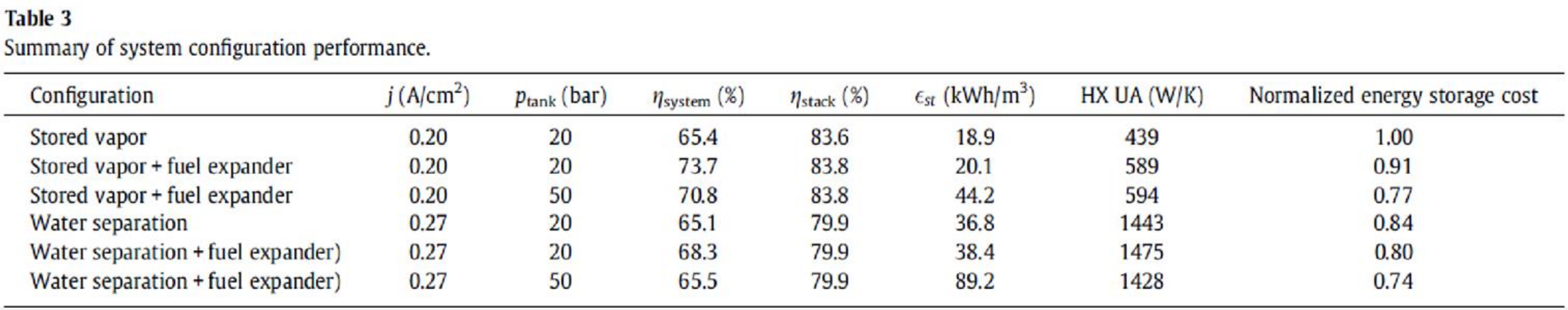


Table 3
Summary of system configuration performance.

Configuration	j (A/cm^2)	p_{tank} (bar)	η_{system} (%)	η_{stack} (%)	ϵ_{st} (kWh/m^3)	HX UA (W/K)	Normalized energy storage cost
Stored vapor	0.20	20	65.4	83.6	18.9	439	1.00
Stored vapor + fuel expander	0.20	20	73.7	83.8	20.1	589	0.91
Stored vapor + fuel expander	0.20	50	70.8	83.8	44.2	594	0.77
Water separation	0.27	20	65.1	79.9	36.8	1443	0.84
Water separation + fuel expander)	0.27	20	68.3	79.9	38.4	1475	0.80
Water separation + fuel expander)	0.27	50	65.5	79.9	89.2	1428	0.74

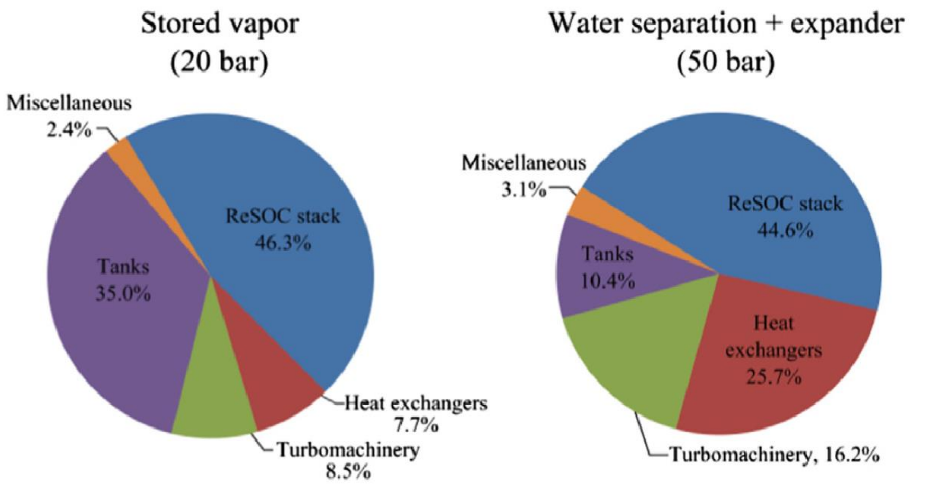


Fig. 10. Annualized component cost contributions for the highest (basecase stored vapor) and lowest (water separation + fuel expander systems) cost systems.

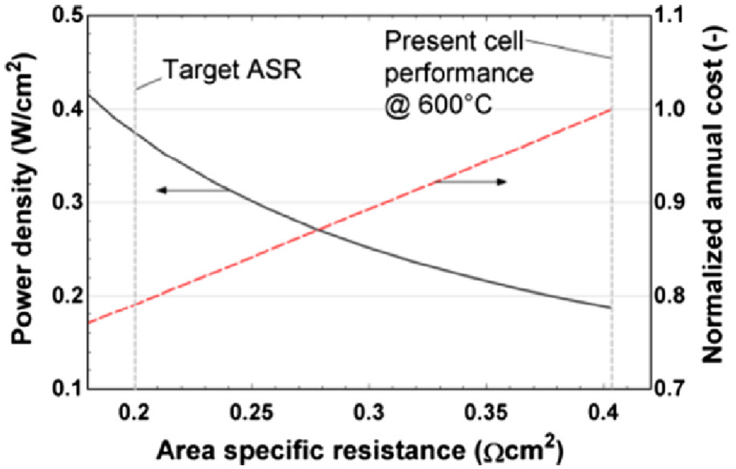
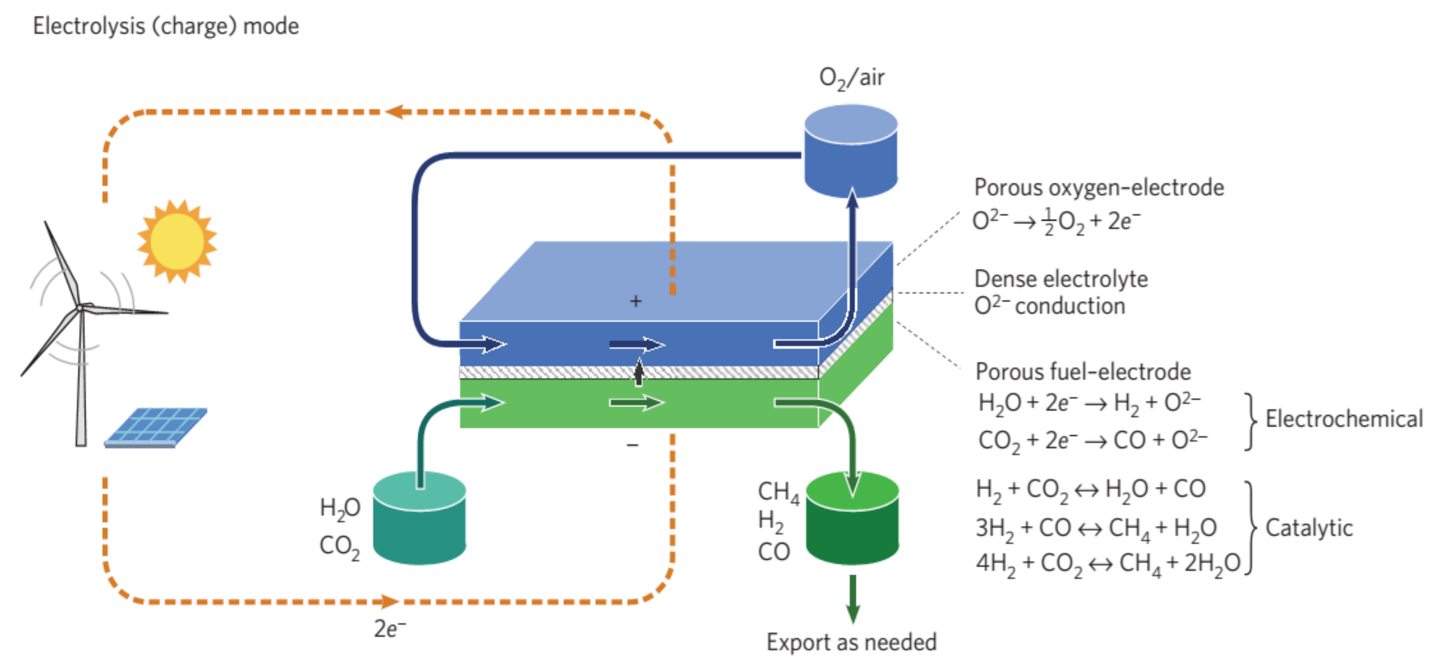


Fig. 11. Power density and normalized annual cost vs. ASR for projected improvements in ReSOC cell-stack performance at constant efficiency of 73.7% for the "stored vapor + fuel expander" configuration at nominal stack temperature of 600°C.

PRODOTTI DI ELETTROLISI: GAS DI SINTESI


Electrolysis (charge) mode
O_2/air
Porous oxygen-electrode
$O^{2-} \rightarrow \frac{1}{2}O_2 + 2e^-$
Dense electrolyte
O^{2-} conduction
Porous fuel-electrode
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Electrochemical
$H_2 + CO_2 \leftrightarrow H_2O + CO$
$3H_2 + CO \leftrightarrow CH_4 + H_2O$
$4H_2 + CO_2 \leftrightarrow CH_4 + 2H_2O$
Catalytic
+
–
H_2O
CO_2
CH_4
H_2
CO
$2e^-$
Export as needed

ACQUA: IDROGENO ED OSSIGENO

ACQUA + ANIDRIDE CARBONICA:

MONOSSIDO DI CARBONIO + IDROGENO (GAS DI SINTESI)

PRODOTTI DI ELETTROLISI: GAS DI SINTESI

The main reaction:

$(2n+1)\ H_2 + n\ CO \rightarrow C_nH_{2n+2} + n\ H_2O$

Prodotti

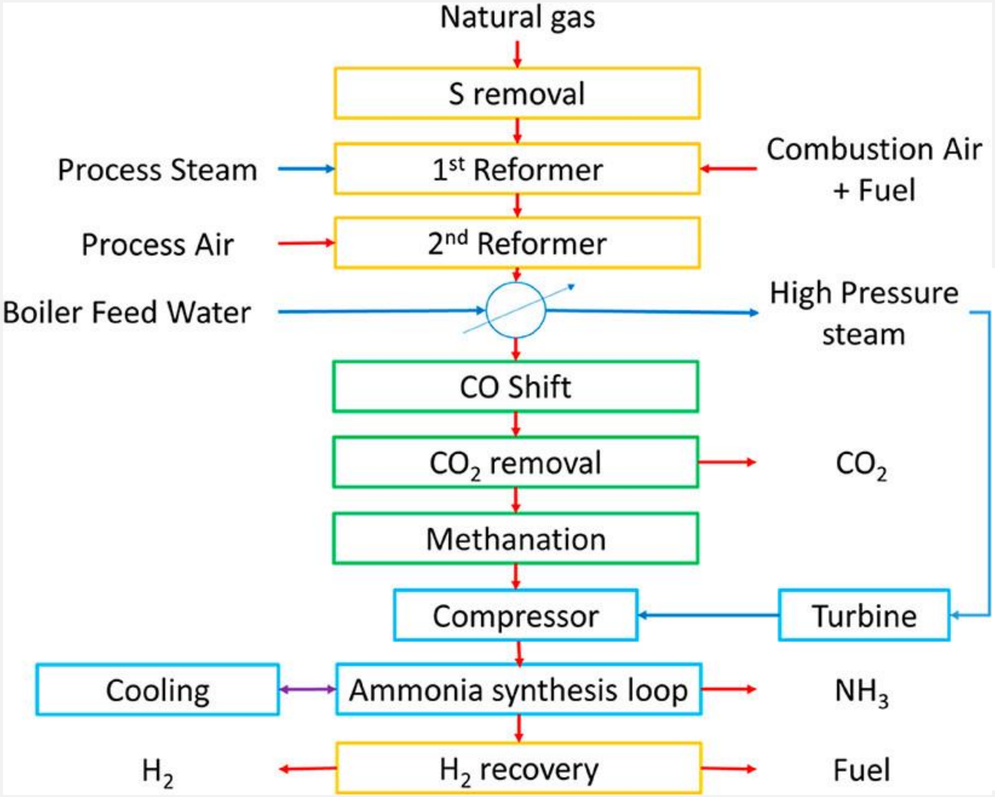
I prodotti di reazione dipendono da pressione, temperature e:.

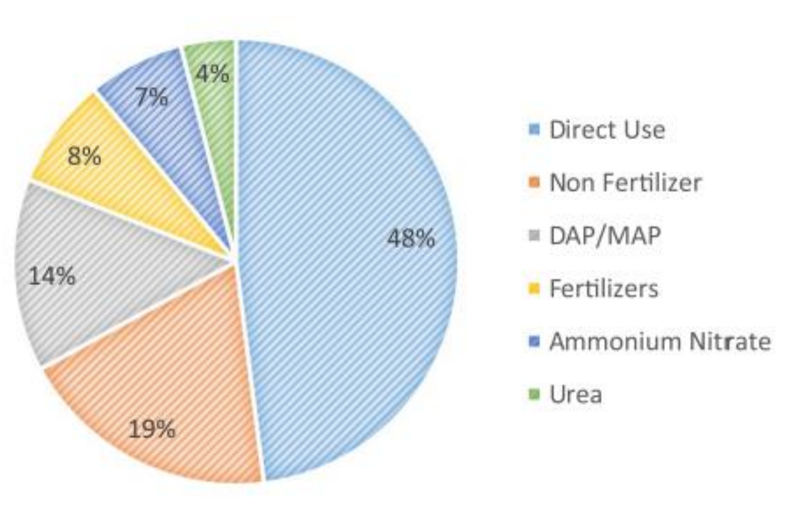
- ✷ Catalizzatori a base di **ferro** a 300-350°C danno idrocarburi leggeri (benzina)
- ✷ Catalizzatori a base di **cobalto** a 200 °C danno prevalenza di idrocarburi pesanti (diesel)

Prodotti a basso contenuto di zolfo (1 ppm vs. 10-500 dei combustibili attuali; meno dell’1% di aromatici)

AMMONIACA: una molecola multiuso

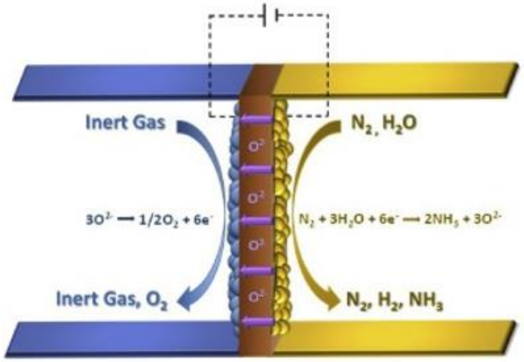
1.87 tonnellate di anidride carbonica per tonnellata di ammoniac
Il processo di Haber-Bosch consuma più dell’1% dell’energia globale


Natural gas
S removal
Process Steam
1st Reformer
Combustion Air + Fuel
Process Air
2nd Reformer
Boiler Feed Water
High Pressure steam
CO Shift
CO2 removal
CO2
Methanation
Compressor
Turbine
Cooling
Ammonia synthesis loop
NH3
H2
H2 recovery
Fuel



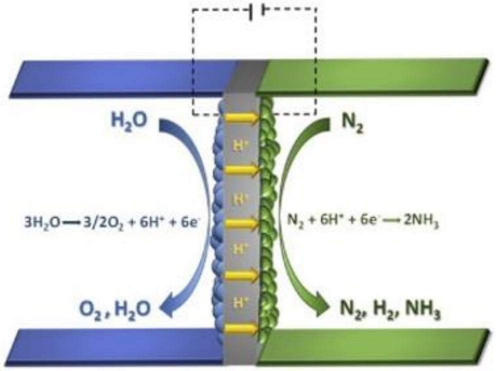
ELETTROLIZZATORI e ATTIVAZIONE DELL’AZOTO

Double Chamber - Solid Oxide Electrolyte
driven by O^{2-} conduction (OD)


Inert Gas
N_2, H_2O
O^{2-}
$3O^{2-} \rightarrow 1/2O_2 + 6e^-$
$N_2 + 3H_2O + 6e^- \rightarrow 2NH_3 + 3O^{2-}$
Inert Gas, O_2
N_2, H_2, NH_3

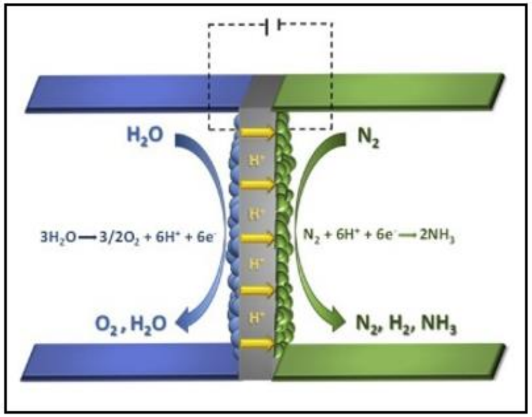
Cathode: $N_2 + 3H_2O + 6e^- \rightleftarrows 2NH_3 + 3O^{2-}$
Anode: $3O^{2-} \rightleftarrows 3/2O_2 + 6e^-$
Overall: $N_2 + 3H_2O \rightleftarrows 2NH_3 + 3/2O_2$

Double Chamber - Solid Oxide Electrolyte
driven by protonic conduction (PC)


H_2O
N_2
H^+
$3H_2O \rightarrow 3/2O_2 + 6H^+ + 6e^-$
$N_2 + 6H^+ + 6e^- \rightarrow 2NH_3$
O_2, H_2O
N_2, H_2, NH_3

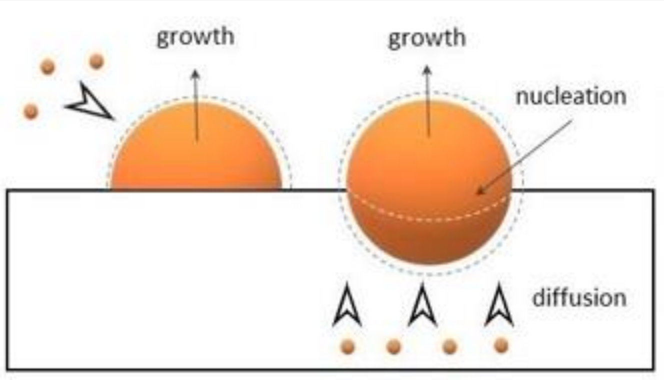
Anode: $3H_2O \rightleftarrows 6H^+ + 6e^- + 3/2O_2$
Cathode: $N_2 + 6H^+ + 6e^- \rightleftarrows 2NH_3$
Overall: $N_2 + 3H_2O \rightleftarrows 2NH_3 + 3/2O_2$

Single Chamber - Solid Oxide Electrolyte
driven by H^+ conduction (PC)


H_2O
N_2
H^+
$3H_2O \rightarrow 3/2O_2 + 6H^+ + 6e^-$
$N_2 + 6H^+ + 6e^- \rightarrow 2NH_3$
O_2, H_2O
N_2, H_2, NH_3

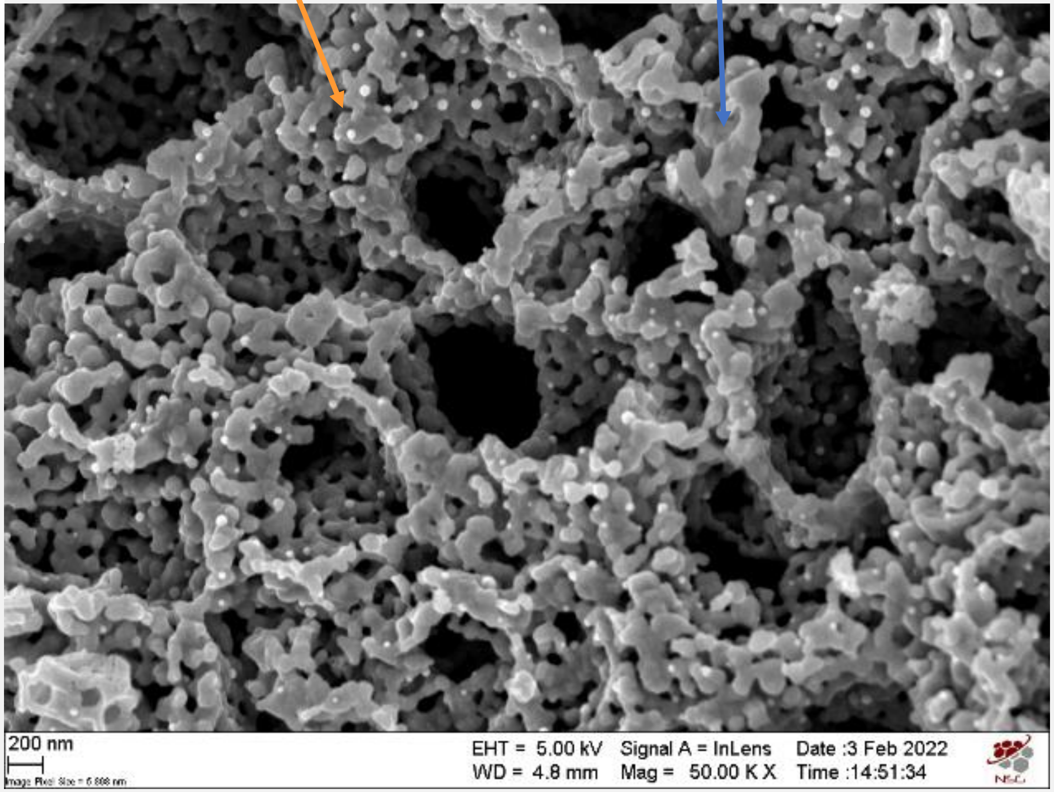
Anode: $3H_2O \rightleftarrows 6H^+ + 6e^- + 3/2O_2$
Cathode: $N_2 + 6H^+ + 6e^- \rightleftarrows 2NH_3$
Overall: $N_2 + 3H_2O \rightleftarrows 2NH_3 + 3/2O_2$

ELETTROLIZZATORI e ATTIVAZIONE DELL'AZOTO: Elettrodi attivi per EXSOLUZIONE


growth
growth
nucleation
diffusion

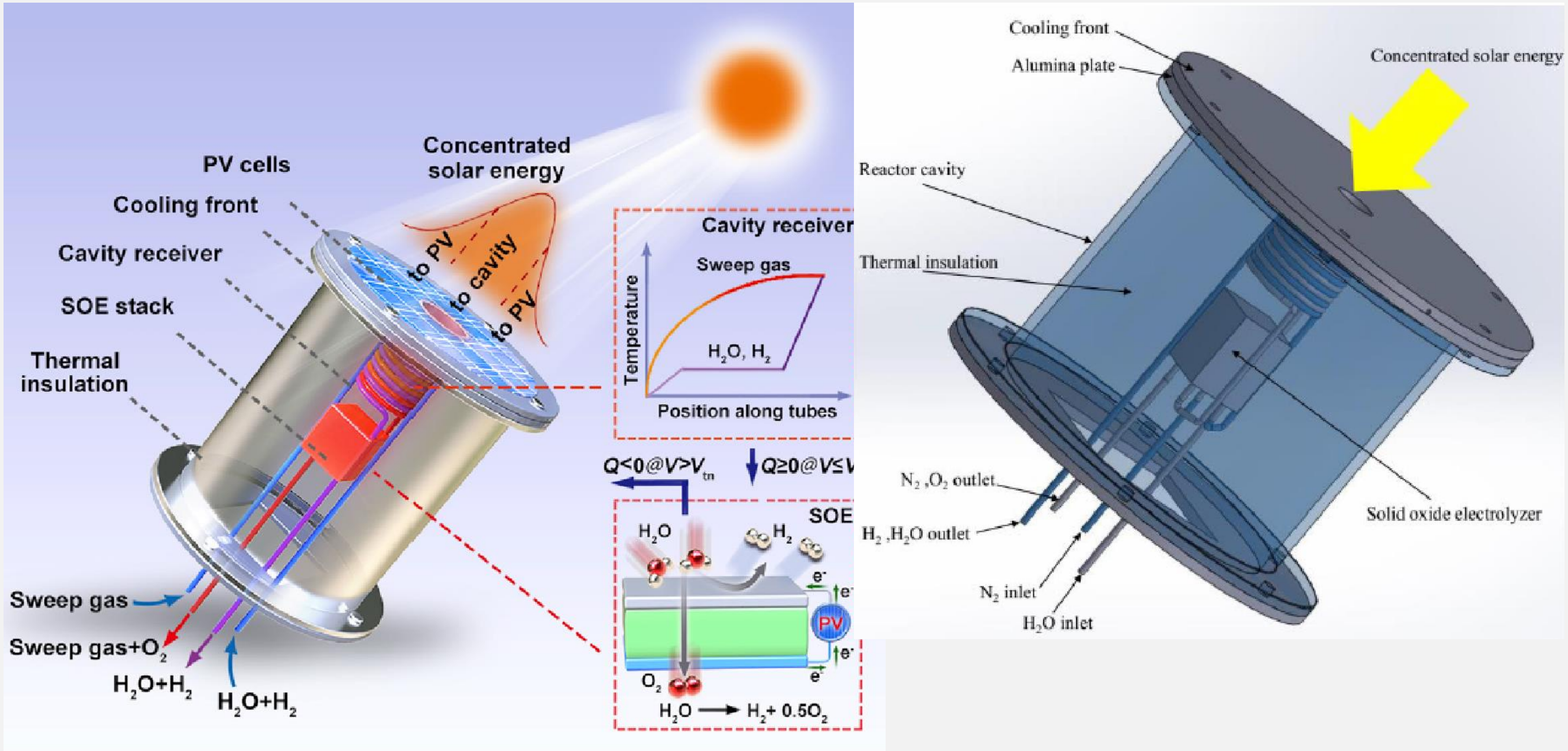
NANOPARTICELLE METALLICHE

MATRICE POROSA DI OSSIDO

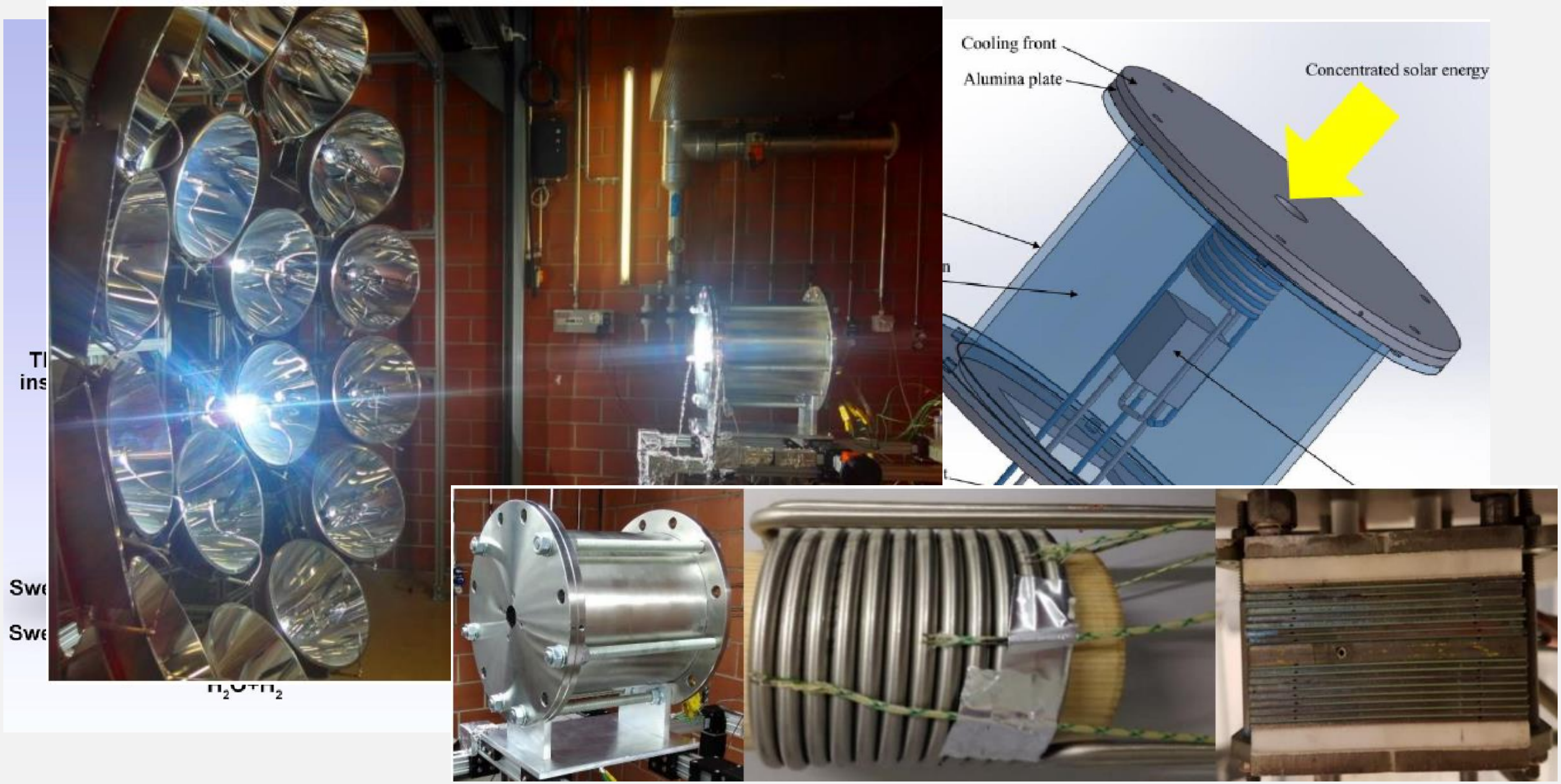

200 nm
Image Pixel Size = 6.808 nm
EHT = 5.00 kV
WD = 4.8 mm
Signal A = InLens
Mag = 50.00 K X
Date :3 Feb 2022
Time :14:51:34

NANOCOMPOSITI METALLO/OSSIDO MEDIANTE SINTESI DA SOLUZIONE ACQUOSA SCALABILI INDUSTRIALMENTE

ELETTROLISI FOTO-TERMO INDOTTA


Concentrated solar energy
PV cells
Cooling front
Cavity receiver
SOE stack
Thermal insulation
to PV
to cavity
to PV
Sweep gas
Sweep gas+O_2
H_2O+H_2
H_2O+H_2
Cavity receiver
Sweep gas
H_2O, H_2
Temperature
Position along tubes
Q<0@V>V_{tn}
Q≥0@V≤V
SOE
H_2O
H_2
e^-
PV
O_2
$H_2O \rightarrow H_2 + 0.5O_2$
Cooling front
Alumina plate
Concentrated solar energy
Reactor cavity
Thermal insulation
N_2, O_2 outlet
H_2, H_2O outlet
N_2 inlet
H_2O inlet
Solid oxide electrolyzer

ELETTROLISI FOTO-TERMO INDOTTA


Cooling front
Alumina plate
Concentrated solar energy
Th
ins
Swe
Swe
H_2O+H_2

GRAZIE DELL’ATTENZIONE