Production of hydrogen and its use in fuel cells

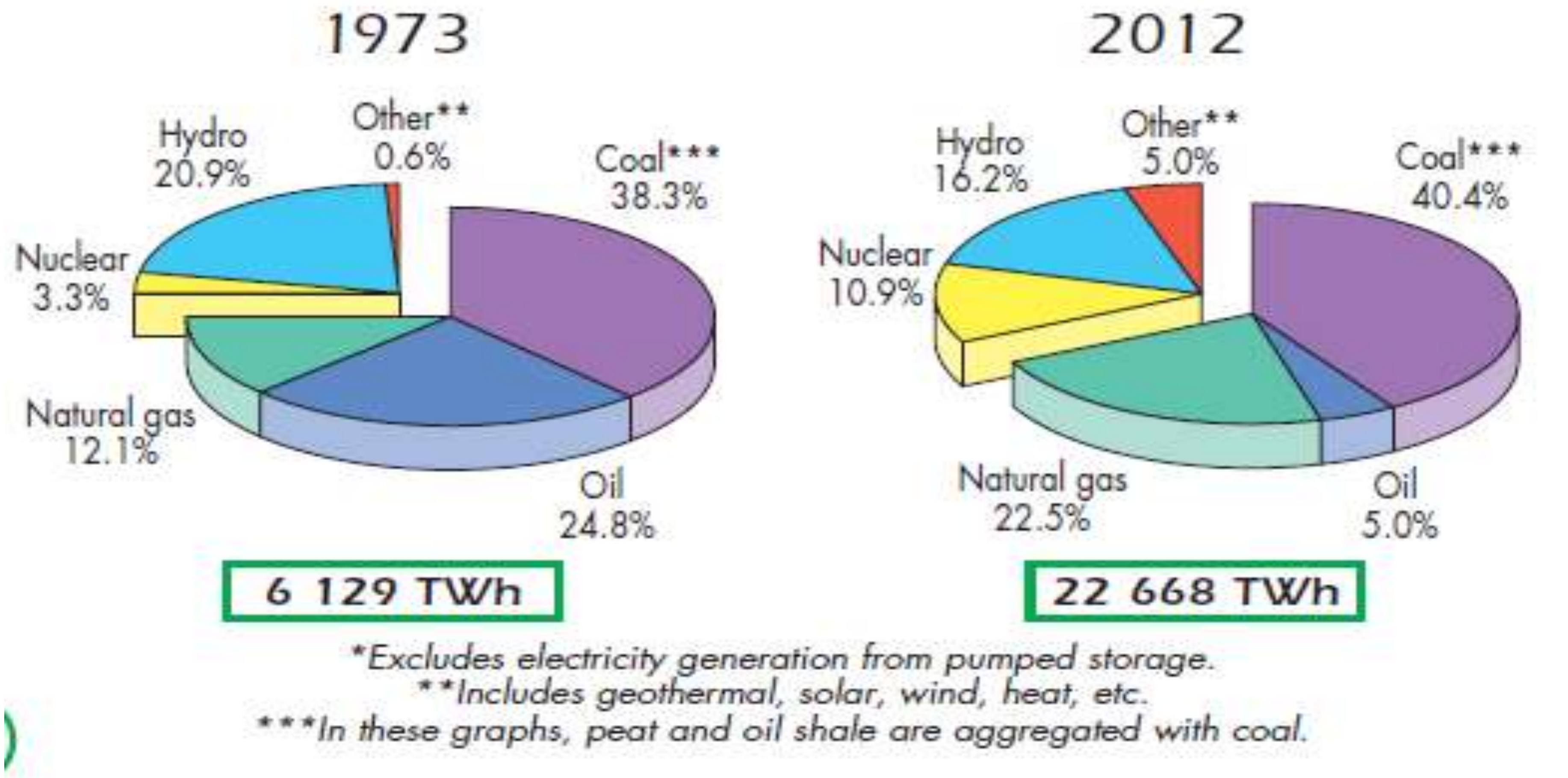
Yohannes Kiros

Department of Chemical Engineering and Technology,

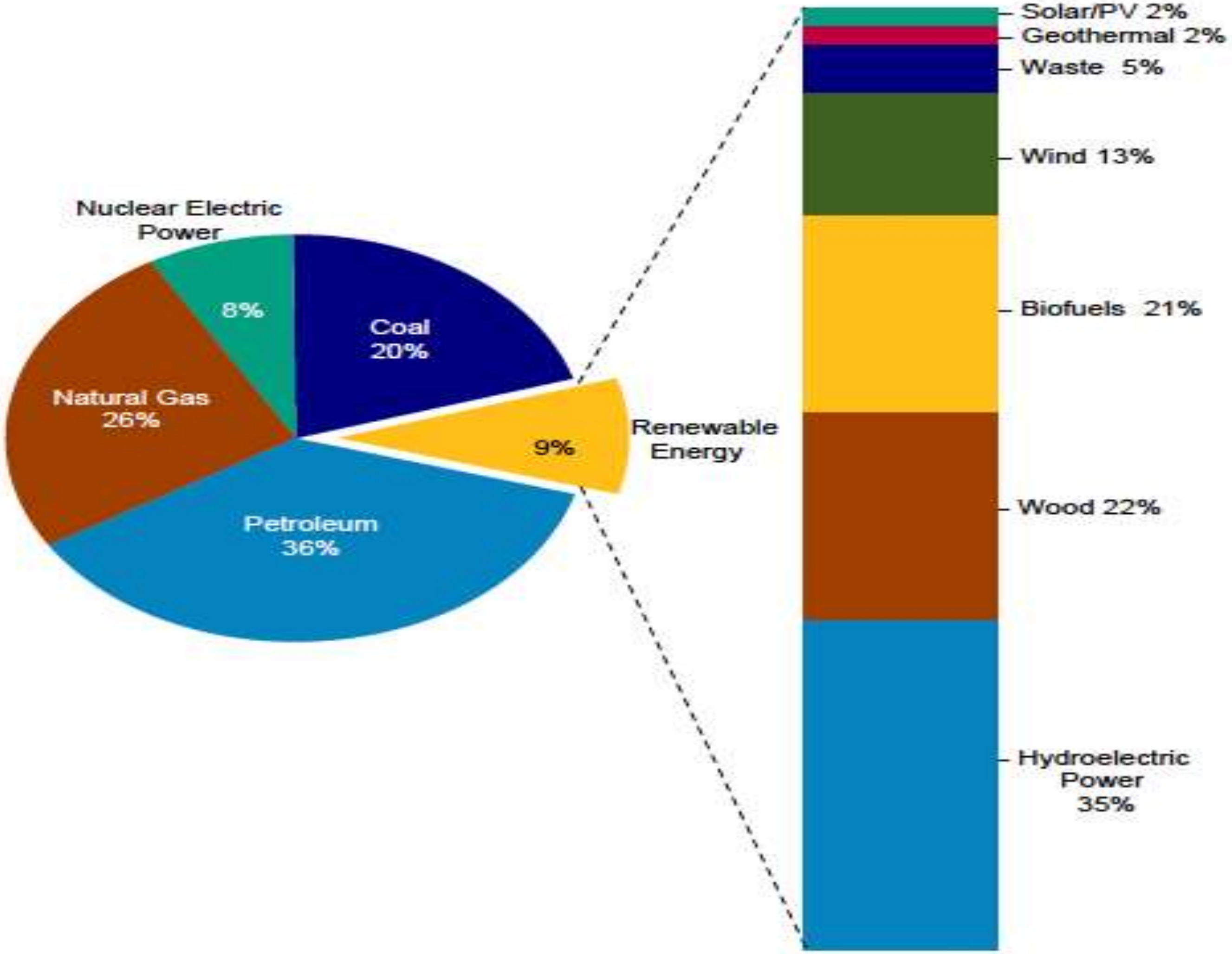
KTH Royal Institute of Technology, 100 44 Stockholm – Sweden

ICNTSE- Alexandria, Egypt **October 3, 2016**

Global fuel shares of electricity generation

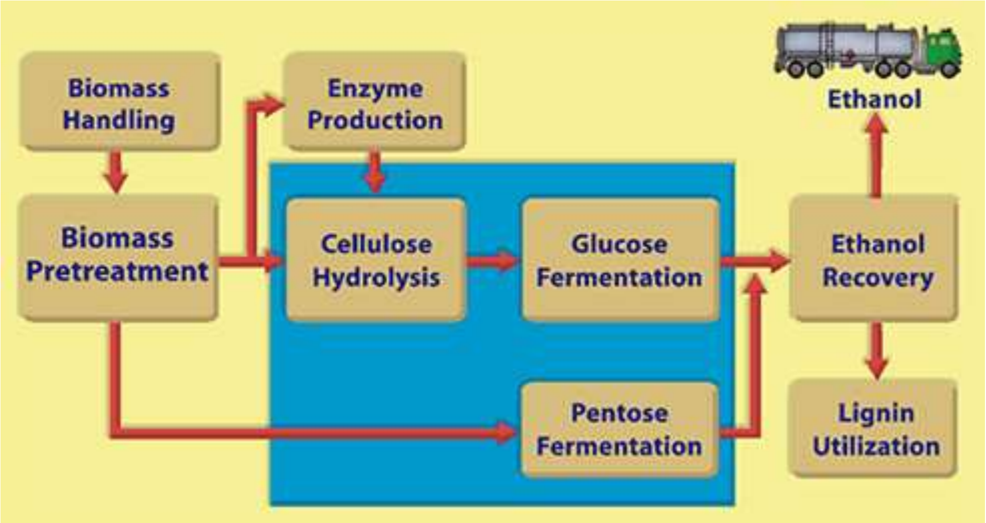


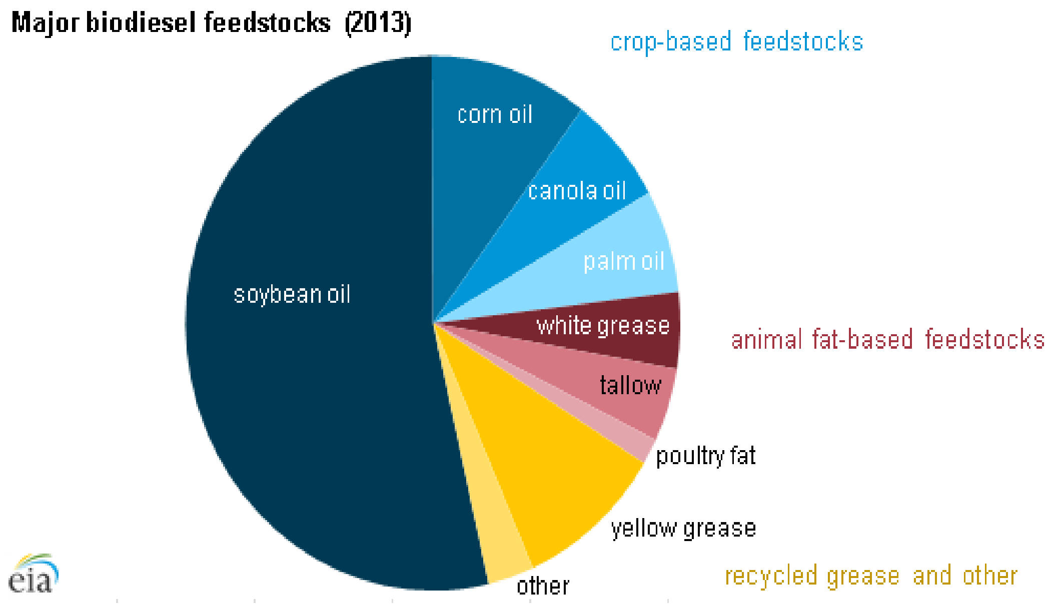
The share of renewables in energy supply



IEA, 2011

Global biofuel production





5406 billion liters of oil/year

95 billion ethanol /year

17 billion biodiesel/year

2% of the total oil supply!

High risk for fuel against food

Available renewable energy sources

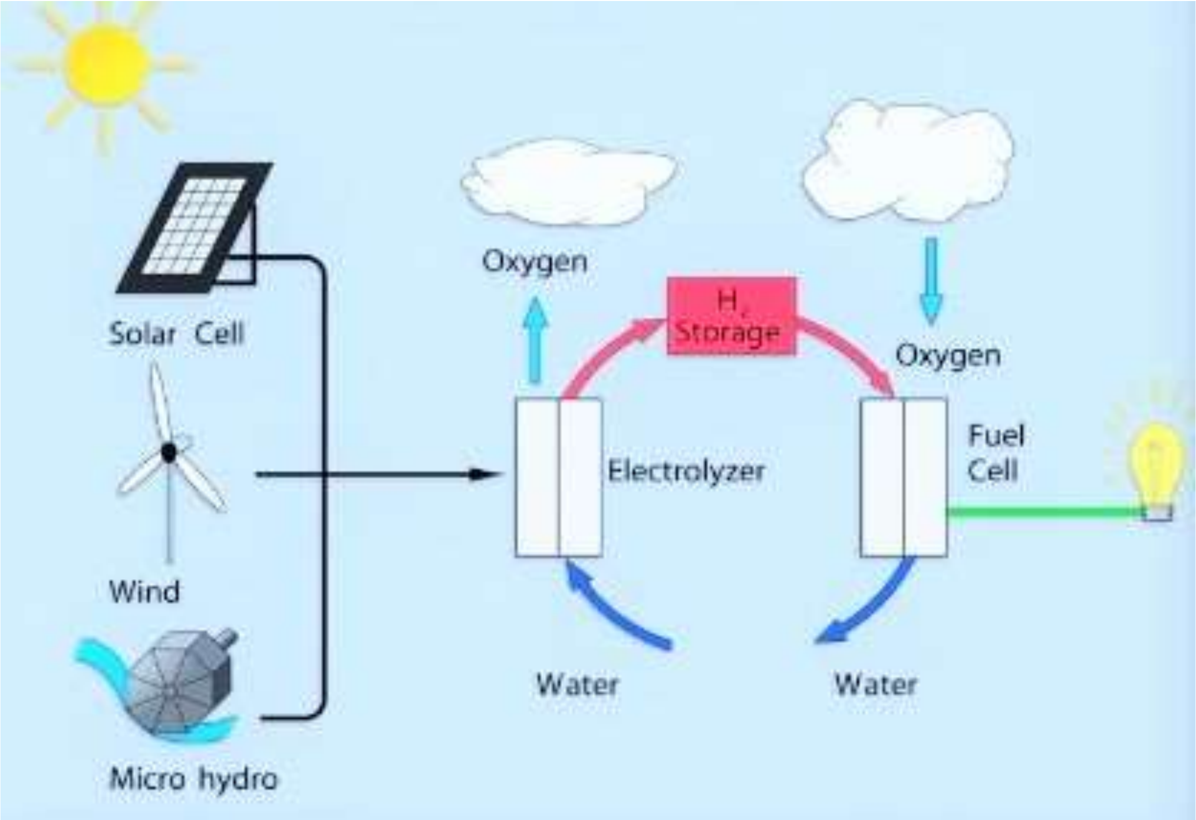
- **Hydropower potential 1,834 TWh/yr[1] (current use at 7%)**
- **Biomass resources 70 billion tonnes[1]**
- **Solar insolation at 1800-2850 kWh/m^2 yr., solar PV at 40,500 TWh/yr[1]**
- **Wind speeds 95 TW[2]**
- **Geothermal 14,000 MW[1]**

[1] World Energy Council (2010)

[2] Greenfacts

The Clean Energy Set-up

With renewable resources such as solar, wind and flowing rivers and springs, Geothermal, biomass there can be a sustainable, clean and safe electric generation by displacing fossil fuels



Solar 227 GW (2015) >26% from 2014[1]
Wind 433 GW (2015) >17% from 2014[2]
Hydropower 1055 GW (2015) 3% from 2014[3]

0 at the end of 1990s for solar and wind

1. IEA, Report PVPS T1-29-2016
2. Global wind energy council (GWEC)
3. HydroWorld.com

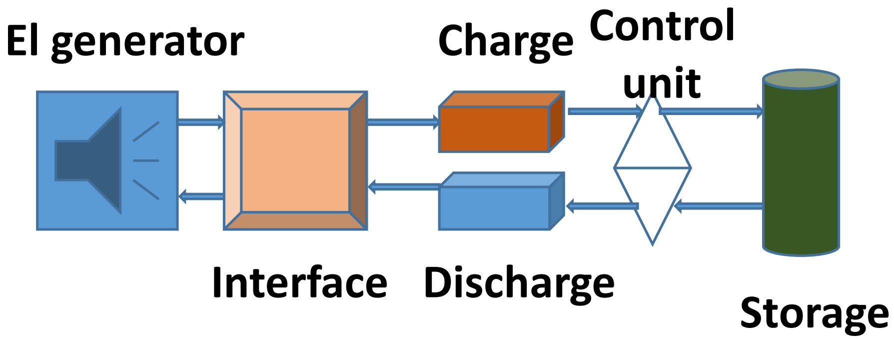
Energy storage systems (ESS)

ESS converts electrical energy from a power network to a form that can be stored and used again at convenience as electrical energy.

Utilization of renewables means

- **Variable energy outputs**
- **Stochastic nature of the sources**
- **Decentralized off-grids or on-grids**
- **Difficulty in integrating to the existing power grids**
- **Supply and demand**

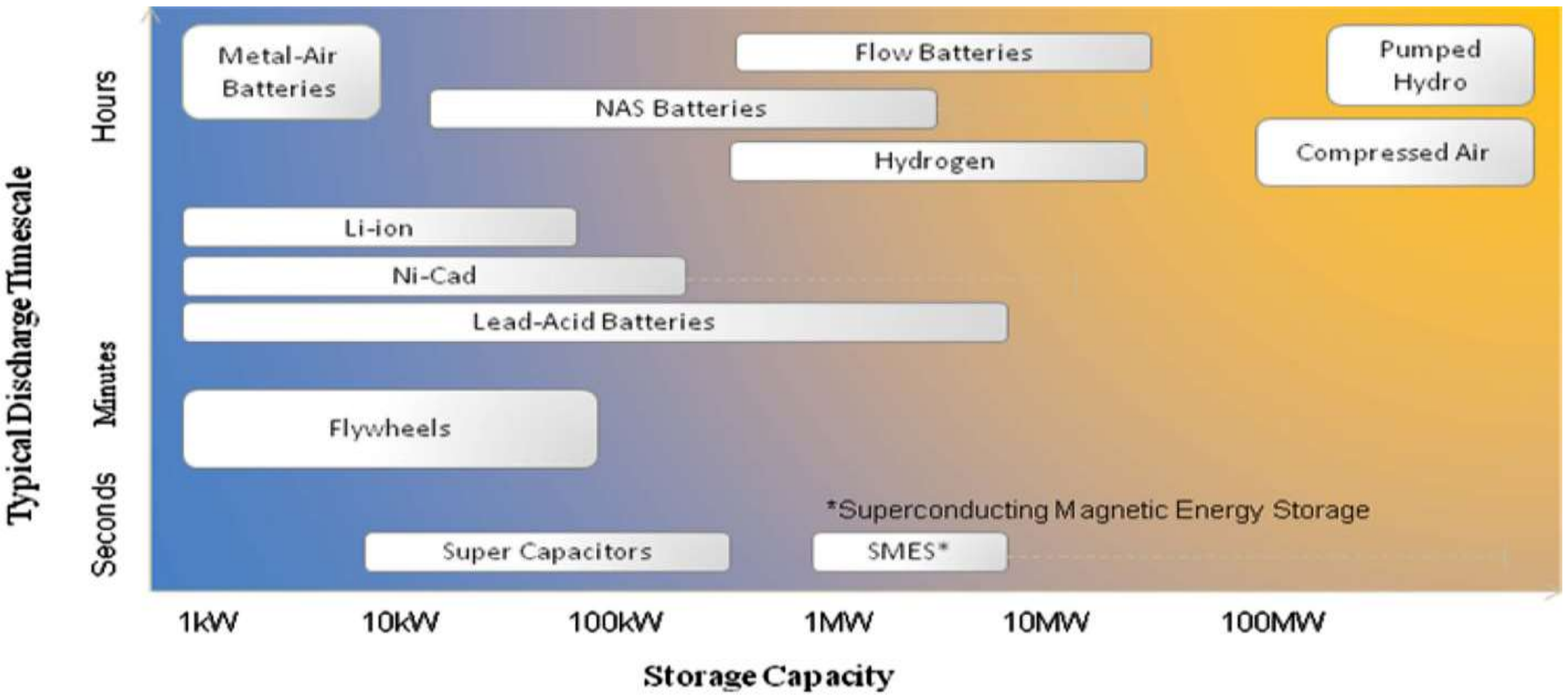
Components of ESS



ESS offers integration and flexibility in power systems by providing

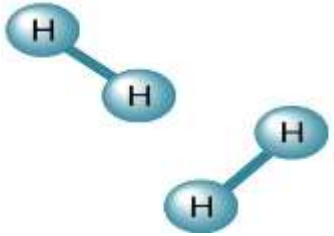
- **Predictability without fluctuations**
- **Energy arbitrage revenues (off-peak to on peak)**
- **High energy utilization**
- **Stable performance**
- **Improvement in power**

Different types of ESS and their capacity



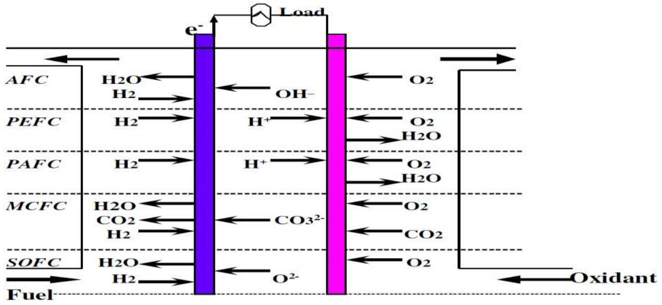
Source: Akinyele et al. Sust. Energy Technol. Ass. 8 (2014) 74

Hydrogen as future energy carrier

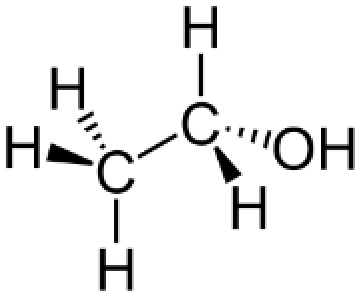


- The simplest molecule, lightest and most abundant element on Earth
- Current use as a bulk chemical in chemical processes

- Acid-base
- Petrochemical industries (hydrotreatment and hydrocracking of compounds, catalytic reforming)
- Fertilizer (ammonia), Methanol, F-T products, ore reduction
- Fine chemicals, polymers, alcohols, Food industry
- Fuel (rockets, cars, fuel cells)



Hydrogen as future energy carrier



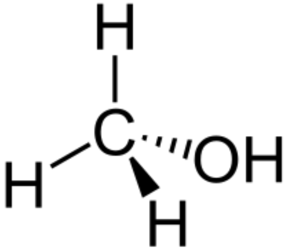
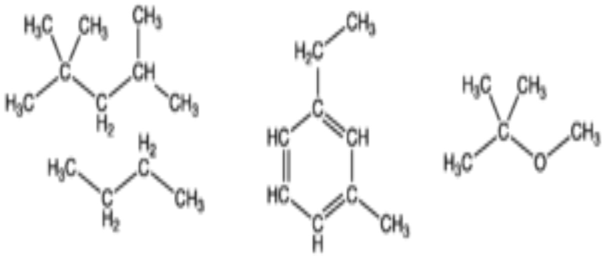


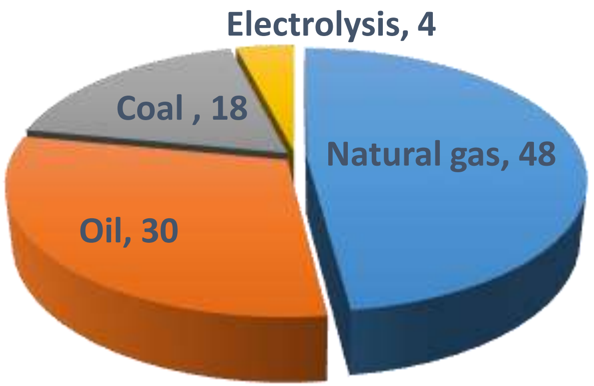
Table 1. Theoretical energy contents of some fuels

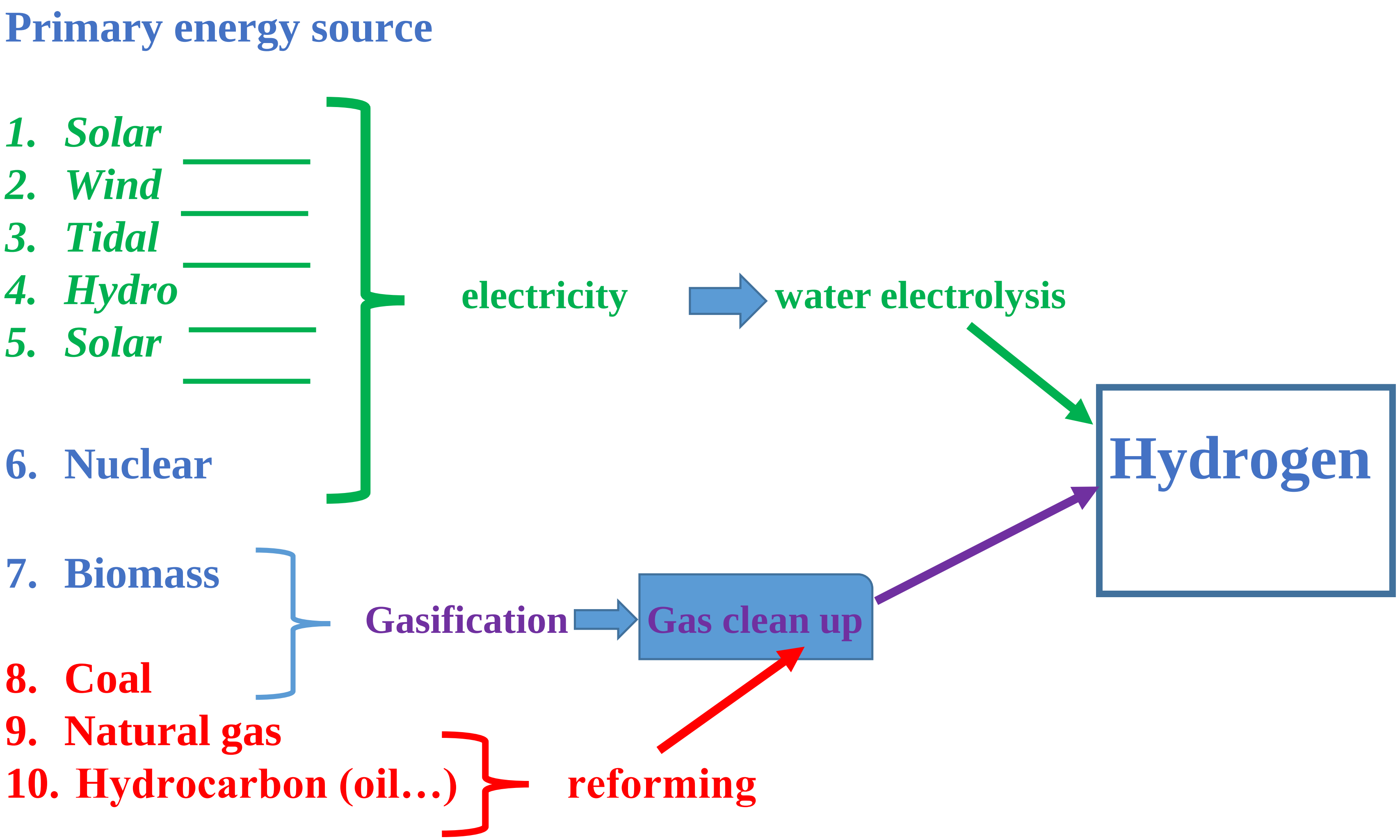
Type of Fuel	Specific energy (kWh/kg)	Energy density (kWh/L)
Compressed hydrogen gas	33	0.56
Liquefied hydrogen	33	2.38
Ethanol	8.7	6.58
Methanol	5.6	4.4
Gasoline	12.8	9.5



Current production of hydrogen

Production share of hydrogen in the world (%) 50 10 ^{6} tons/year*





*R. Kothari et al. Ren Sust Energy Rev. 12 (2008) 553
US DOE, Washington DC 20585 (2013)

Current production of hydrogen

Hydrogen production from fossil fuel feedstock through a set of processes

1. **A hydrocarbon fuel (petroleum, coal, natural gas** ⇨ **Sulfur removal**

2. **Gaseous sulfur on metal oxide** ⇨ **Another step of sulfur removal**

3. **fuel and water ⇨ hydrogen +CO** ⇨ **High temperature conversion to hydrogen**

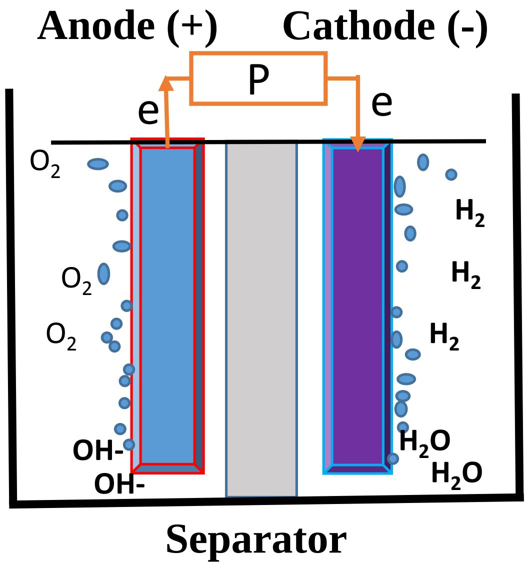
4. **Carbon monoxide removal**

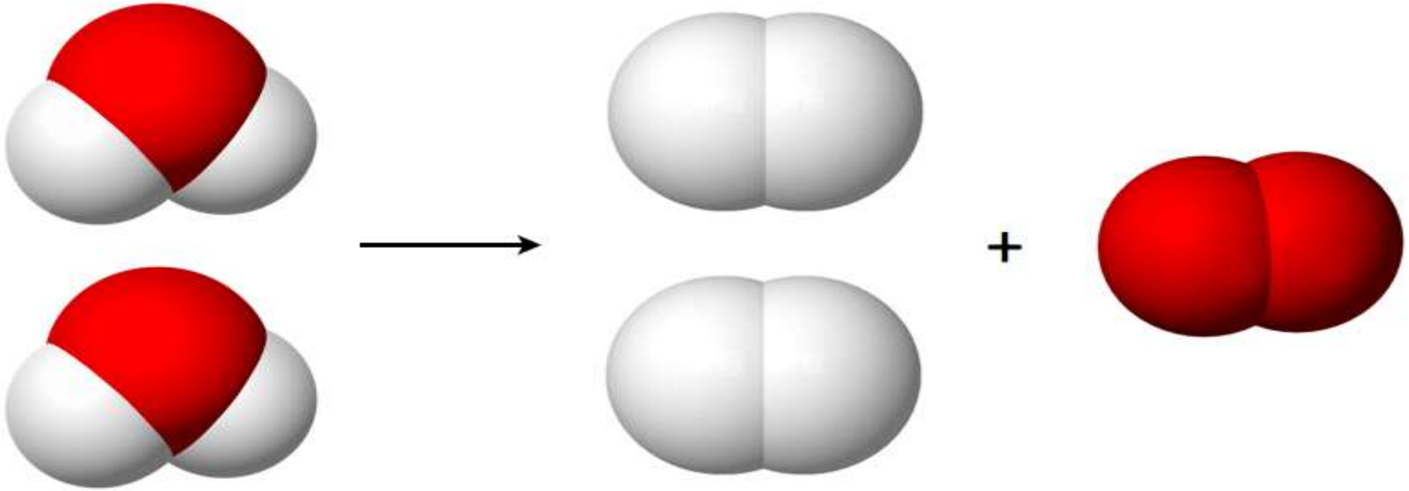
5. **Gas clean up** **Removal of carbon dioxide and water**

6. **>99% H_2**

Electrolysis cell and the reactions

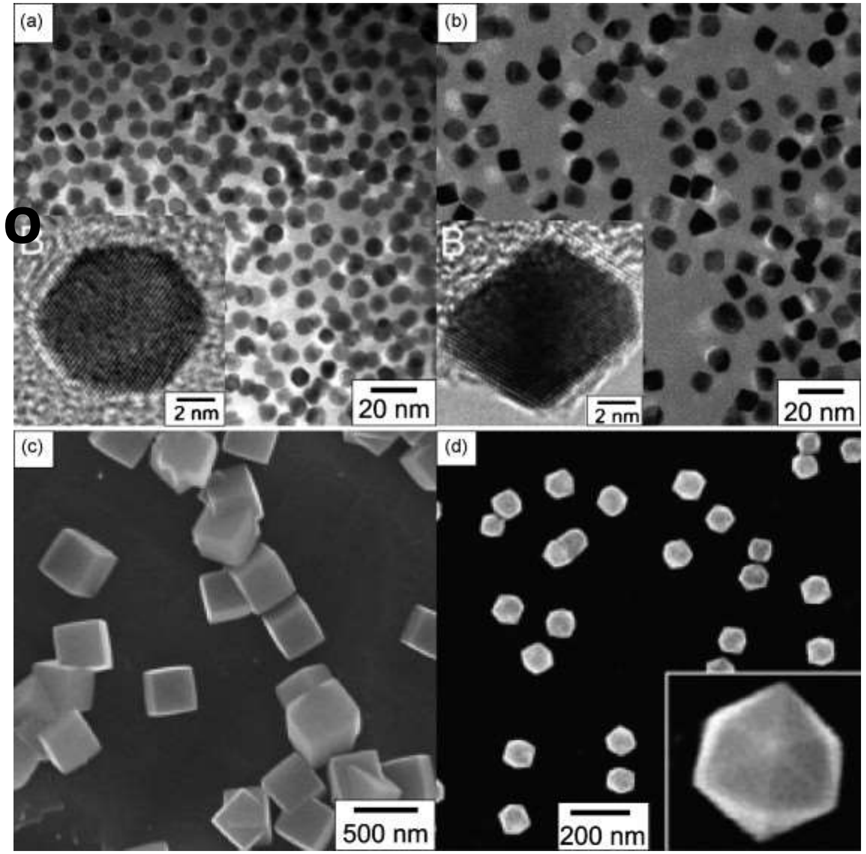
Electricity needed 33.3 kWh/kg H_2





$$2H_2O \longrightarrow 2H_2 + O_2$$

Catalysts and alternatives for the reactions



TEM images of Pt nanostructures[3]

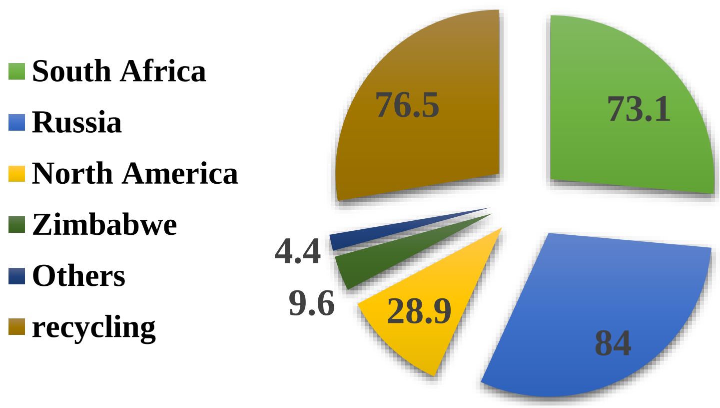
An electrocatalyst is a substance which increases the rate of the reaction without being consumed in the reaction.

Most of the active catalysts are based on platinum group metals such as platinum, ruthenium, rhodium and iridium.

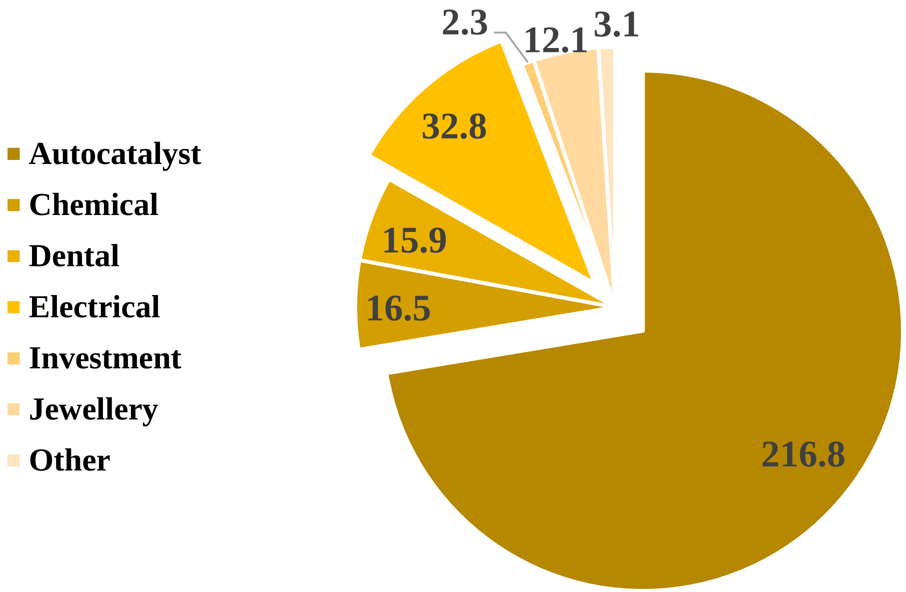
1 Z. Peng et al., Nano Today 4 (2009) 143

Would the PGM survive large scale applications as catalysts?

Total supply of Pt in tons (276.5) 2013 (JM)

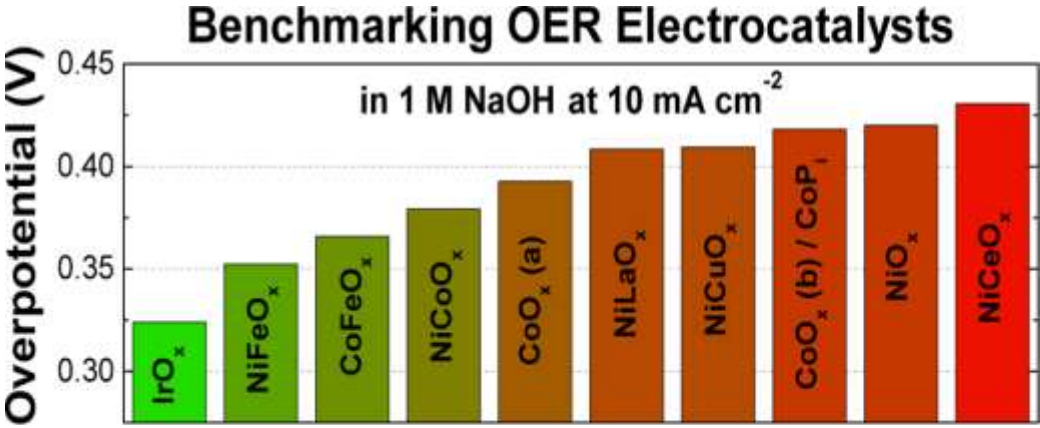


Total demand of Pt in tons (300), 2013 (JM)



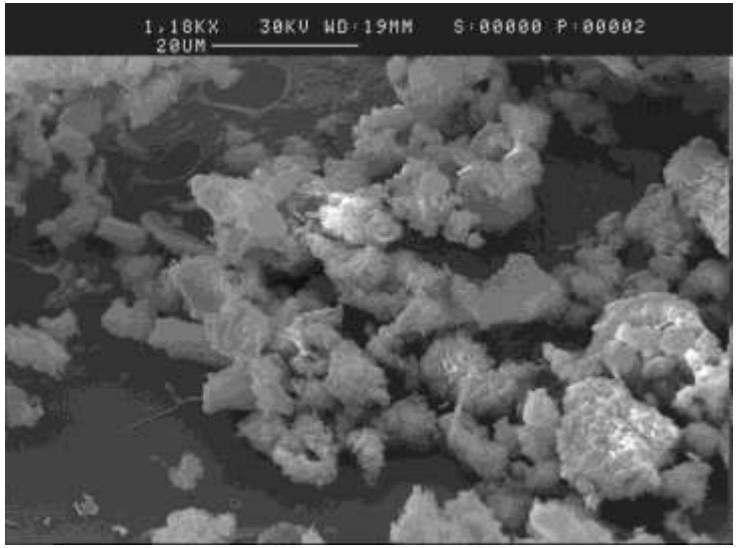
Ir, Rh, Re are by presence and weight among the rarest PGM among the mined in the Earth!

Thus, the incentive and drive to find alternative catalysts with low-cost and abundance

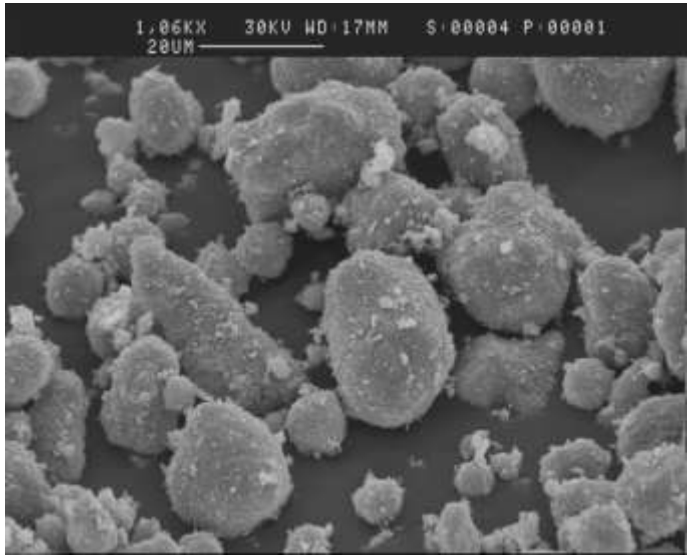


Ref. CCL McCrory et al. JACS, 135 (2013) 16977

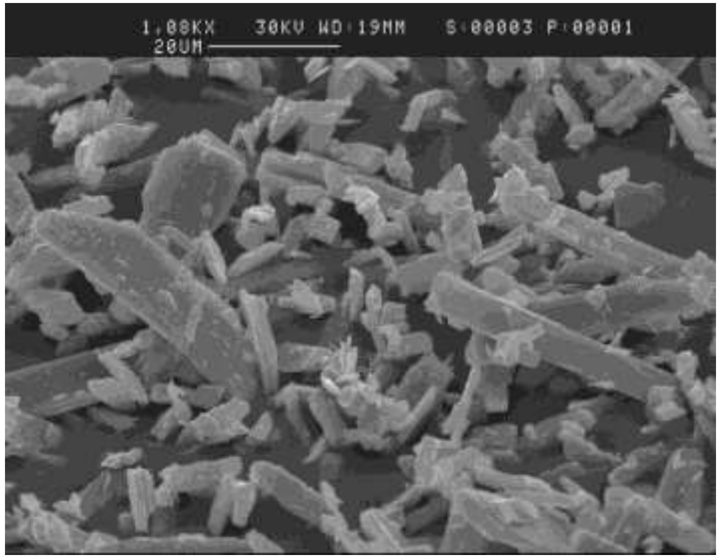
Catalysts and additives by SEM characterization



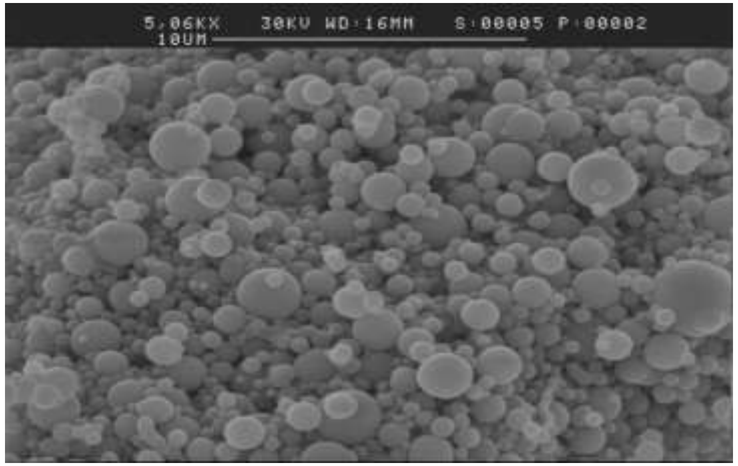
Ni-Fe Raney: ~ 80wt% Ni, 7wt% Al, 13wt% Fe



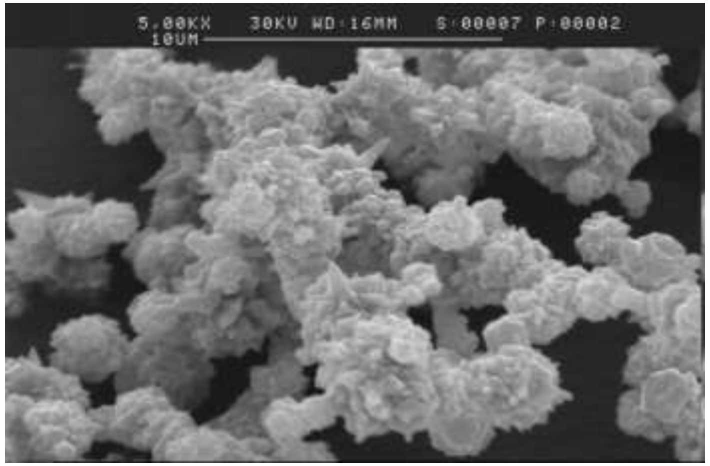
Co_3O_4



MoO_3

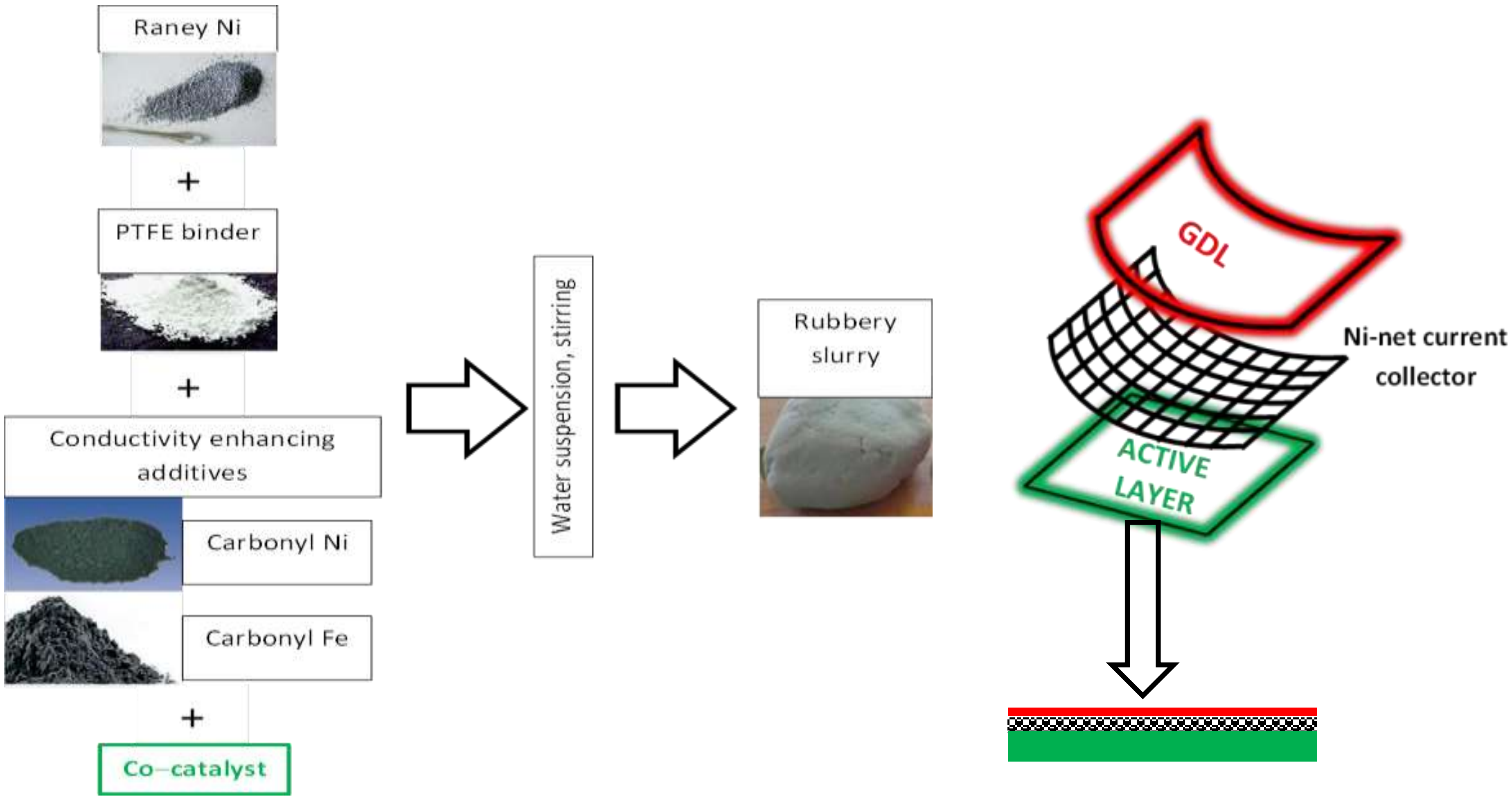


Carbonyl iron



Carbonyl Nickel

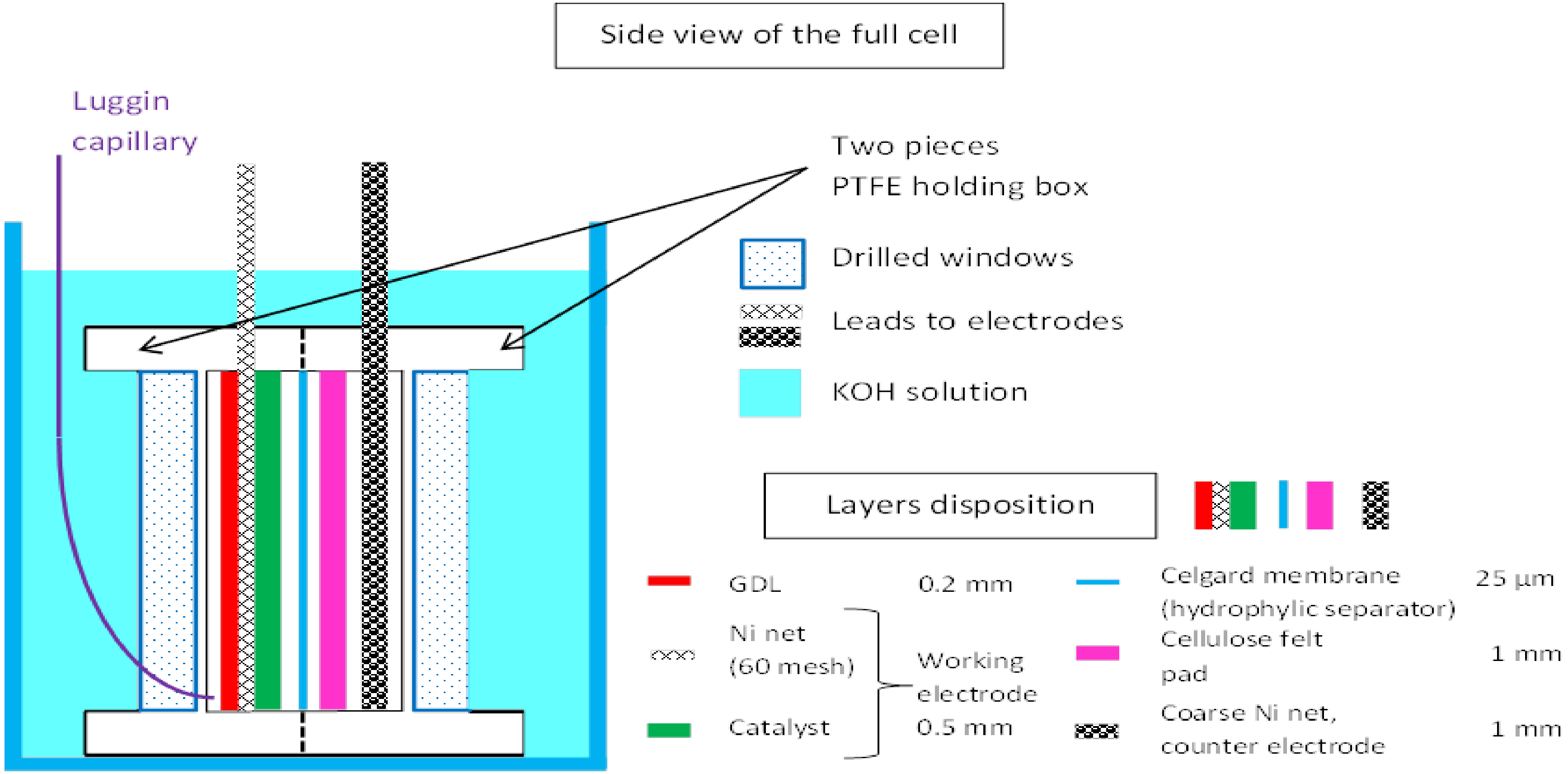
PTFE bonded Raney-Ni with ad-atoms/mixtures



Test of electrodes for electrolysis

Alkaline electrolyte

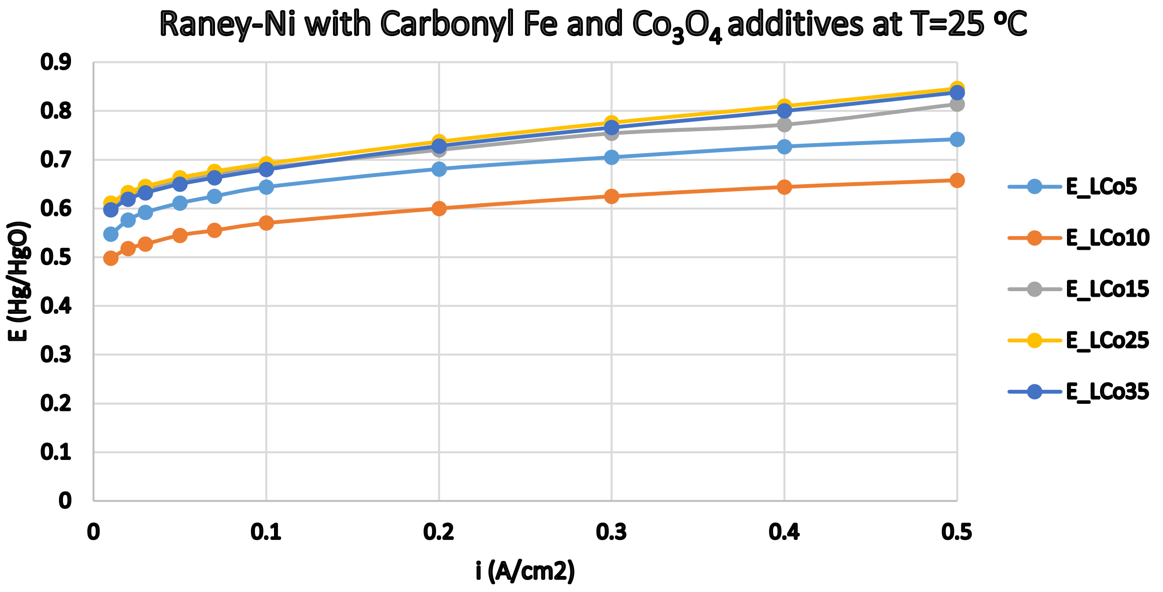
At 25-100 ^{o}C.

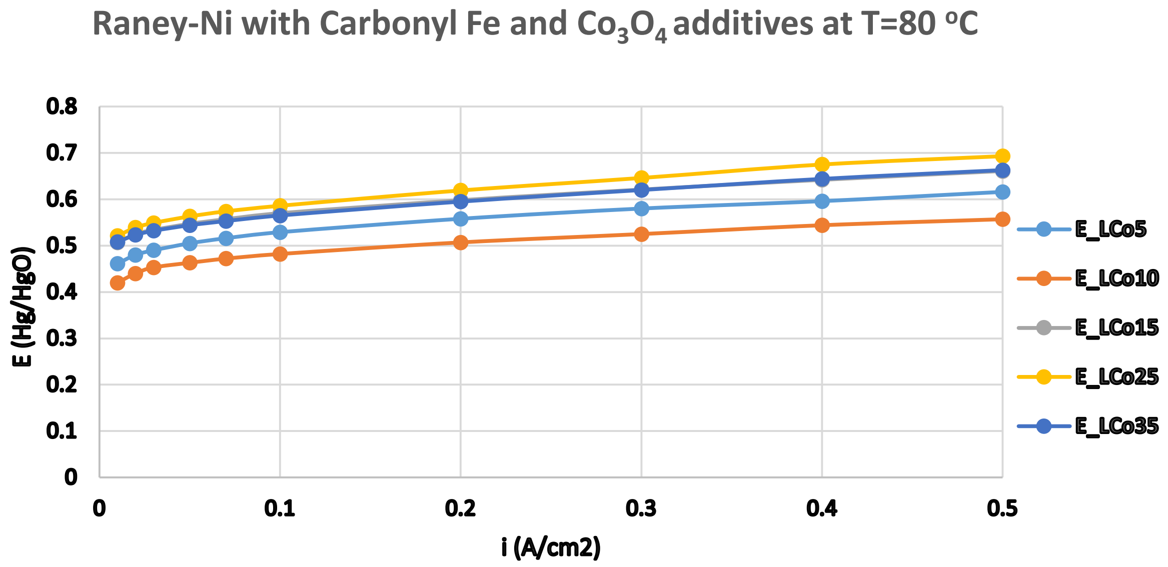


Half-cell design and "Zero gap" cell

Results of half-cell measurements

Anodic materials





Improvement of activity and stability

-The presence of oxyphil materials

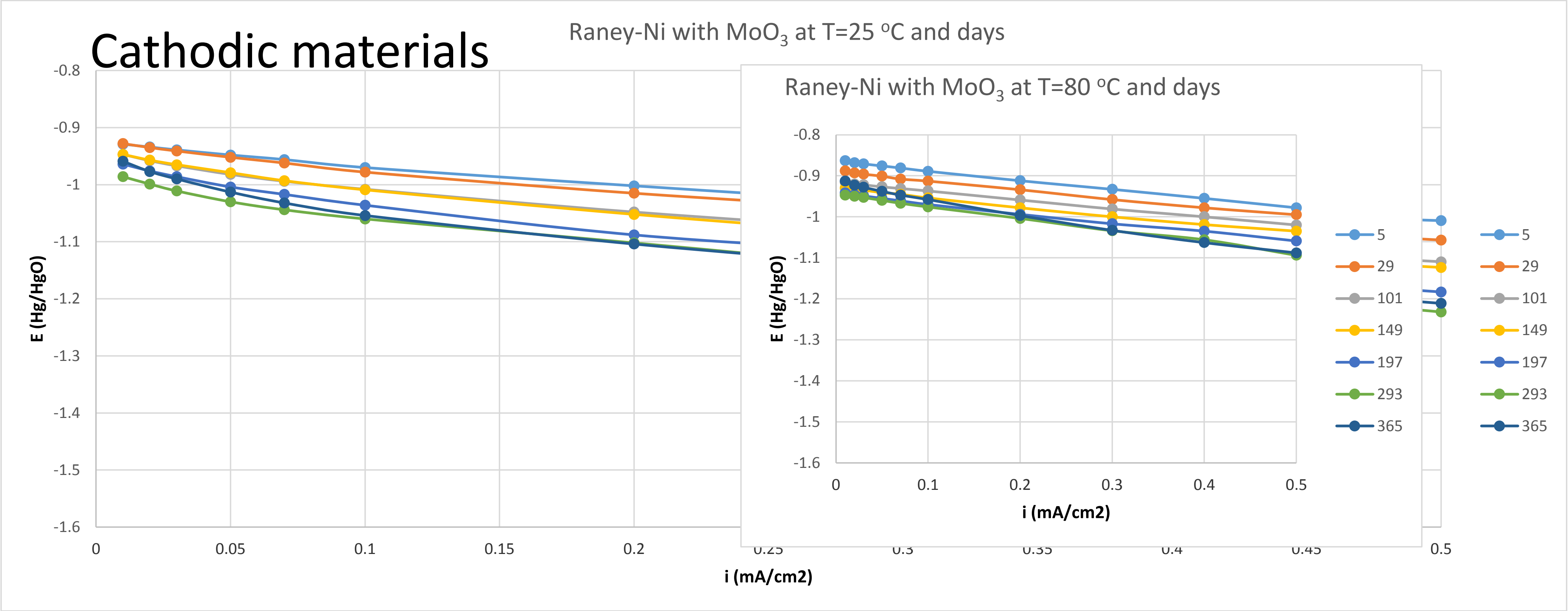
-10 wt.% of Co_3O_4

-Thickness of active layer ca. 0.5 mm

-Higher temperature, higher kinetics (100 to 175 mV)

Half-cell measurements

Cathodic materials



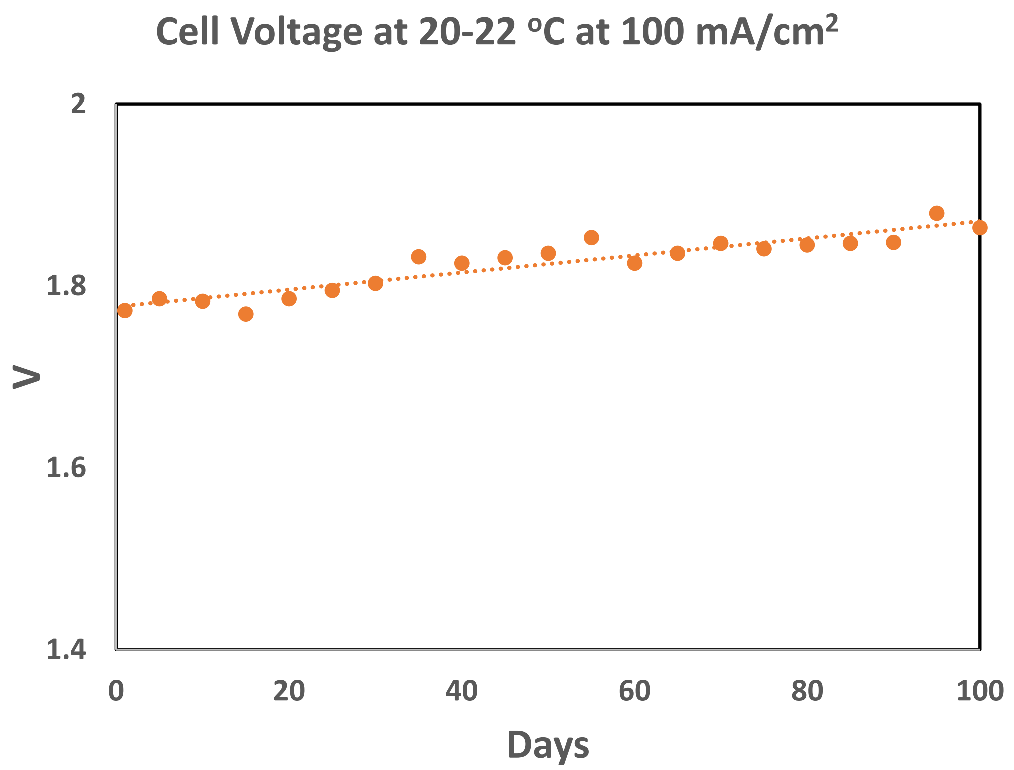
Improvement of activity and stability

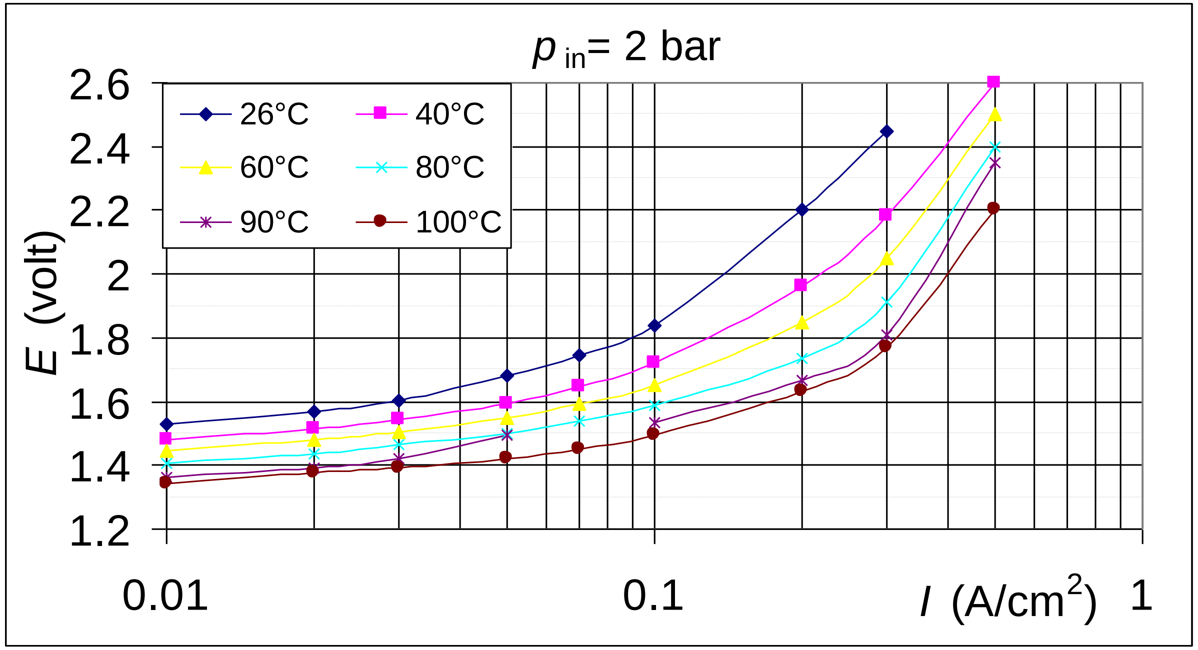
-Additive of MoO3 (10 wt.%)

-Higher temperature, higher kinetics (100-200 mV)

-Thickness of active layer ca. 0.5 mm

Test of electrolysis cell





Temperature dependence of the zero-gap cell

Stable performances at room temp.
Low decline rate
Gas bubble formations results in cell voltage fluctuations

Fuel cells

A fuel cell converts the chemical energy of the fuel directly to electrical energy

- ***High theoretical energy conversion efficiency (η)***

$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$ + Electricity+ Heat

$\eta > 83\%$ (HHV on aqueous product)

$\eta > 94\%$ (LHV on gaseous product)

Advantages of Fuel Cells

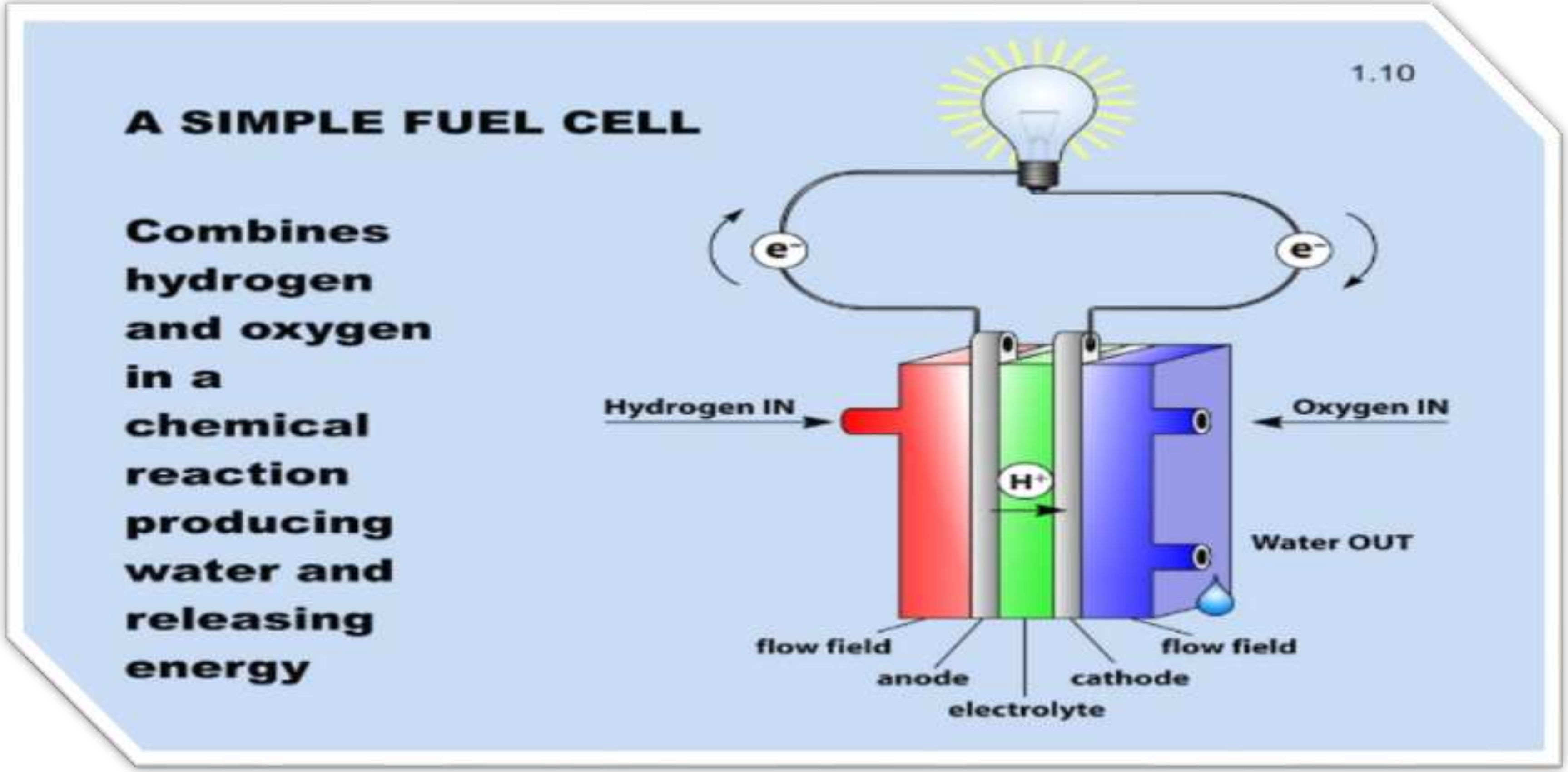
- **High efficiency**
- **Co-generation of heat**
- **Flexibility in the source of fuel**
- **Modular size and stand-alone**
- **Applicable to transport systems**
- **Non-pollutant and noiseless**

Principles of a fuel cell operation

H_2=2H^++2e^- (anode)

1/2O_2+ 2H^++2e^-=H_2O (cathode)

Overall cell reaction 1/2O_2+ H_2=H_2O+heat+ elctricity



Types of Fuel cells

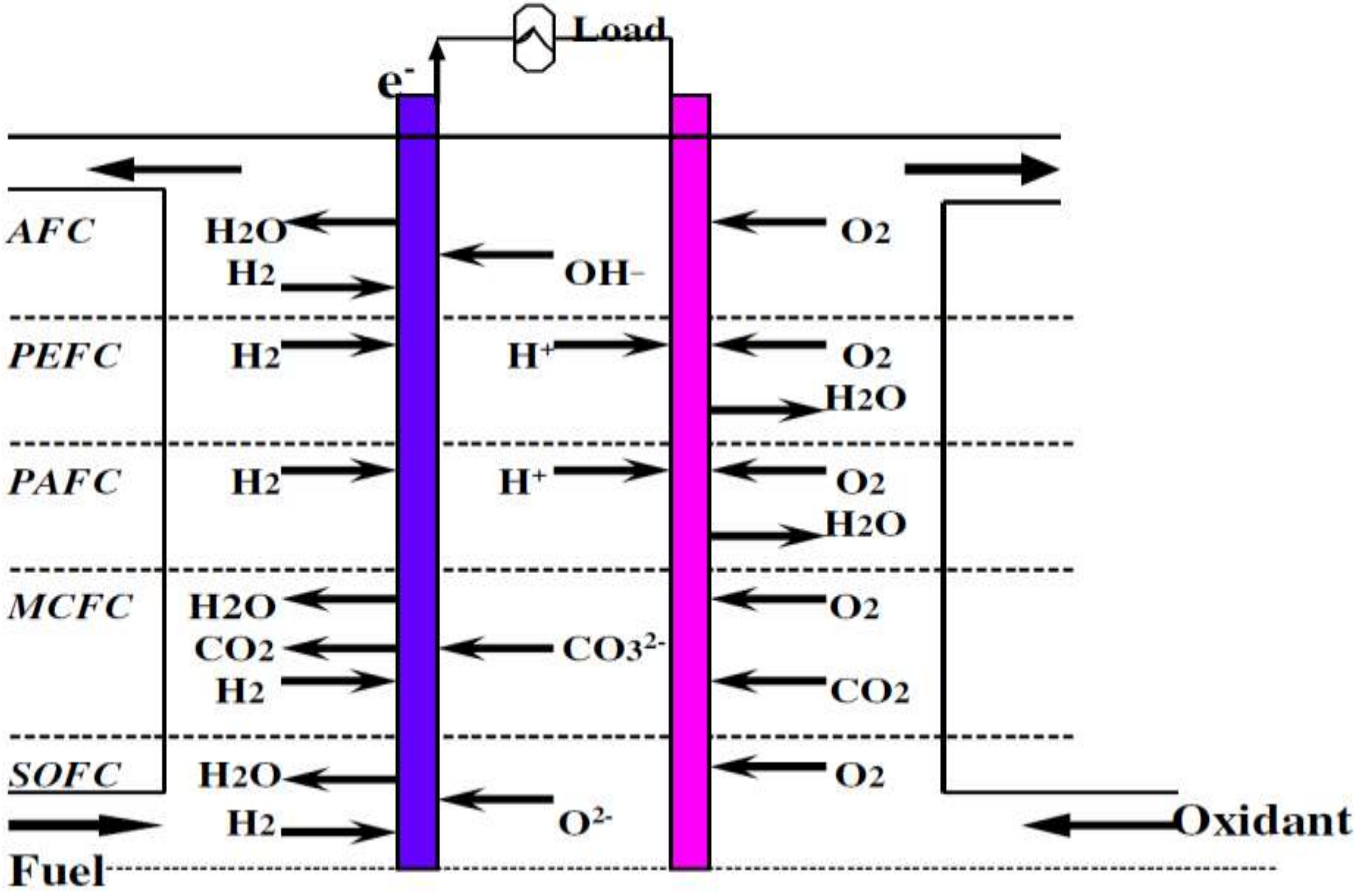
Type	AFC	PEFC	PAFC	MCFC	SOFC
Electrolyte	KOH	Membr.	H3PO4	K/Li-CO3	Zr/Y2-O3
T (C)	50-100	50-100	200	650	<1000
Electrode	C/metal	C	C	metal	cermets
Anode	Pt/ Ra-Ni	Pt	Pt	Ni	NiZrO2
Cathode	Ag/Pt/oxi-des/TPP	Pt	Pt	NiO	Perovskite
Fuel	H2	H2	H2	H2	H2-CO
Oxidant	O2/air	O2/air	O2/air	O2/air	O2/air

DMFC-Direct methanol fuel cell, DBFC-borohydride

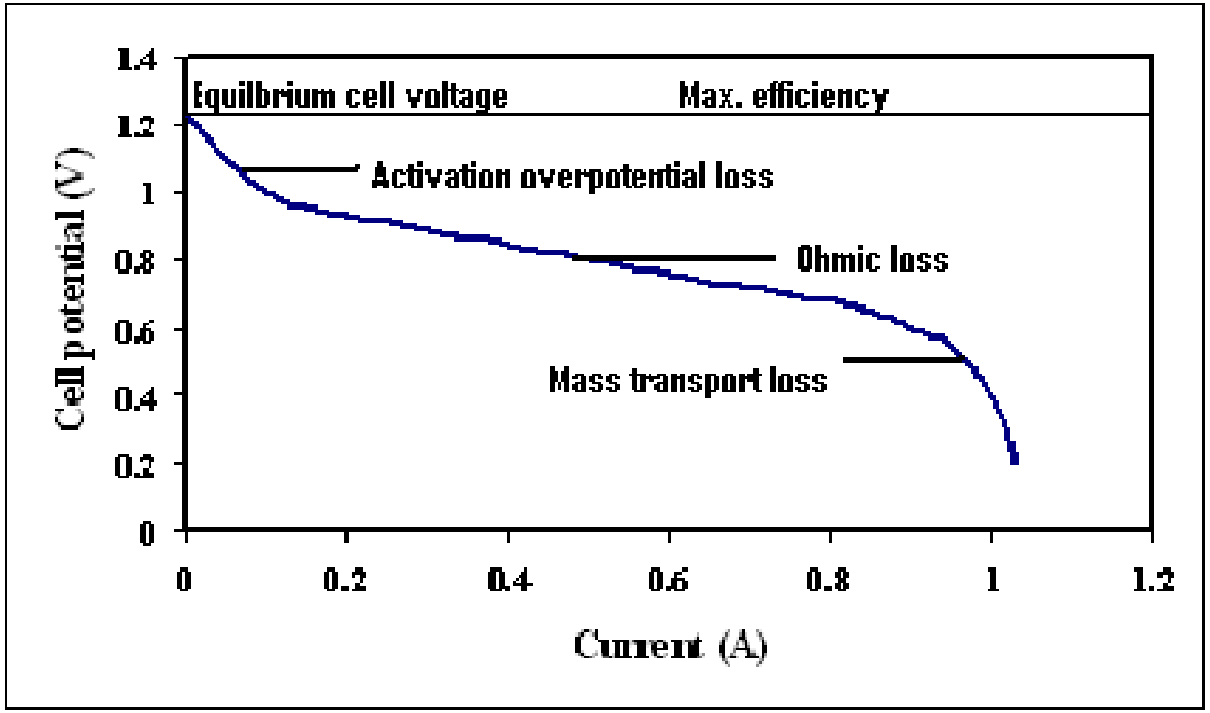
BioFC-Biological fuel cell, DHFC- hydrazine

DEFC-Ethanol fuel cell, DFAFC-formic acid

Main types of fuel cells with flow directions of reactants and products



Irreversibel Thermodynamics



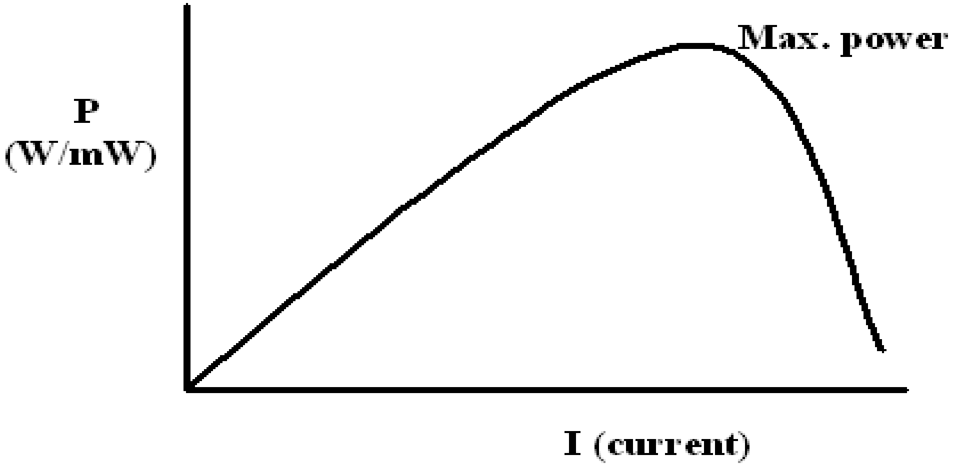
Polarization curve of a fuel cell and its inherent losses

Power (W or mW)

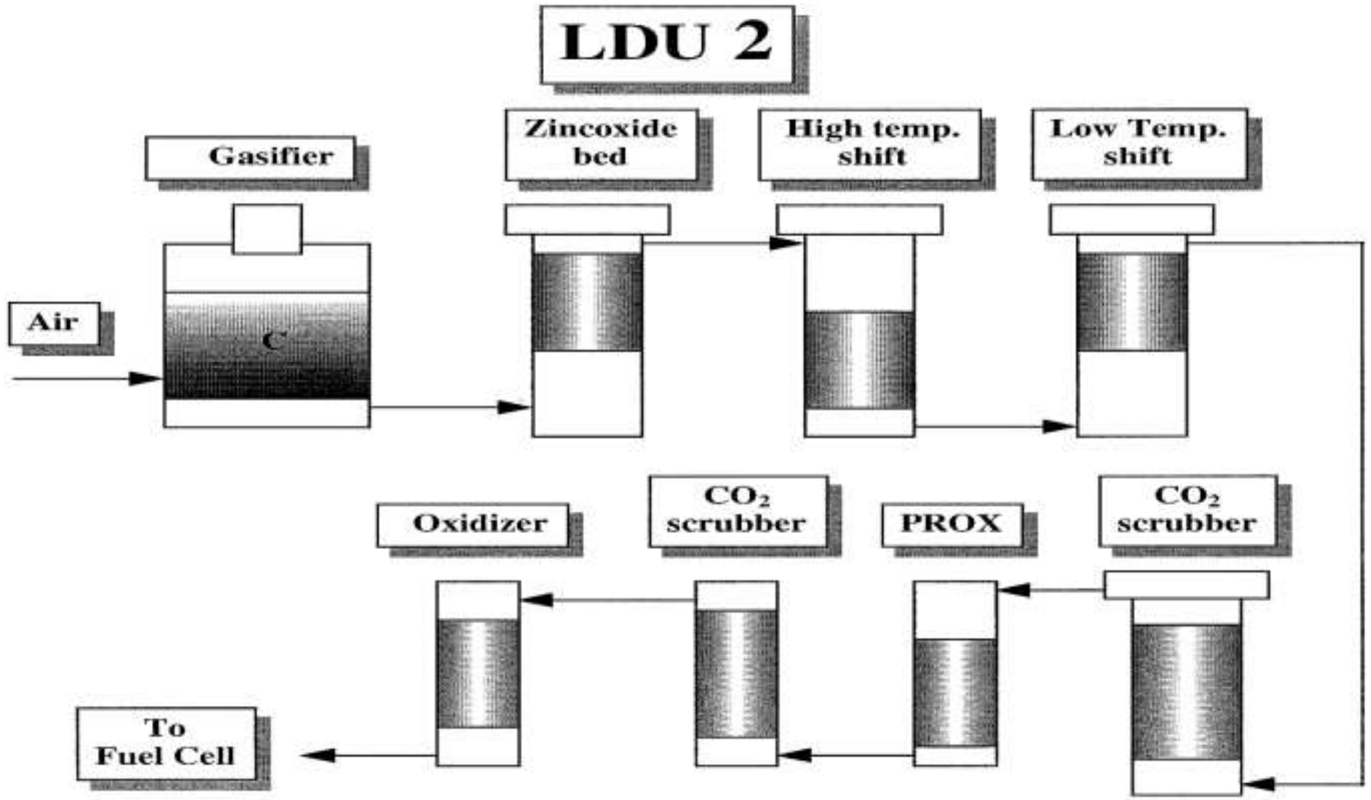
$P = E_{cell} \times I$

Power density (W/cm² or mW/cm²)

$P = E_{cell} \times I/A$



Integration of gasifier for H_2 production with AFC

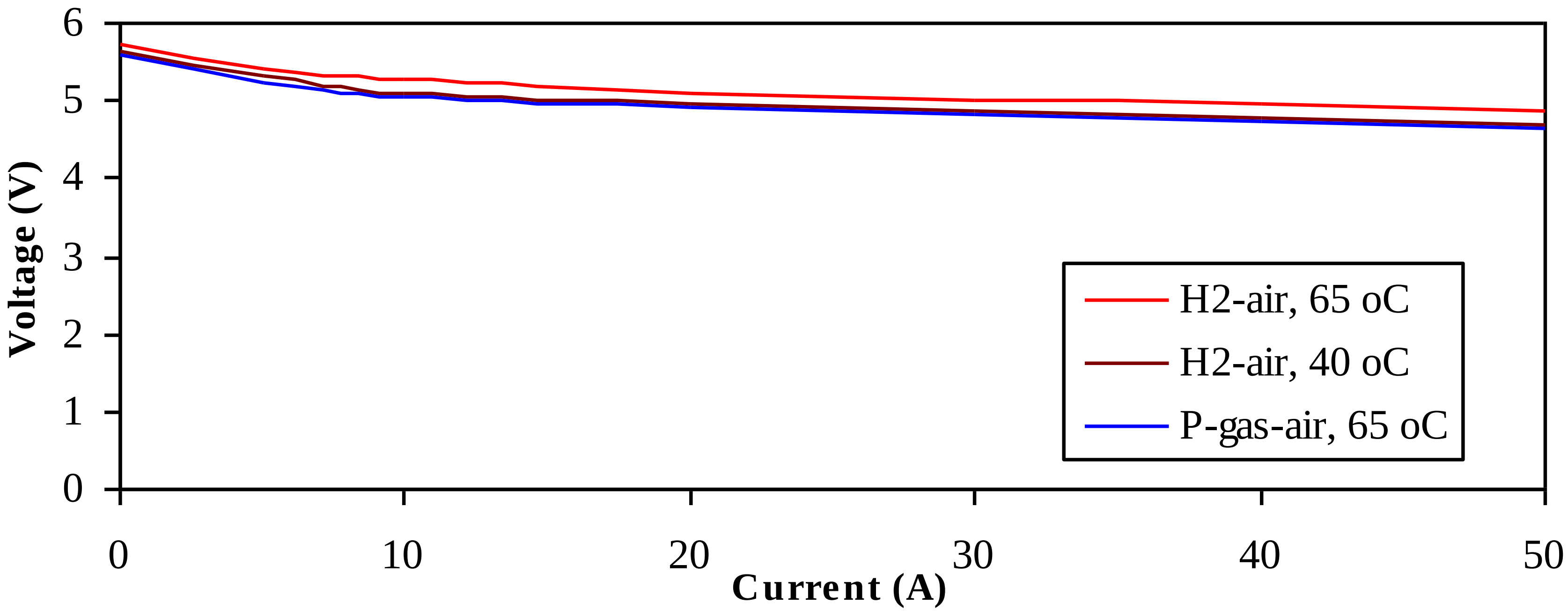


Fuel Enrichment and gas clean-up

Gas composition after the gasifier & the whole system

Gas	After gasifier (Vol.%)	After the whole system (Vol.%)
CO	15-21	0-15 ppm
H_2	3-6	20-30
CH_4	0.5-1	-----
CO_2	8-12	20-90 ppm
N_2	65-70	70-80

Fuel Cell performance with P-gas

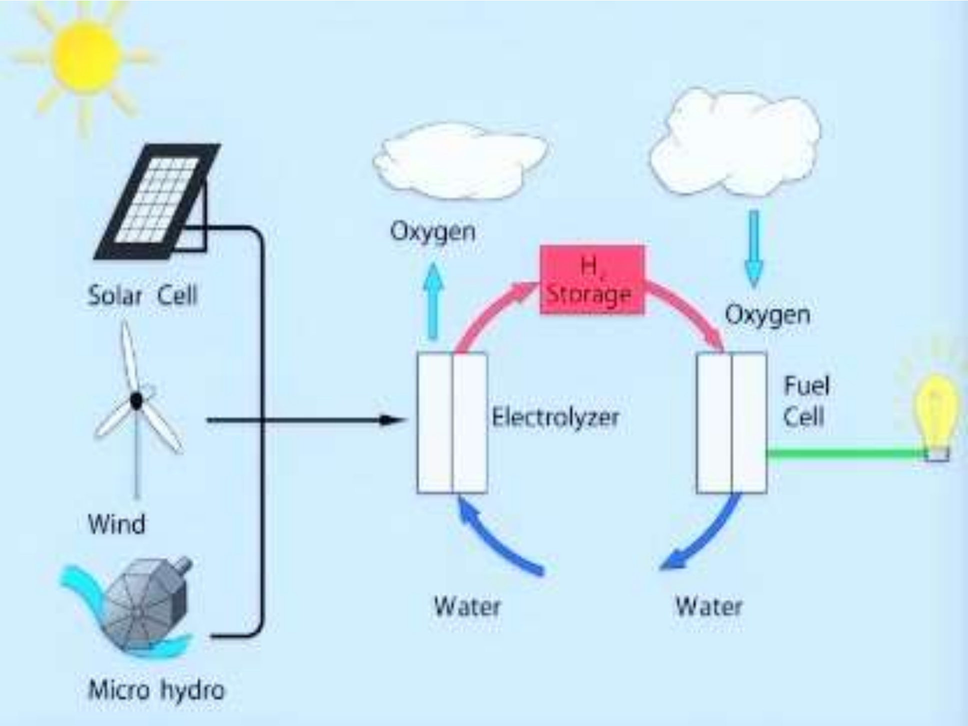


Performance of an AFC stack module.

Pure hydrogen 260 W

Producer gas 250 W

Conversion to hydrogen and storage in fuel cells



Geothermal

Biomass

Thank you for your attention