Air Liquide
creative oxygen

H_2 essential molecule for industry and Society

UNAFIC

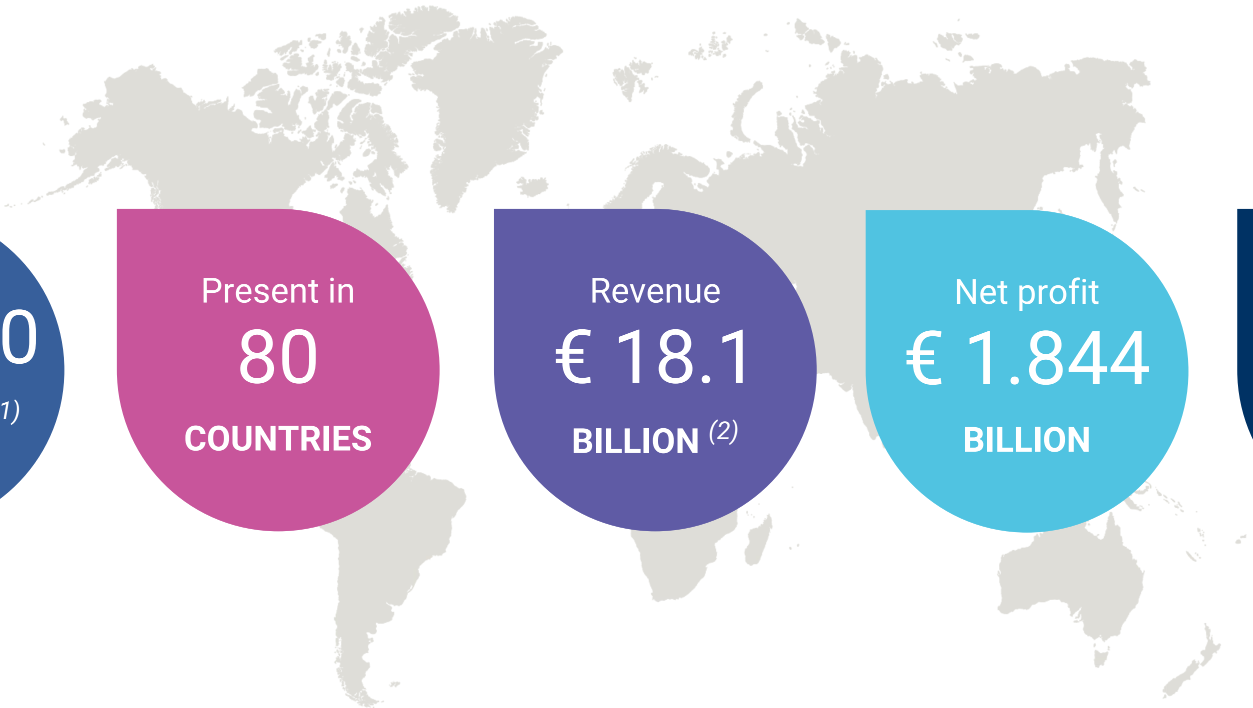
Régis Réau - 21st November 2017

Air Liquide
creative oxygen

1
The Air Liquide Group

2016 key figures

(Following the acquisition of Airgas on May 23rd, 2016)



~65,000
EMPLOYEES (1)

Present in
80
COUNTRIES

Revenue
€ 18.1
BILLION (2)

Net profit
€ 1.844
BILLION

More than
3 MILLION
CUSTOMERS & PATIENTS

(1) As of August 1st, 2017.
(2) Excluding Welding and Diving, restated as discontinued operations.

Unique expertise and skills

Separating the components of the **air** to take advantage of their properties

- O_2 — **OXYGEN**
- N_2 — **NITROGEN**
- Ar — **ARGON** AND **RARE GASES**

Producing molecules from **natural resources** of the Planet

- H_2 — **HYDROGEN**
- He — **HELIUM**
- SiH_4 — **SILANE**
- C_2H_2 — **ACETYLENE**
- CO — **CARBON MONOXIDE**

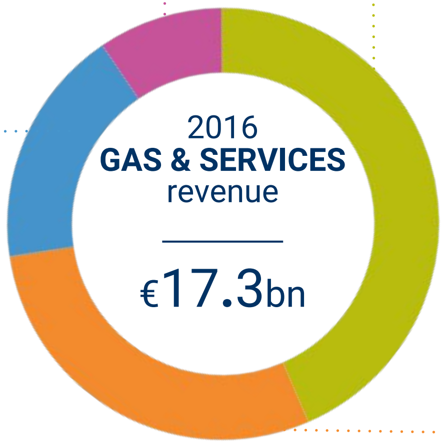
A diversified and solid business mix

ELECTRONICS
9%

Carrier gases
Electronic materials
Equipment & installations; Services

HEALTHCARE
18%

Hospitals
Home Healthcare
Hygiene
Specialty ingredients



INDUSTRIAL MERCHANT
44%

Bulk and cylinder gases
Wide variety of sectors and customer sizes

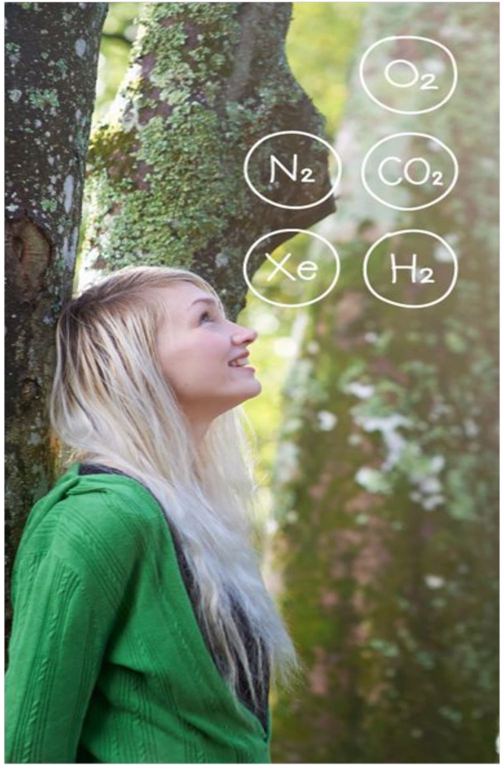
LARGE INDUSTRIES
29%

Air gases, hydrogen and CO
15-year or more contracts
Pipeline networks
Industrial basins

From Properties and Reactivity to Applications

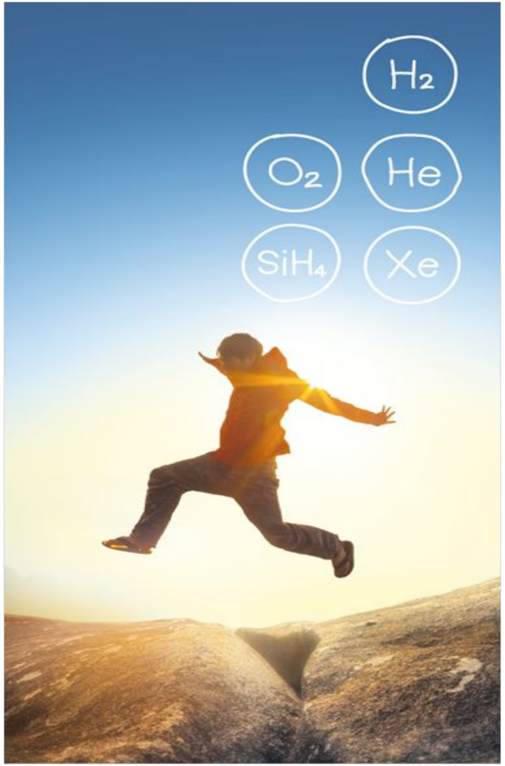
Air Liquide Territory: Essential Small Molecules

to life



to matter

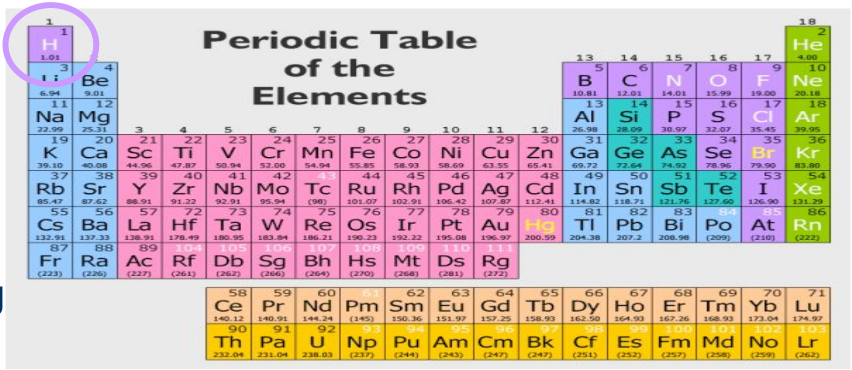
to energy



What is the H atom? What is the H2 molecules ?

- The first element of the periodic table
- The lightest element : atomic weight: 1.008
- Isotopes : H (99.98%), D (0.01%), T (t1/2 = 12.3 y)

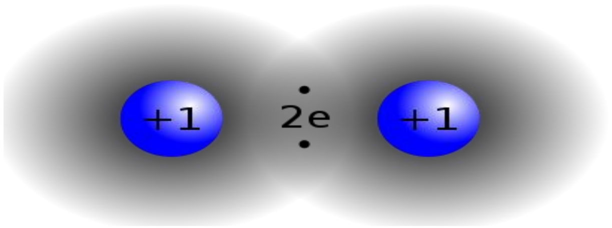
  Exists as H+, H-, H. (H_2O, CH_4, MgH_2…)



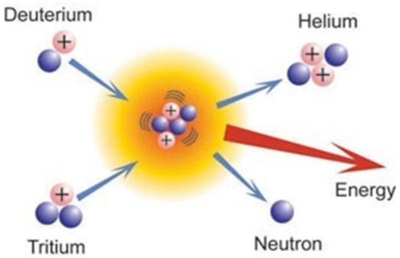
- The simplest molecule : low gas density (0.0852 kg
- Very stable bond : 436 kJ/mol (C-C, 350 kJ/mol)
- Combustible gas : $H_2 + ½ O_2 \rightarrow H_2O$ (- 242 kJ/mol)
- Energy density :

	Wh/kg	Wh/l
H_2	39	1.6
CH_4	15	10
Diesel	13	10
Jet Fuel	12	10

H-H molecule



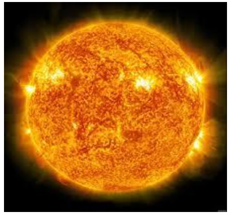
H (D, T, H+, H-, H.) and H_2 in Nature



Universe

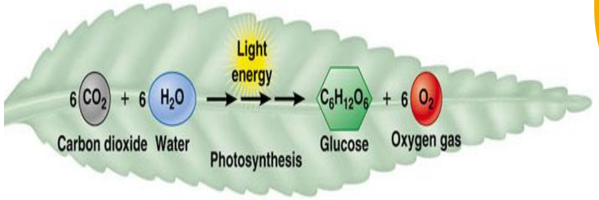
H-feedstocks

H_2O, fossil fuels
C_nH_{2n+2}, biomass -(CH_2O)-



the most abundant element
essential to energy

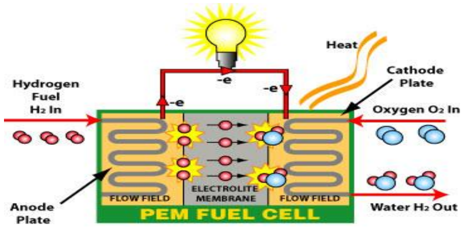
Photosystem(I)



$H_2O \rightarrow 2\,H^+ + 2\,e^- + O_2$

Fuel Cells :

$H_2 + \frac{1}{2}\,O_2 \rightarrow H_2O$
+ electricity



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

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

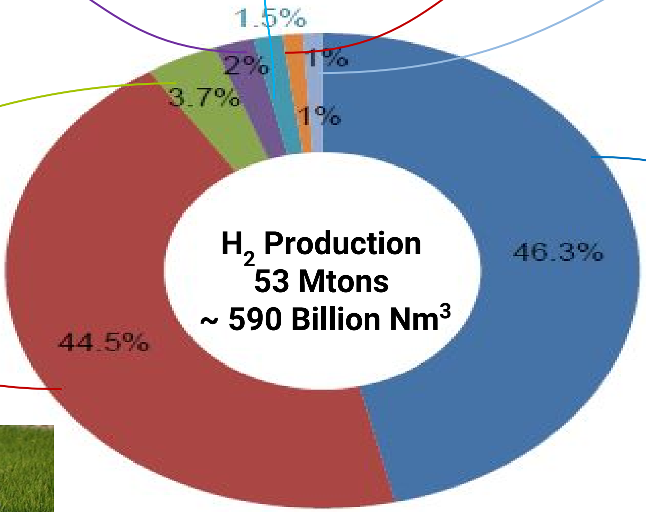
H_2 in modern life : a versatile molecule

Materials processing
Flat glasses,
Heat treatment
Reducing atmospheres

Electronics
Reactant & gas carrier for semiconductors fabrication

Food industry
Oil hydrogenation

Space
Rocket fuel



Methanol production

$CO + 2\ H_2 \rightarrow CH_3OH$

Petroleum refining
Hydrodesulfurization
Hydrocracking

Ammonia synthesis
Haber-Bosch process
$N_2 + 3\ H_2 \rightarrow 2\ NH_3$

2015: Towards H_2 mobility
Hydrogen fuel cell vehicle

Energy : GreenHouse Gases (CO_2, CH_4 , N_2O…)

Cities : 2%

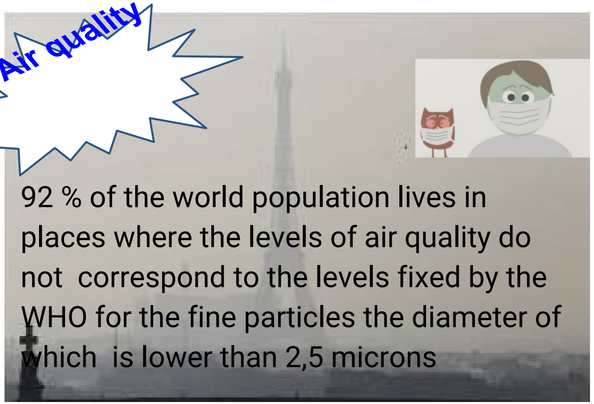
global land area but 70% of CO_2 emissions

COP21 · CMP11
PARIS 2015
UN CLIMATE CHANGE CONFERENCE

GHG emissions

Europe & Japan, -80% (2050); USA -28% (2030), China -20% (2030)…

Air quality



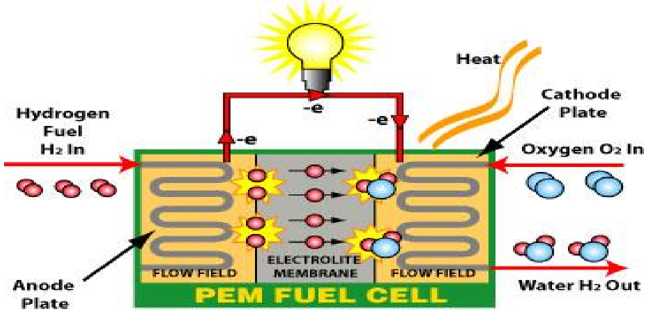
92 % of the world population lives in places where the levels of air quality do not correspond to the levels fixed by the WHO for the fine particles the diameter of which is lower than 2,5 microns

Transportation

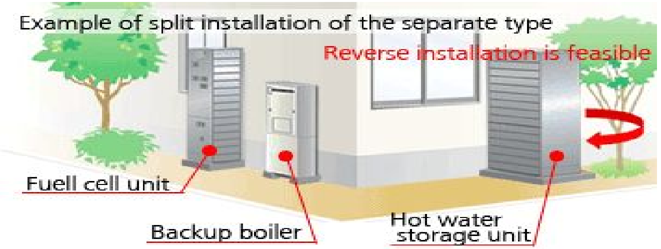
26% of total GHG emissions

H2

Fuel Cell : Electrical Vehicules, H_2-mobility



and also residential: Smart cities !



RESIDENTIAL FUEL CELL ENE·FARM

Panasonic

> 150000 installations (Japan)

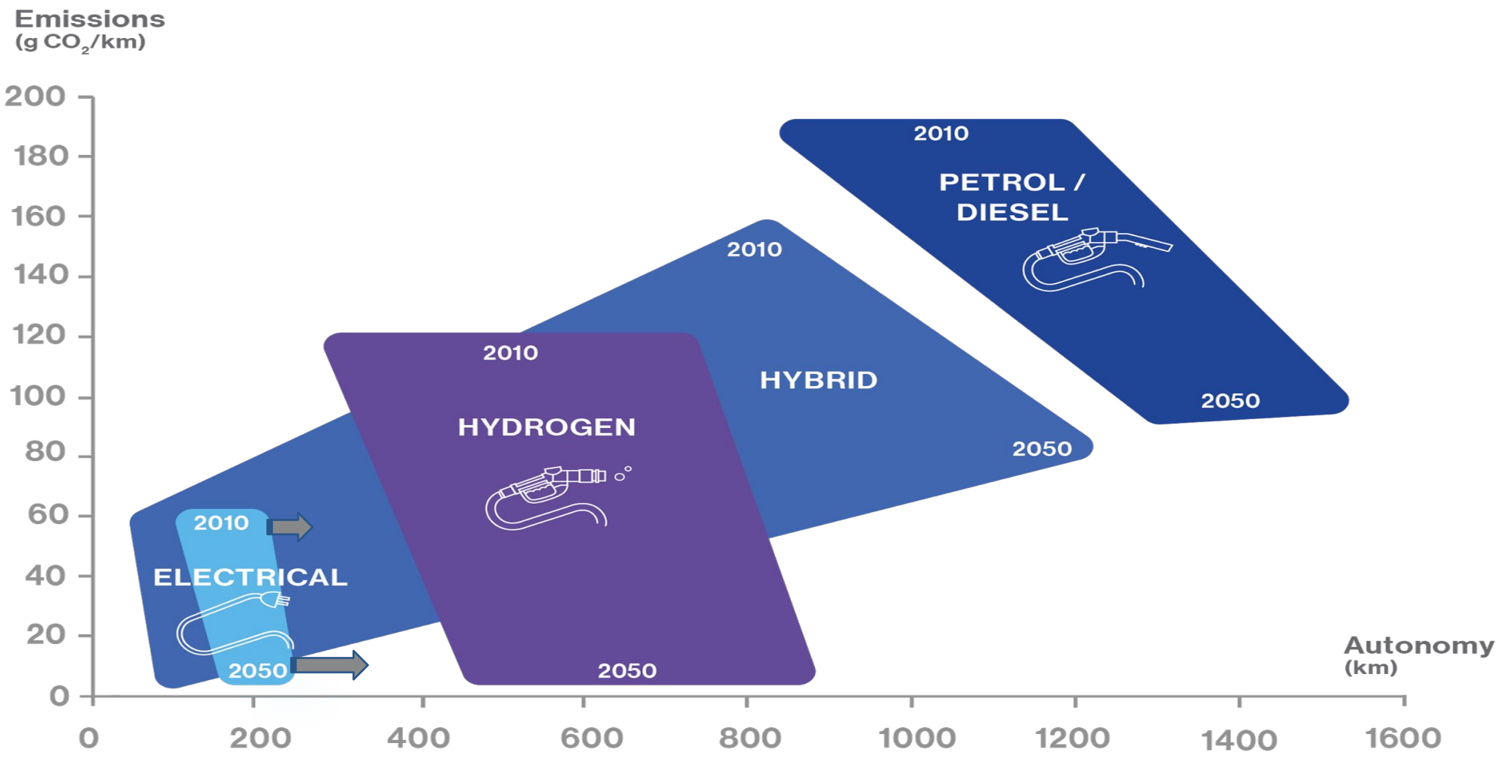
H_2 + ½ O_2 → H_2O + electricity

No CO_2/particules emissions

Good efficiency

H_2: the molecule for energy storage

Hydrogen: a competitive solution for clean transportation



Smart Governance & smart citizens to accompany new usages…

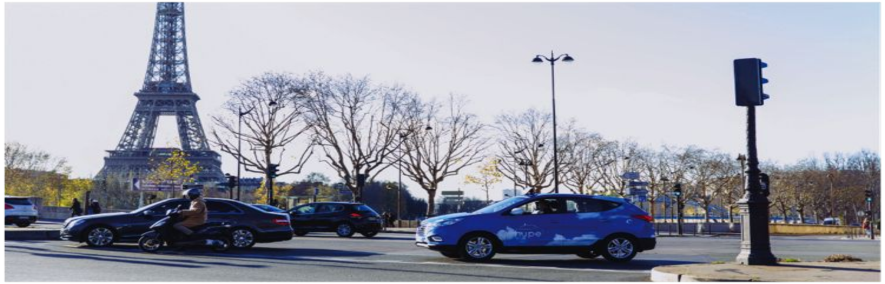
hype The «taxi of tomorrow»

An emission-free Paris

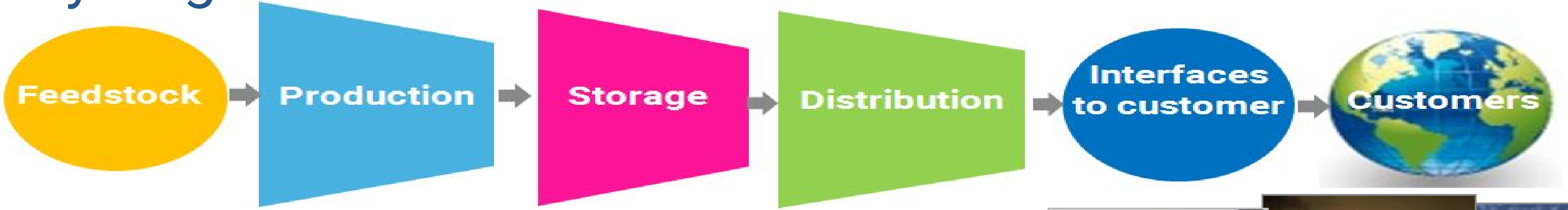
Targeting
70 taxis
by the end of 2016

and 600
within 3 years

Speeding-up energy transition for taxis



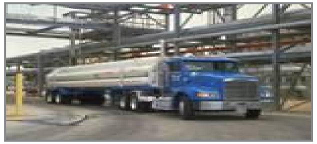
Air Liquide: + 50 years of experience on the hydrogen value chain



95% in large central plants
Mainly from fossil fuels

Pipeline

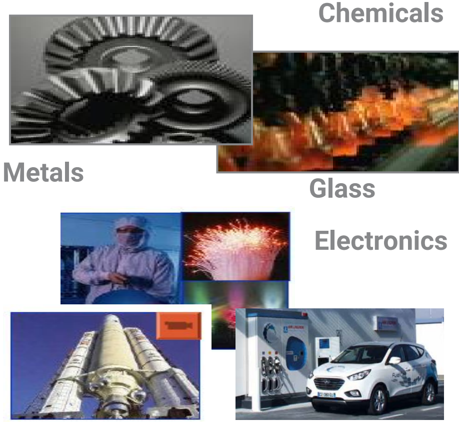
Tanks (liquid)



Trailers (gas)

Cylinders (gas)

H_2 charging stations

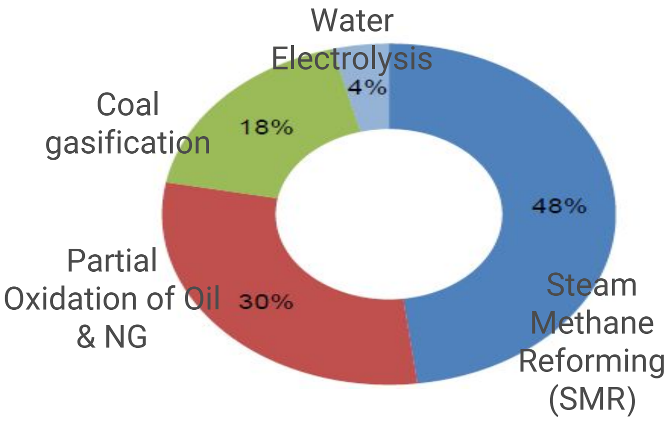


SUPPLY CHAIN
12.5 Billion Nm^3 H_2 /year

Safe | Efficient | Reliable Competitive Sustainable

Hydrogen generation today

- Hydrogen is produced at large scale (>> 150,000 Nm^3/h)
- 96 % H_2 produced is from fossil fuels : $CH_4 + 2 H_2O \rightarrow 4 H_2 + CO_2$
- 4 % H_2 produced is from water: $H_2O \rightarrow H_2 + ½ O_2$



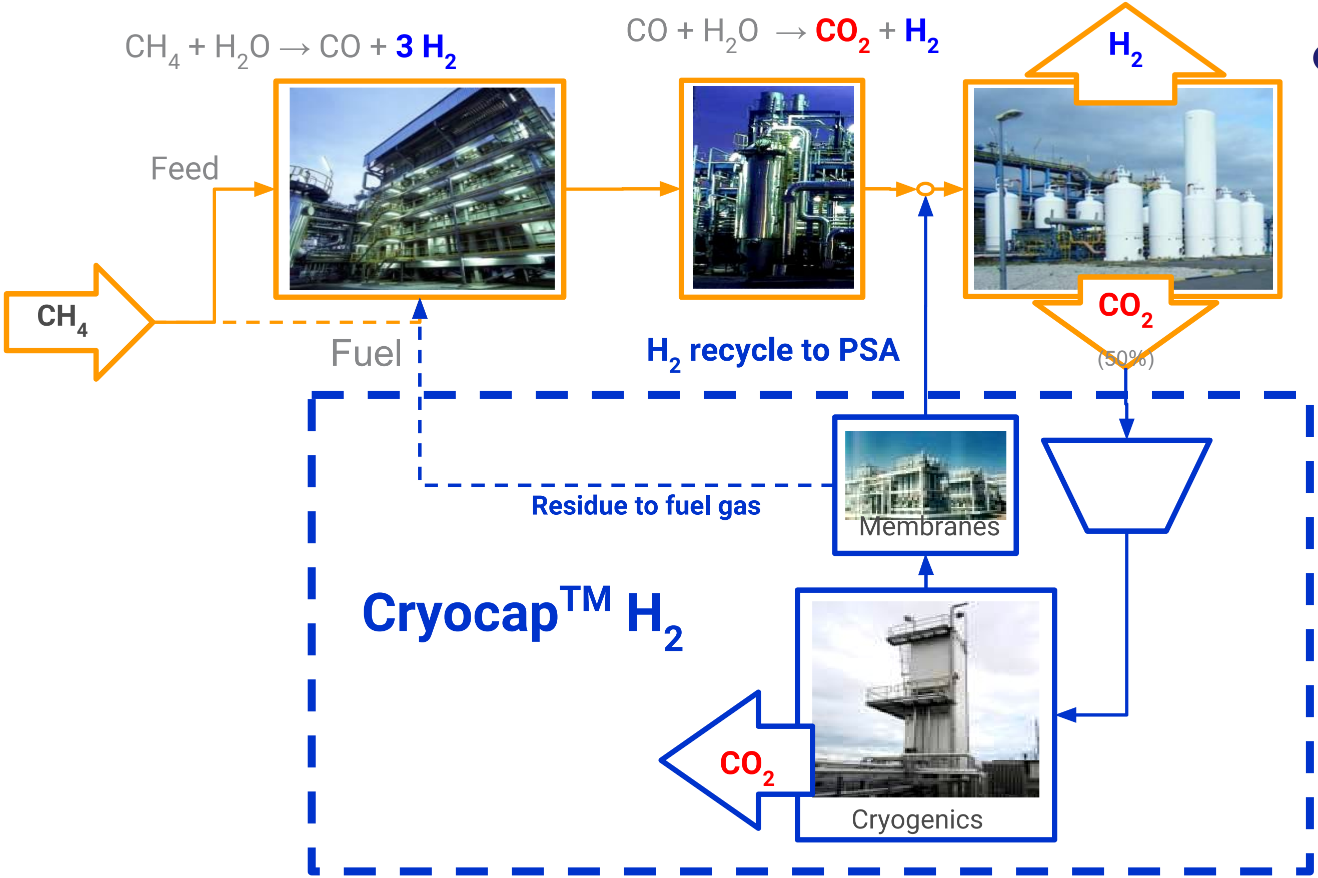
2010 Global H_2 Production

53 Mtons (~ 590 Billion Nm^3)

Air Liquide Yanbu H_2 SMR plant (Saudi Arabia Kingdom)

Total hydrogen capacity of 340,000 Nm³/hour

CO_2 capture from SMR plants (Cryocap™ H_2)

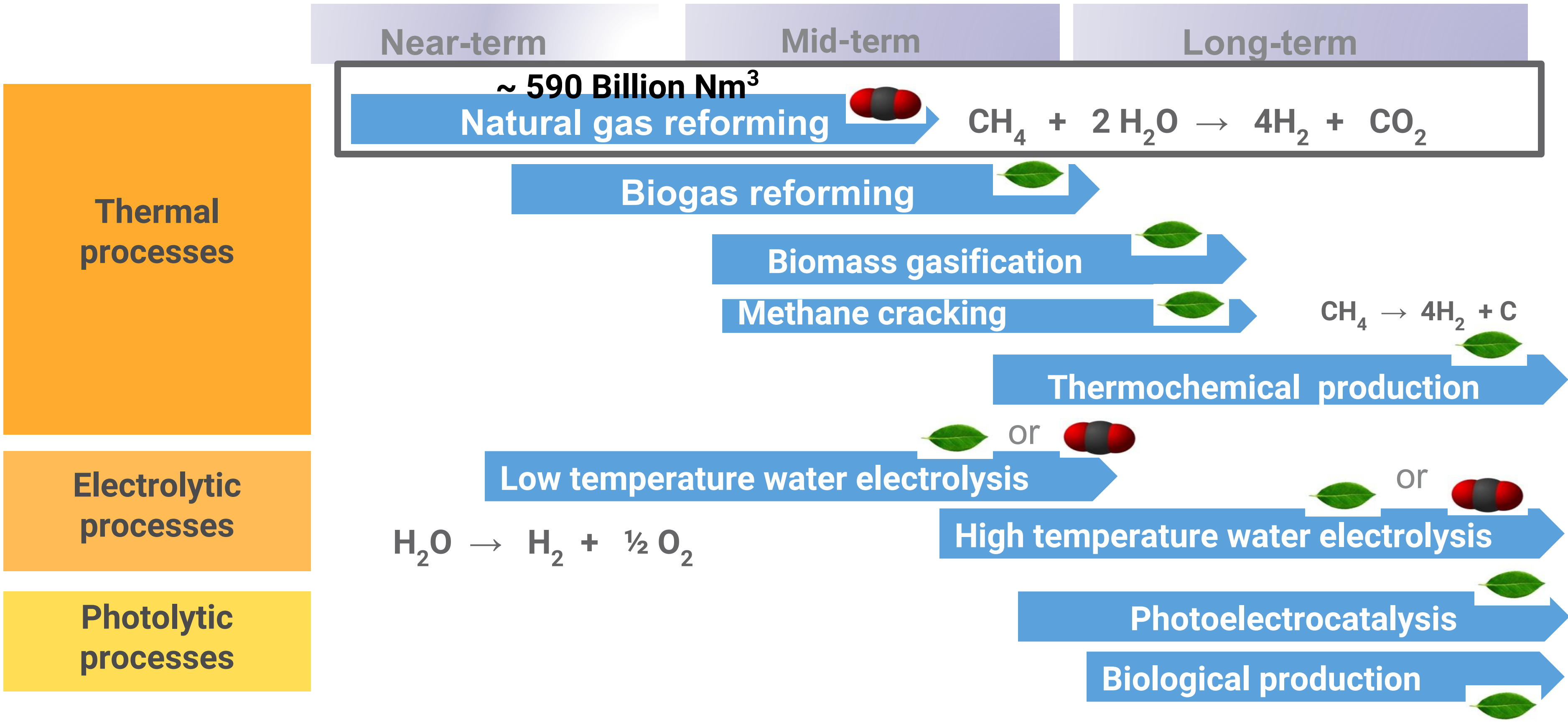


First demo at

Port-Jerome SMR

(47,000 Nm^3/h H_2)

Challenge : environmental friendly H_2 productions



Urban agriculture / vertical farms : feeding the cities

World's largest vertical farm
opens this year in the US
(Newark, April 15)

Waste (organic)

Fermentation

Electricity

Biogas (CH_4 + CO_2)

Biogas Upgrading

Steam

Bio-CH_4

SMR

Bio-H_2

+ Bio-energy for Cities….

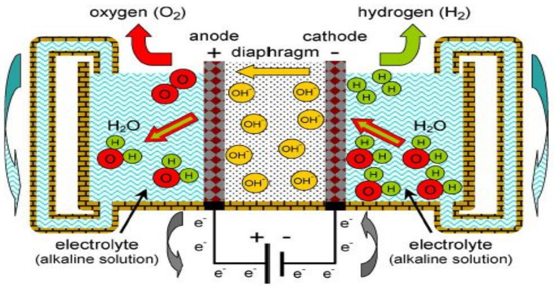
micro-methanisation
(Tryon)

Polymeric hollow
fiber bundle

"New York City converts waste to biogas …" April 2014

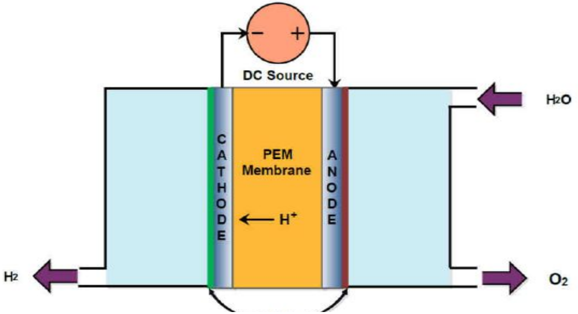
H_2 Production by low temperature water electrolysis

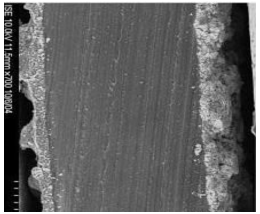
Electrochemical reaction: H_2O + electricity → H_2 + ½ O_2



Cathode (HER): $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

Anode (OER): $2OH^- \rightarrow ½ O_2 + H_2O + 2e-$





Cathode (HER): $2H^+ + 2e- \rightarrow H_2$

Anode (OER): $H_2O \rightarrow ½ O_2 + 2H^+ + 2e-$

Alkaline electrolysis

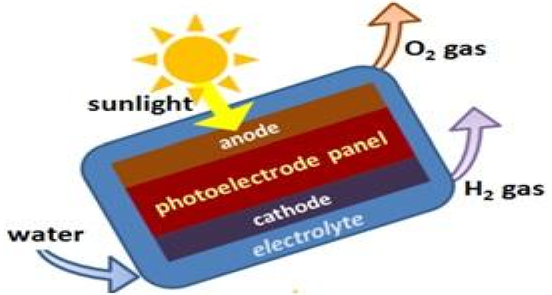
- Low temperature: 70-100°C
- Well established technique up to large scale systems
- Cheap materials: mainly Ni-based electrocatalysts

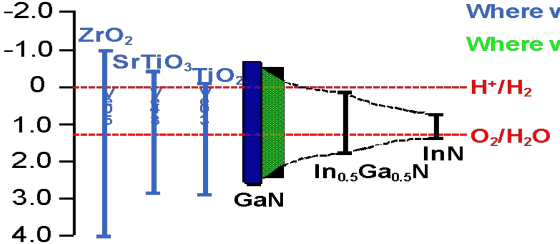
Proton exchange membrane (PEM) electrolysis

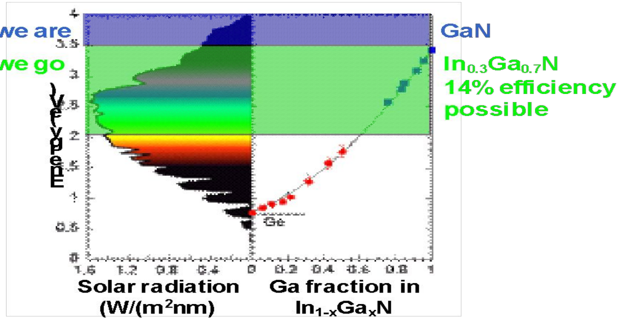
- Low temperature: 80 °C
- Hydrogen side: Platinum (1-6 mg/cm2)
- Oxygen side: Platinum, Iridium, Ruthenium and their oxides and mixtures (1-2 mg/cm2)
- The most difficult part: the oxygen electrode (oxidation of water to oxygen)

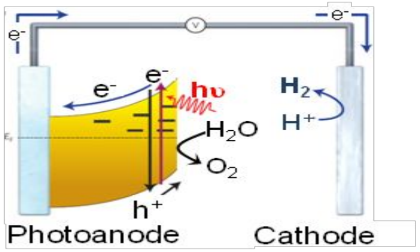
Challenges
- Reduce cost
- Replace or reduce amount of noble & rare metals

H_2 Production by photoelectrocatalytic water splitting







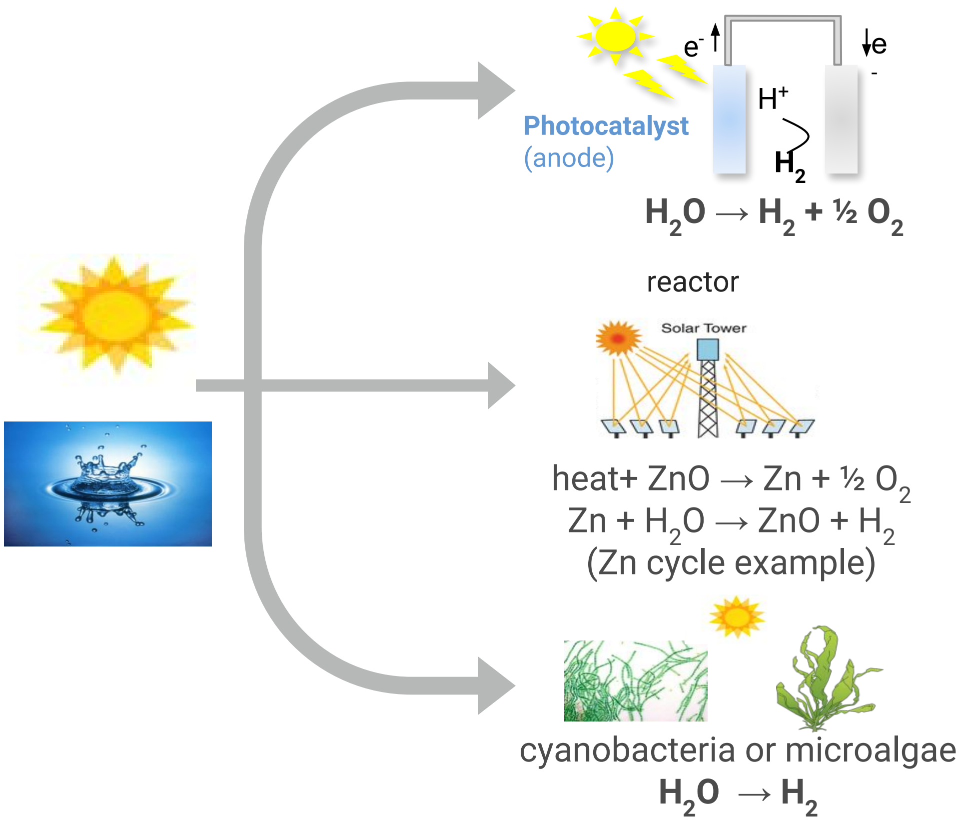


$$H_2O \rightarrow H_2 + ½\, O_2$$

Challenges

- Materials efficiency (photocatalyst bandgap for maximum absorption of solar spectrum)
- Materials stability and durability in aqueous solution
- Materials cost

The future ?????? Solar-H_2 !



Photoelectrochemical water splitting

More research needed:

- highly efficient photocatalyst durability
- low cost materials
- large scale process

Thermochemical H_2 production

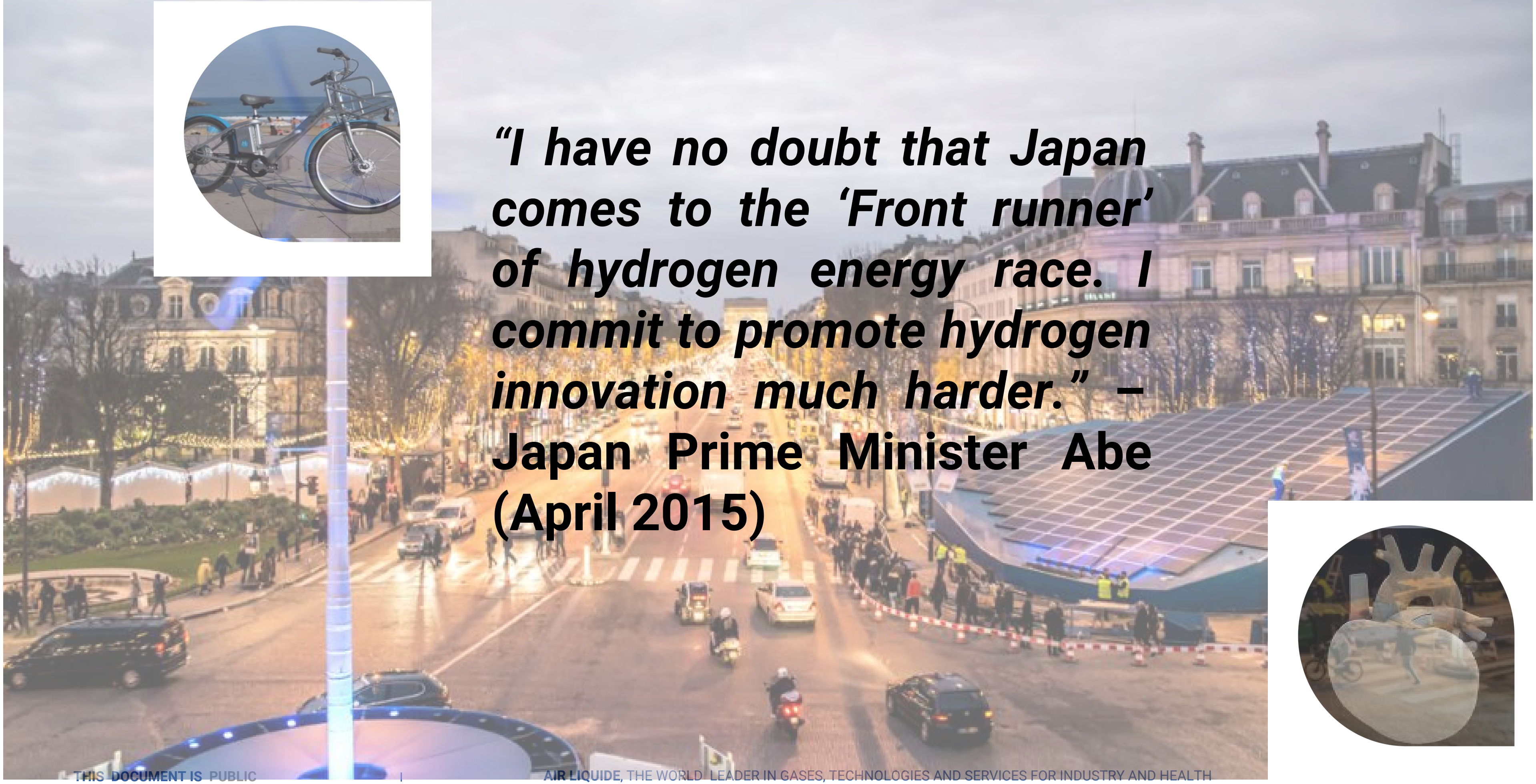
More research needed:

- durable materials
- low cost receivers/reactors
- heat transfer for chemical cycle

Biological H_2 production

More research needed:

- efficient microorganisms
- single organism system
- high volume manufacturing process



“I have no doubt that Japan comes to the ‘Front runner’ of hydrogen energy race. I commit to promote hydrogen innovation much harder.” – **Japan Prime Minister Abe (April 2015)**

Thank you for your attention

For further information

encyclopedia.
airliquide.com

airliquide.com

Open Innovation
@Air Liquide

Régis REAU

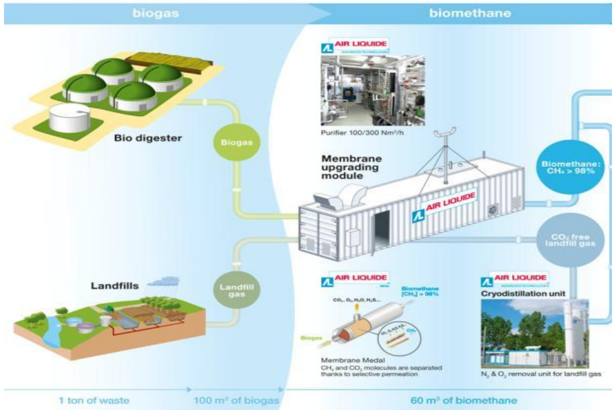
Scientific Director
regis.reau@airliquide.com

New catalytic routes to produce clean hydrogen from methane

Biogas reforming

$$CH_4 + CO_2 \rightarrow 2H_2 + 2CO$$

(dry reforming)



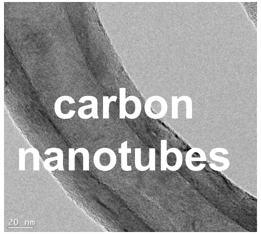
Challenges for catalysts due to CO_2

- Efficiency
- Durability
- Activity (carbon formation higher than SMR)

Catalytic CH4 cracking

$$CH_4 \rightarrow 2\,H_2 + C$$

- Pure hydrogen
- High value carbon nanomaterial
- No CO_2 emissions



Challenges for catalysts

- Efficiency
- Durability
- Activity
- Regeneration ?

PV/electrolyzer system

<u>Principle:</u> PV cell and water electrolyzer are **spatially separated systems** with power conditioning system

PV array

Electrolyzer powered electricity

$$H_2O \rightarrow H_2 + ½ O_2$$

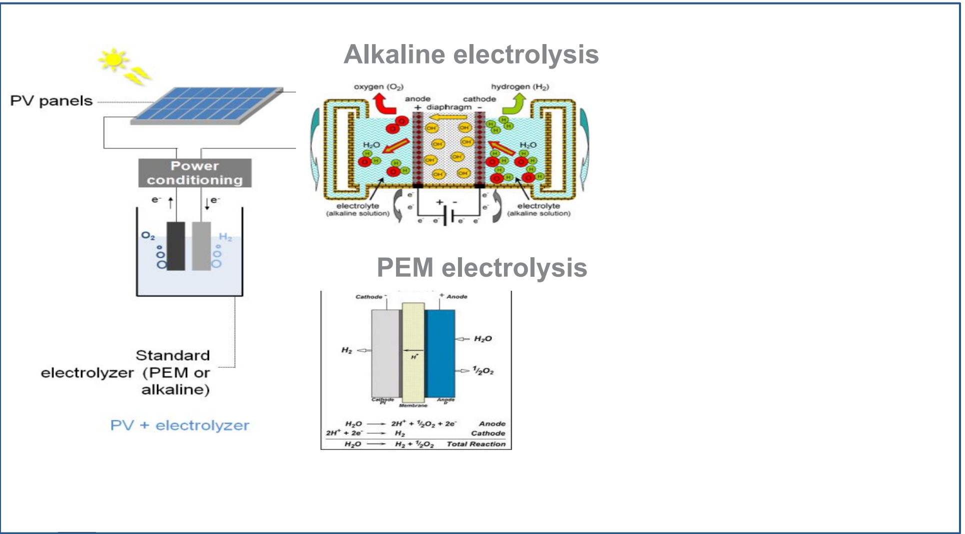
ΔH (25 °C, 1 bar) = 285.83 kJ/mol

(3.54 kWh/Nm3 H_2)

<u>Strengths:</u> available technologies

<u>**Current limitations**</u>:

- solar electricity is the dominant cost
- high capital costs (materials)



Sun to H_2 efficiency: up to 13 %
(65 % for electrolyzer and 20 % for PV cell)

possible improvements but no disruptive technologies are expected