

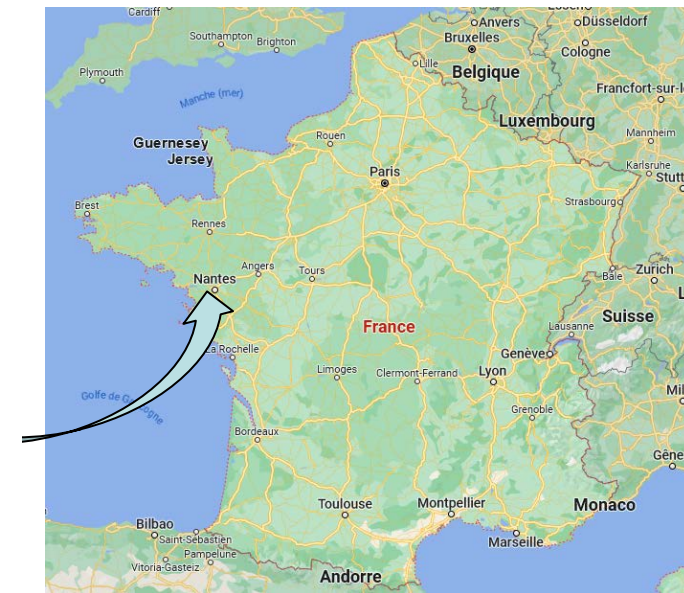


Production, storage and conversion of hydrogen into electricity: technological achievements and remaining challenges

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Jean Rouxel - France
Electrochemical Storage and
Conversion of Energy group:
Fuel cells & Electrolyzers team



Outline

Challenges...

Conclusion

Recycling

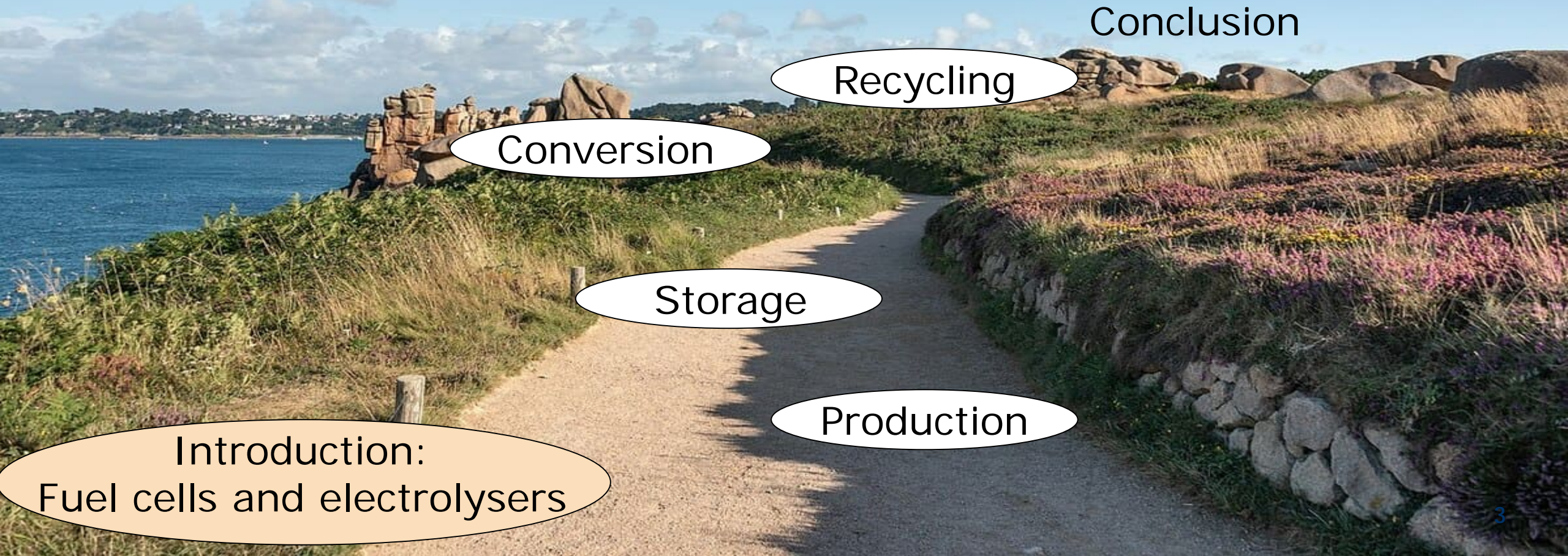
Conversion

Storage

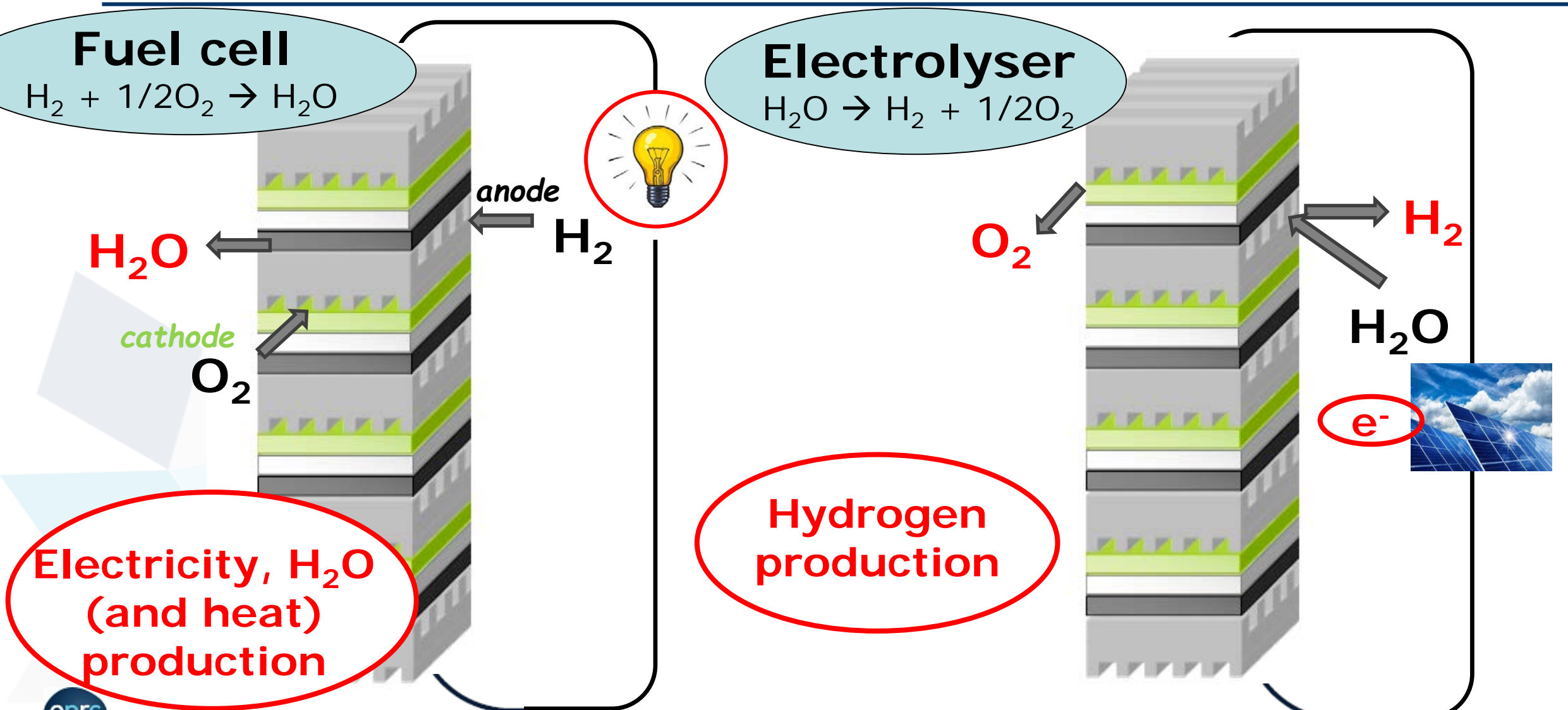
Production

Introduction:
Fuel cells and electrolysers

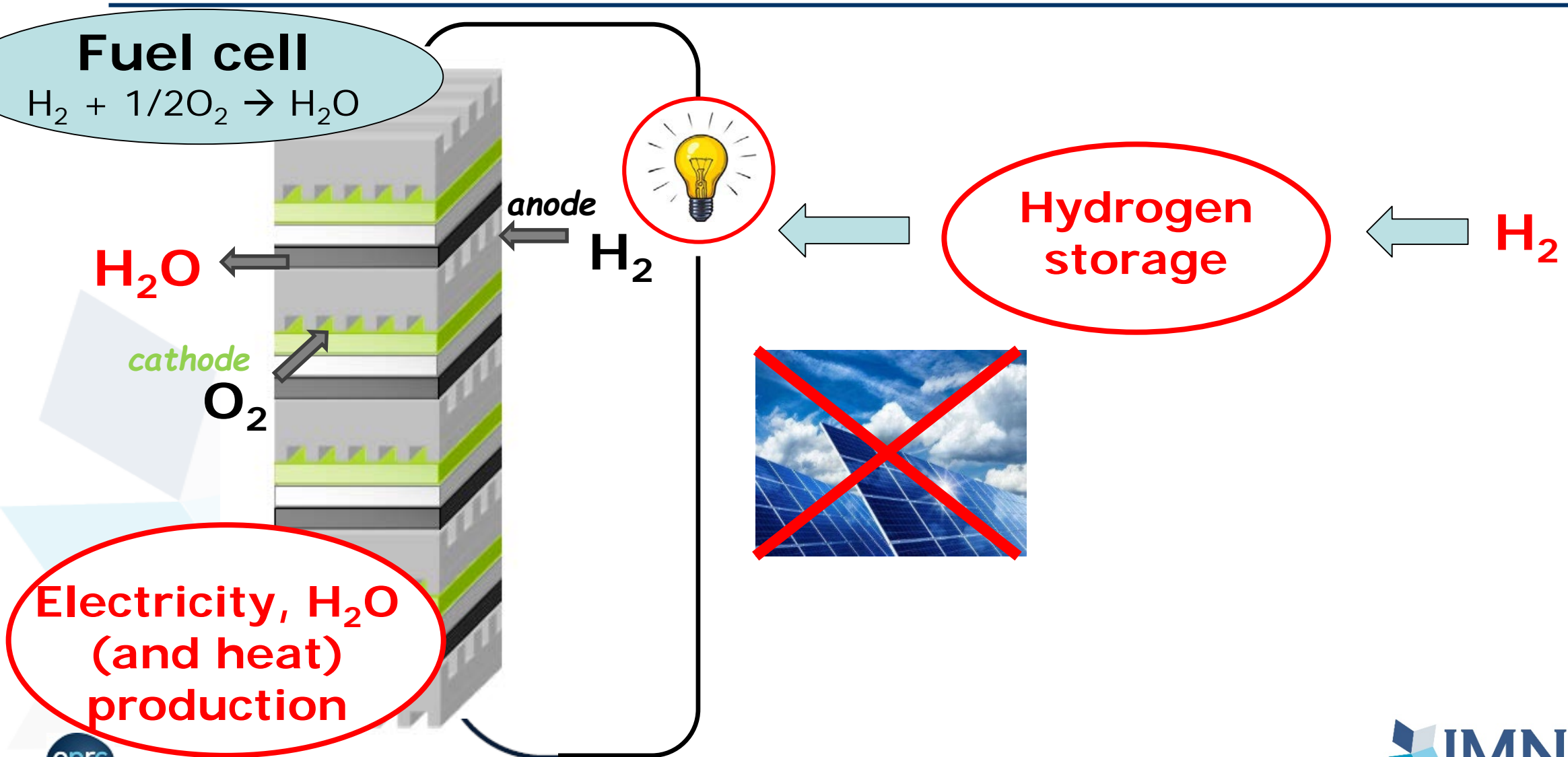
Outline



What is a fuel cell? An electrolyser?



What is a fuel cell? An electrolyser?



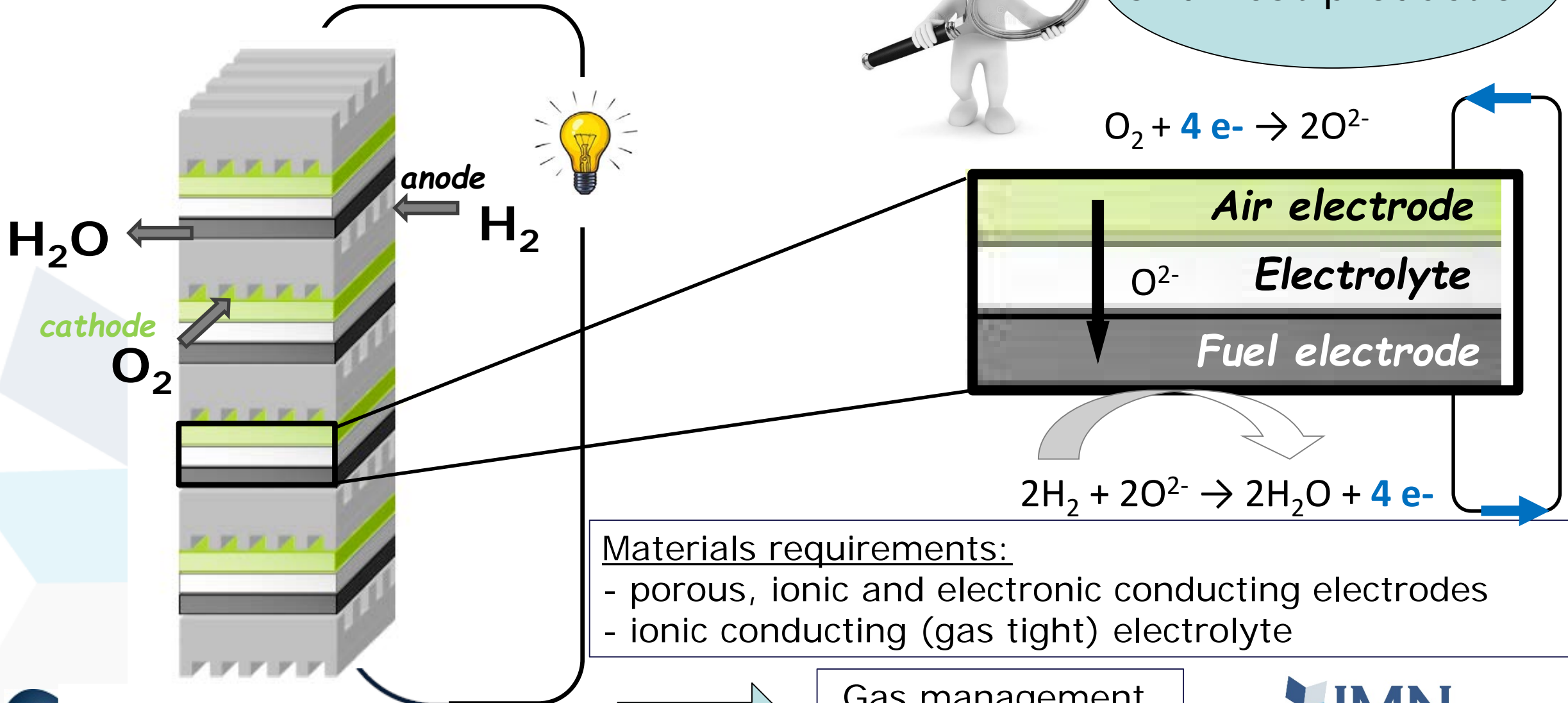
Fuel cell
 $H_2 + 1/2O_2 \rightarrow H_2O$

Hydrogen storage

Electricity, H_2O (and heat) production

What about the cell?

FC: Electricity, H₂O and heat production

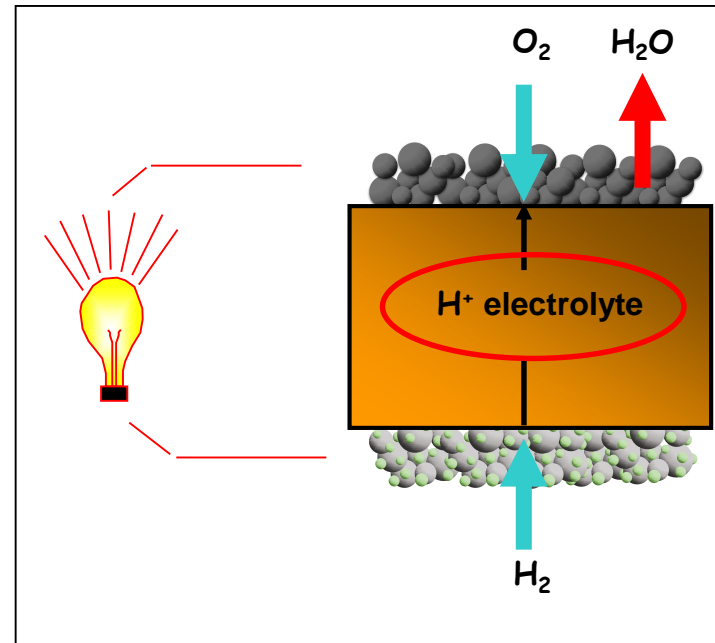
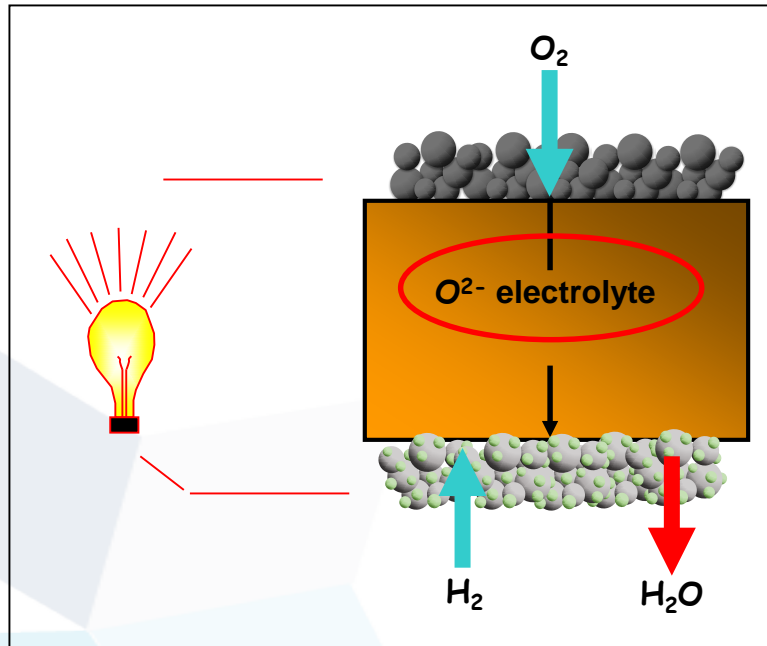


- Materials requirements:
- porous, ionic and electronic conducting electrodes
 - ionic conducting (gas tight) electrolyte

stack →

Gas management, connections...

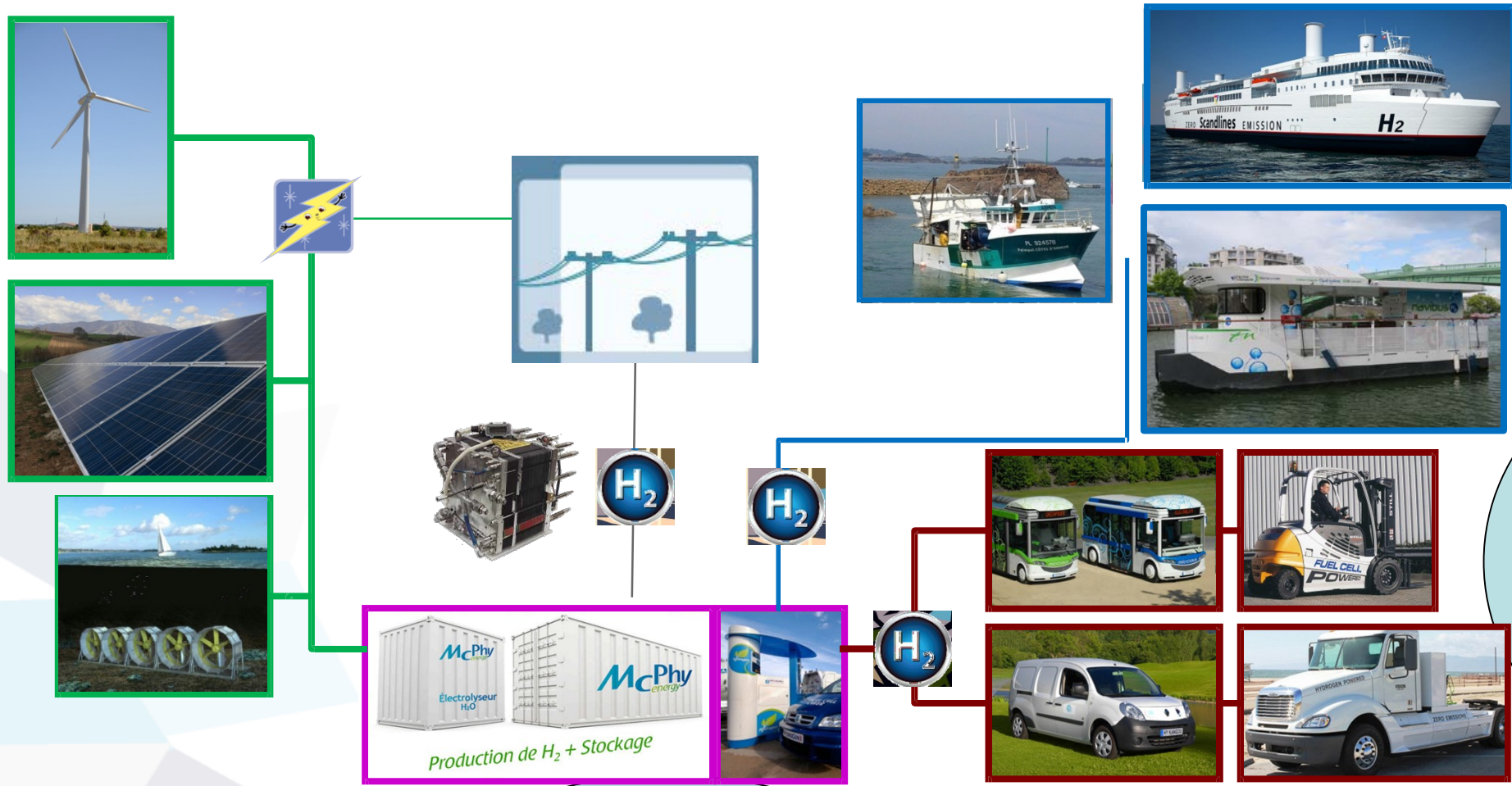
Different types...



... depending on electrolyte:

- Ion transported...
- Temperature allowing conductivity...

Hydrogen... associated to renewable energies

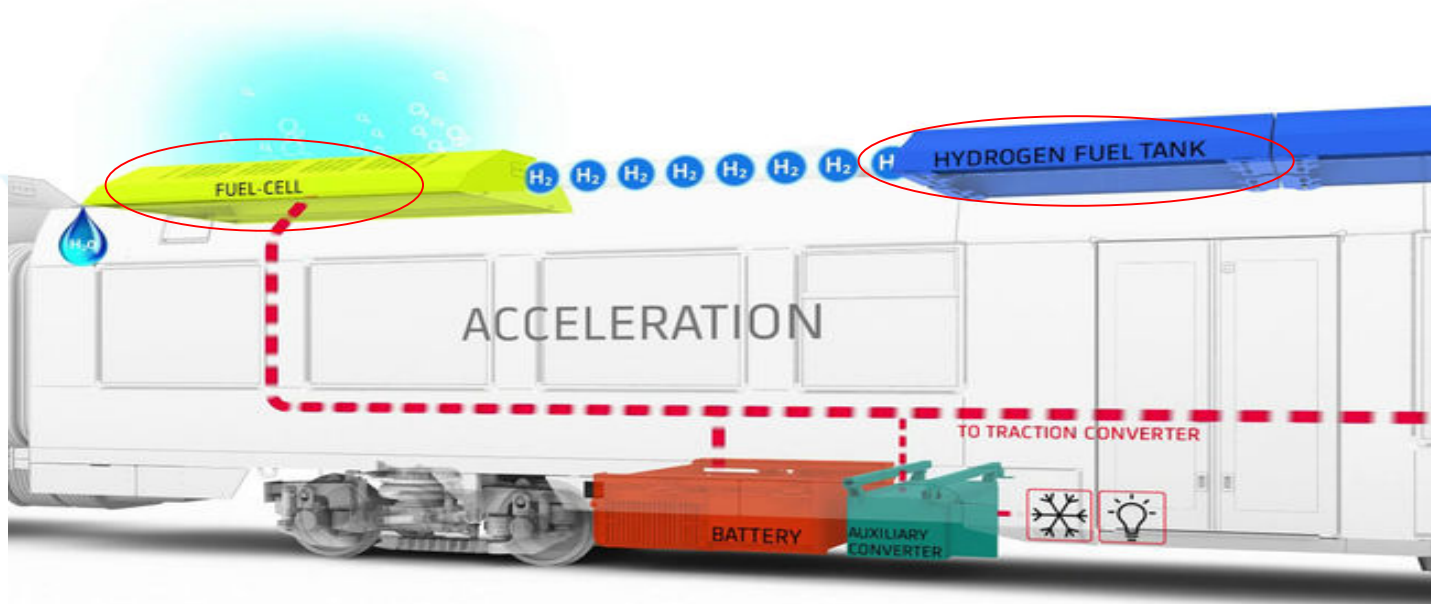


Applications in « heavy » mobility: ships, trains, trucks...

Stationary applications



Heavy mobility...



ALSTOM CORADIA ILINT
(Germany)

Reaching carbon-free autonomy of isolated territories

Pass « Le Palet » : Refuge powered by solar electricity...



- wasted during a part of the year for lack of means to store it
- completed by a diesel or gasoline generator during other parts of the year (numerous visitors)



In 2015, electrolyzers, H₂ storage, FCs (+ batteries)

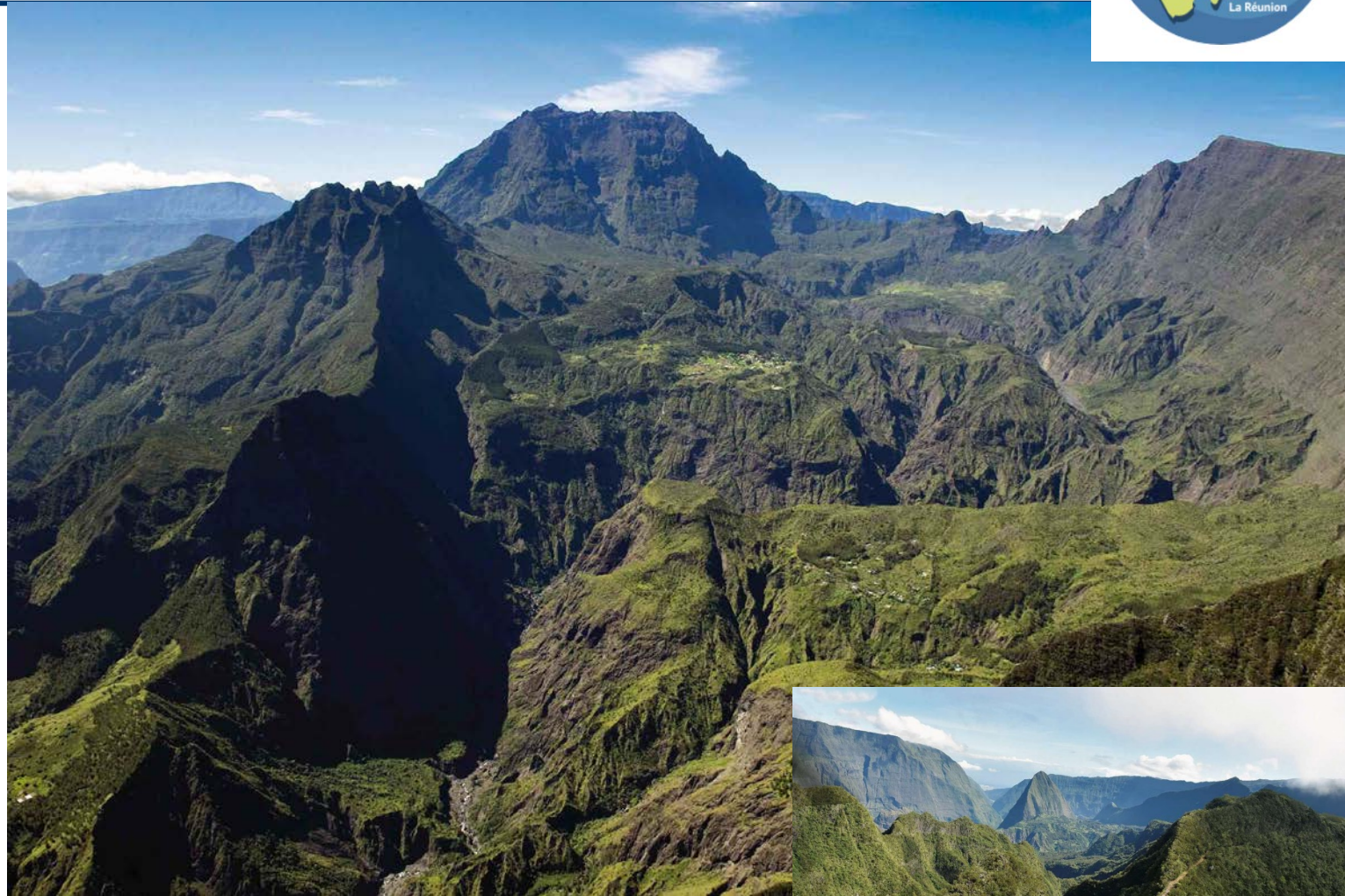
Total autonomy of the building, with better comfort for visitors (charge of electronic devices!) (1-30 MWh/y, -30→30°C)

- Financial support from FEDER,
- 5 companies: Gest'Hydrogène, Gest'Performance, MaHyTec, Powidian, WaechterÉnergies.

Carbon-free autonomy of isolated territories



La Nouvelle at La Réunion:
(excluded from the electrical grid and
the road network: foot path or
helicopter!)



In 2016, micro-grid with batteries,
electrolysers, H₂ storage, FCs*

→ Total autonomy of some buildings
(school, health center, ONF, ...)

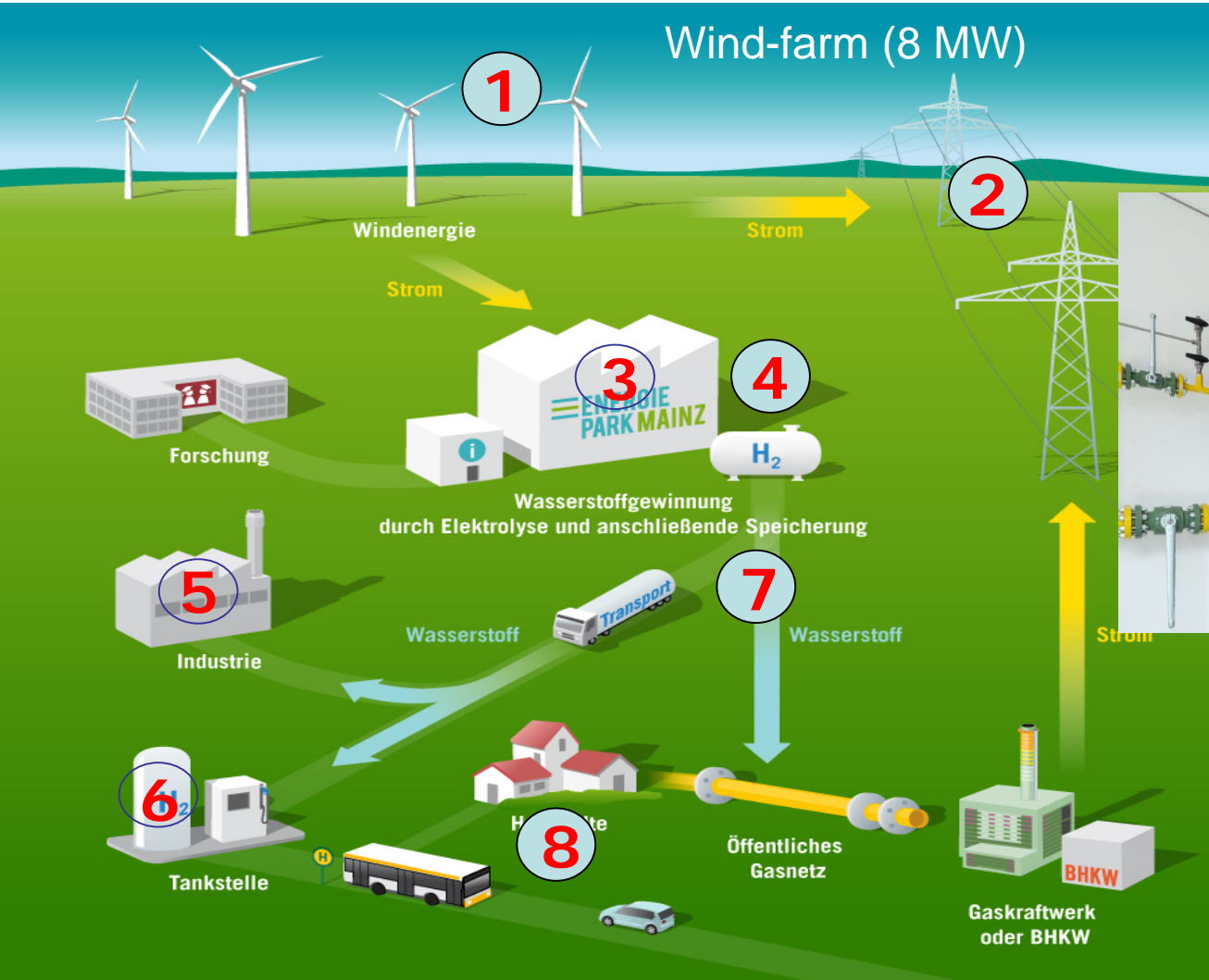
*European Regional Development Fund (ERDF)
... EDF and SIDELEC for local distribution

Carbon-free autonomy of isolated territories



Coupling with wind farms...

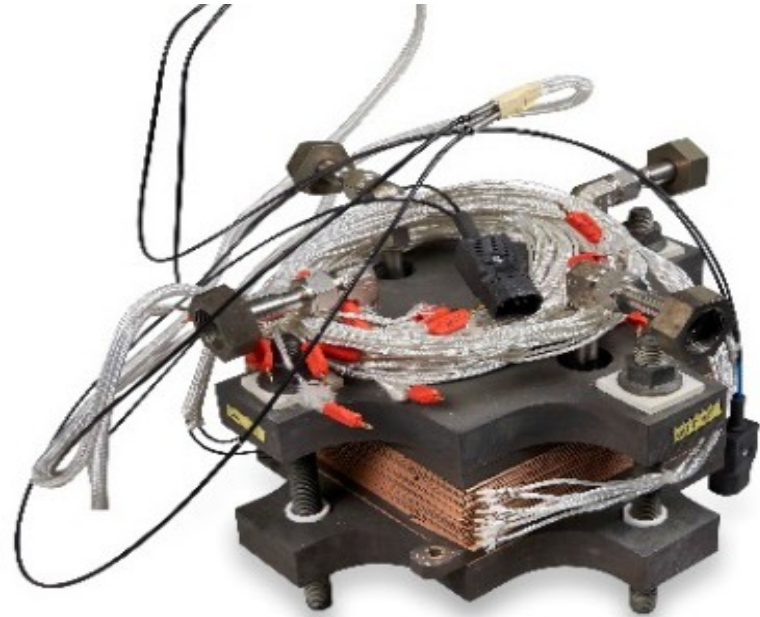
Mainz Energie Park (Germany)



Domestic cogeneration heat/electricity



To develop hydrogen uses... simultaneously...



Hydrogen production
(électrolyzers)



Hydrogen storage

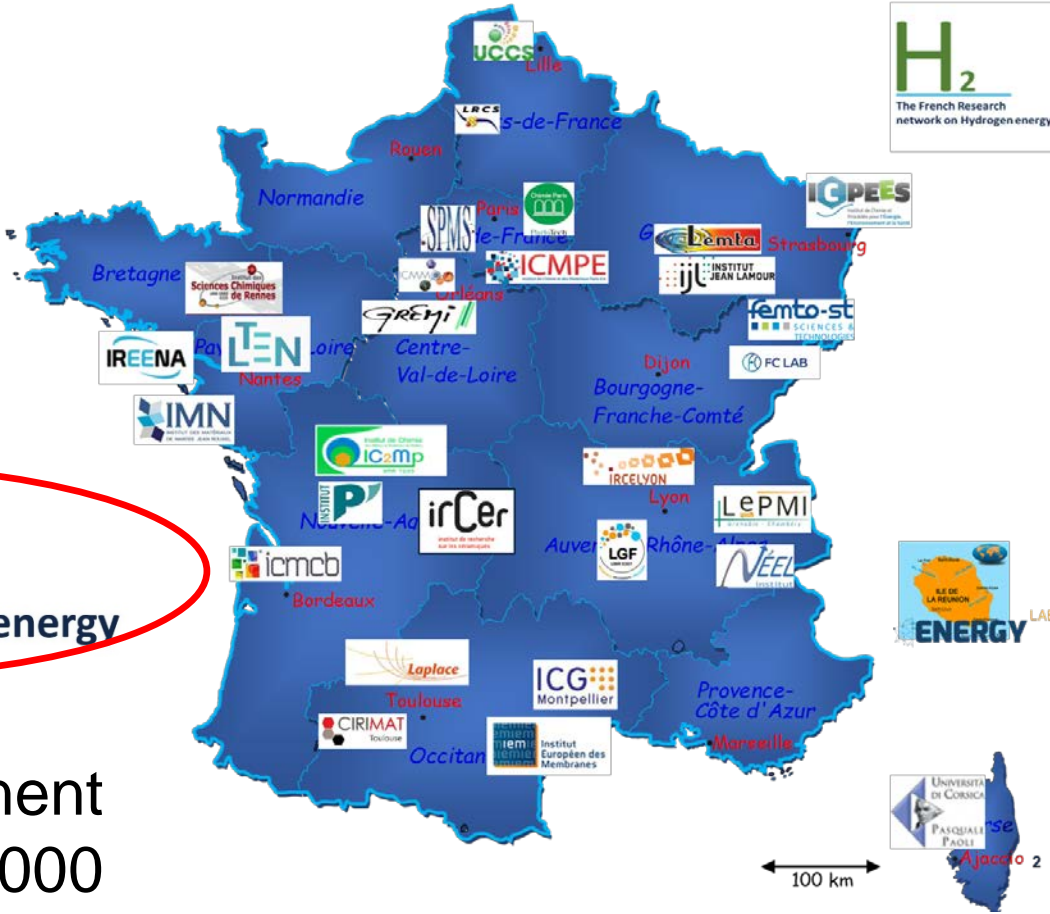
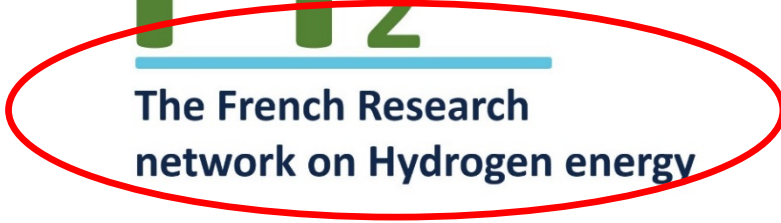


Hydrogen conversion
(FC)

specific issues

Hydrogen issues adressed all around the world...

→ in France, one program:

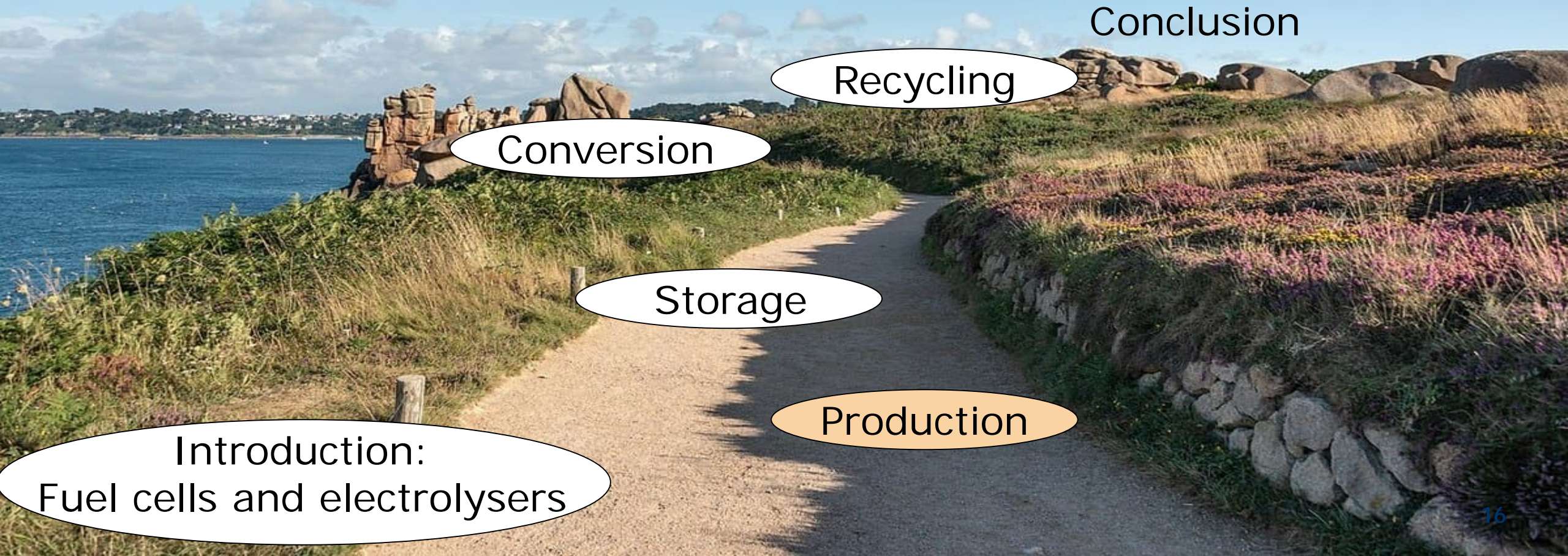


Organization: 30 laboratories, 300 permanent CNRS researchers and lecturers (70%), 4000 publications (2014-2019) 4 start-ups from CNRS

Aim: synergy between complementary skills: Materials, Processes, Components, Systems...

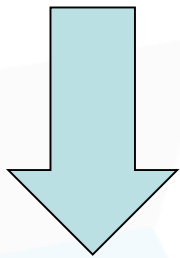


Outline



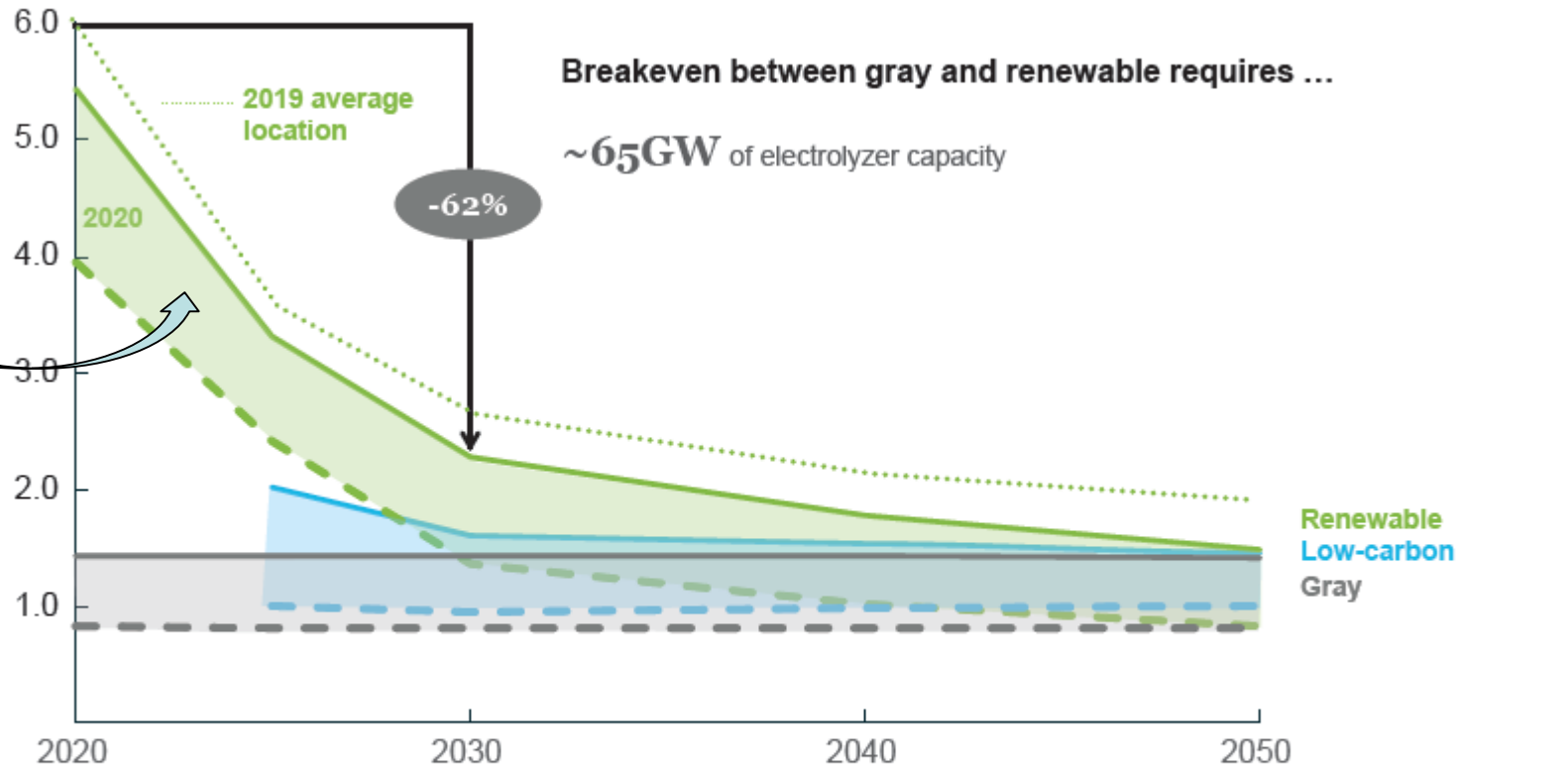
1. Hydrogen production...

Today, 95% of hydrogen is issued from fossil sources (grey H₂)...
... and green H₂ expensive



Need for **clean** production of (green) H₂ at **low cost**

Production cost of hydrogen USD/kg



Renewable hydrogen

- Dedicated renewable/electrolyzer system
- Fully flexible production
- Scale up of renewable hydrogen production
- Additional costs to reach end supply price

Low-carbon hydrogen

- Development of CO₂ pipelines and at-scale sites
- Scale-up of low-carbon hydrogen production
- Scale-up of CCS outside of hydrogen production

Key assumptions

- Gas price 2.8–8.8 USD/Mmbtu
- LCOE USD/MWh 25–73 (2020), 13–37 (2030) and 7–25 (2050)

LCOE: levelized cost of electricity
1m³ GNV = 0,0353 Mmbtu



1. Green hydrogen production (electrolysis)

Currently:

- low temperature technologies are mature

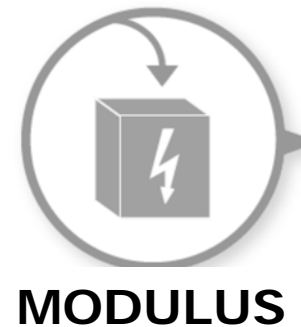
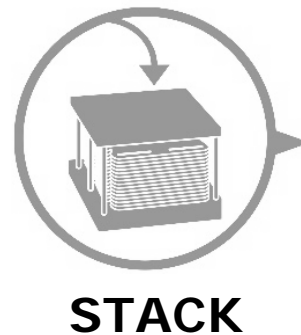
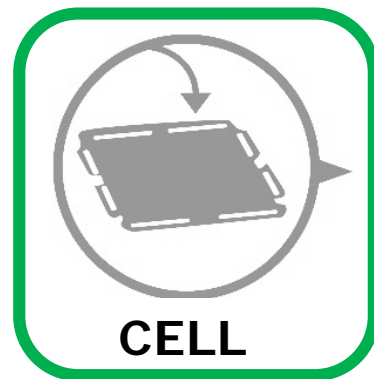
... but costly catalysts (platinum ou PGM)

→ Technologies without PGM, but low yields

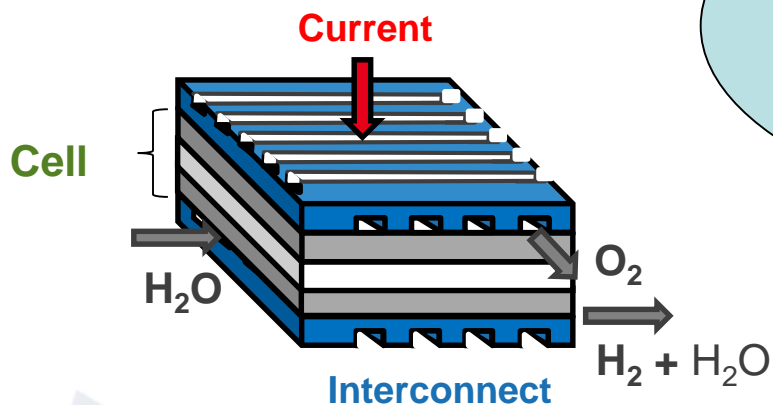
→ **High Temperature Electrolysis*** :

→ higher yields... without PGM

*Technological
improvements
at the cell scale*



1. HTE cells



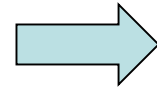
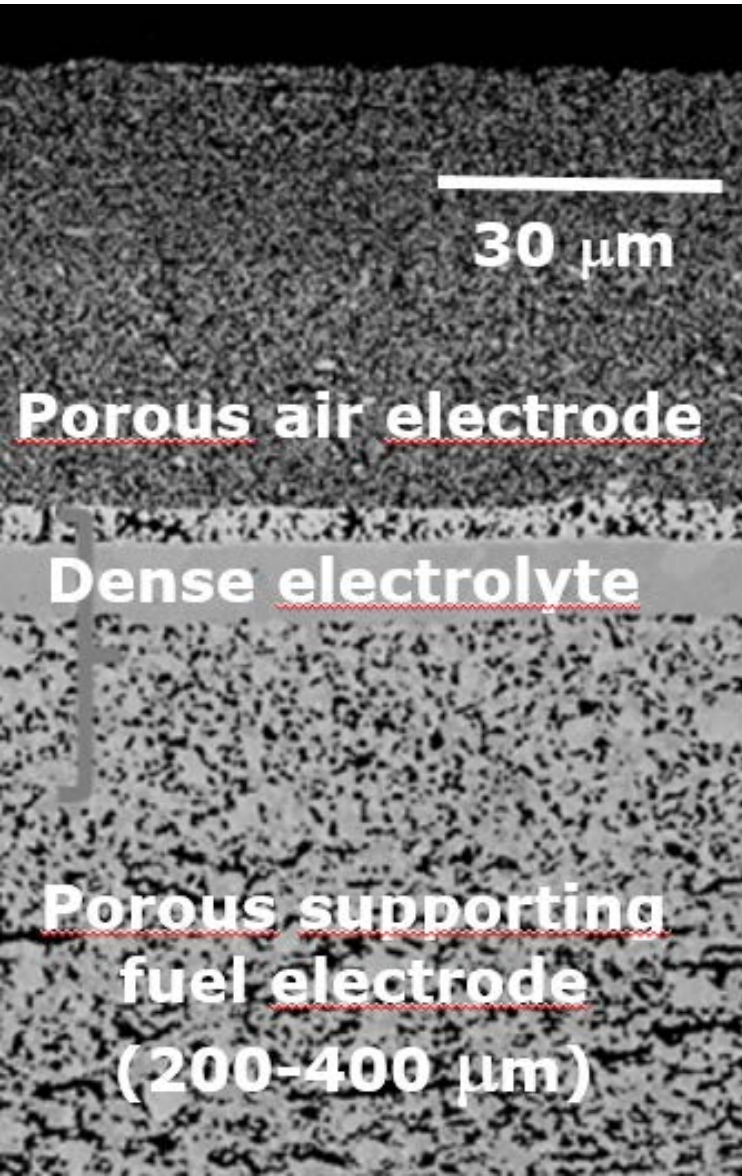
Ageing of the cell:
redox reactions
→ segregation (porosity),
diffusion, delamination,...

Today, electrode-supported cells

- High performance $\geq 1 \text{ A/cm}^2$ à 1,3V
- Weak durability: loss of 2 to 5%/1000h
at 1.3V and 0.5 à 0,6 A/cm^2



1. In order to increase the durability of the HTE cells...



PC CELCER-HT, *F. Lefebvre-Joud et coll.*



1. Improvement of current materials

Morphology (nanomaterials), barrier layers, shaping...

2024 :

Cells degradation rate :

- 1%/1000h at 1.3V and 0.85 A/cm²
- on cells of 200 cm²

Cells robustness :

- Low temperature starting time = 8h
- High temperature starting time = 300s

2. New materials

Composition (modelling, calculations...)...

2026-2027 :

Cells degradation rate :

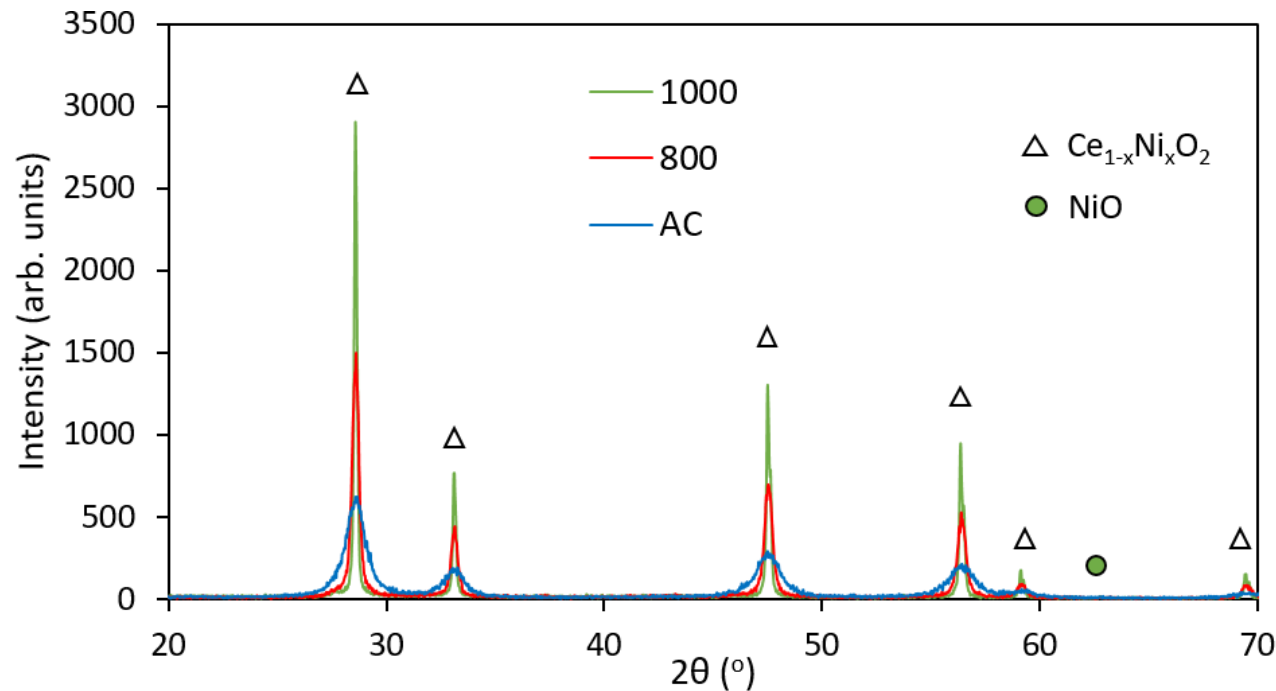
0,7%/1000h at 1,3V and 1 A/cm²

1. IMN's involvement in CELCER project ...

New materials for H₂ electrode: 1. New Ce & Ni-based materials: Ni exsolution
(homogeneous distribution)

→ Previous studies: Ni-introduction limited to 15%: Ce_{0.85}Ni_{0.15}O_{2-δ}*

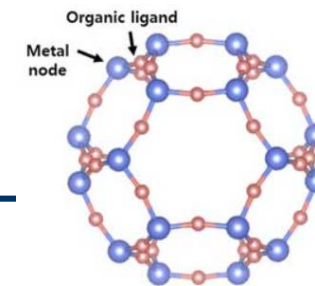
→ Ce_{0.95}Ni_{0.05}O_{2-δ} prepared at IMN**:



→ No crystallized secondary phase

→ Ni exsolution

1. IMN's involvement in CELCER project



New materials for H₂ electrode: 2. Use of Metal–organic frameworks (MOFs):

Porous Zirconium Terephthalate UiO-66

- ❖ MOFs : porous and tunable materials composed by organic structures and inorganic nodes¹.
- ❖ High porosity after burning the organics ².
- ❖ Easy synthesis of Zr-based MOFs ³.
- ❖ Possible doping of Zr-based MOF with Yttrium ⁴.
- ❖ Possible infiltration (due to their high porosity) ⁵.

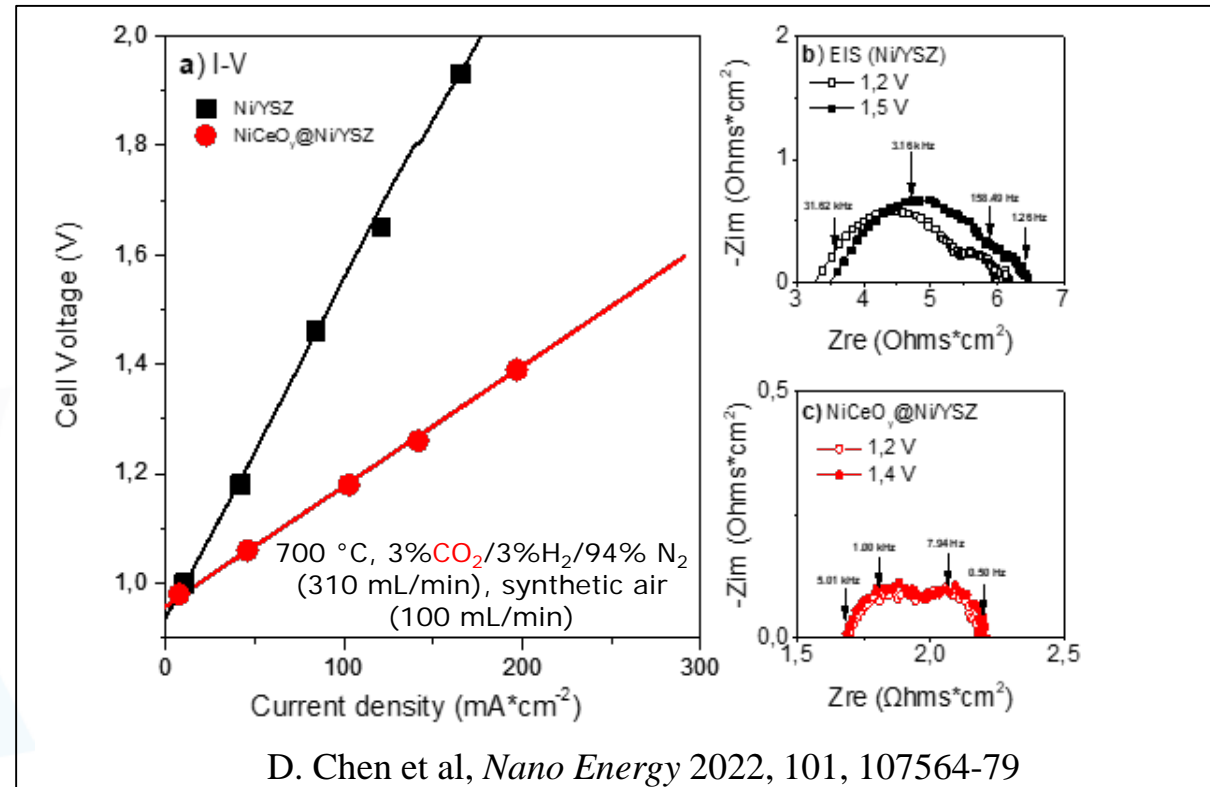


Next step: Addition of NiO?

1. F. Ragon et al. Inorg. Chem. 53 (2014), 2491 – 2500.
2. R. Quin et al. Adv. Funct. Mater. 29 (2019), 1903264.
3. M.J. Katz et al. Chem Commun., 49 (2013), 9449.
4. Z. Yue et al. RSC Adv. 5 (2015), 10619.
5. R. Lippi et al. J. Mater. Chem. A 5 (2017), 12990.

1. Versatile High temperature electrolyzers: fuel electrode

Adaptation of classical fuel electrode material for CO₂/H₂O electrolysis:

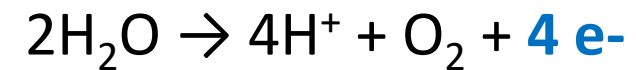
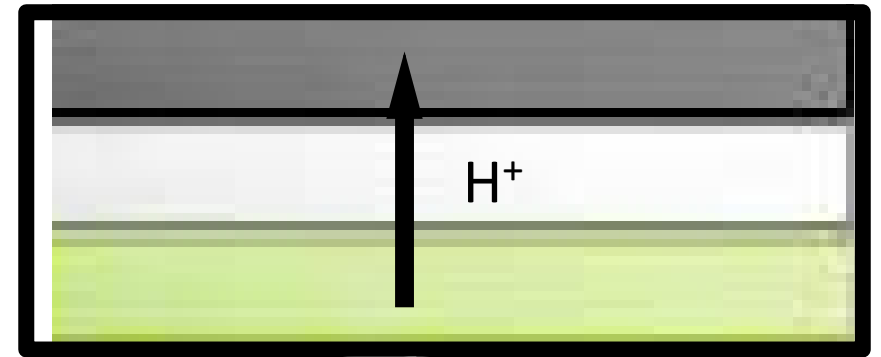
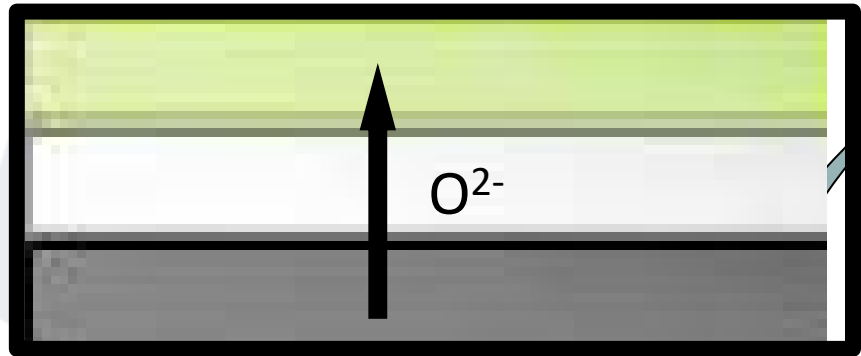


... and also seawater electrolysis...

1. Another route to improve HTE...

Anionic conductor based cells

Protonic conductor based cells

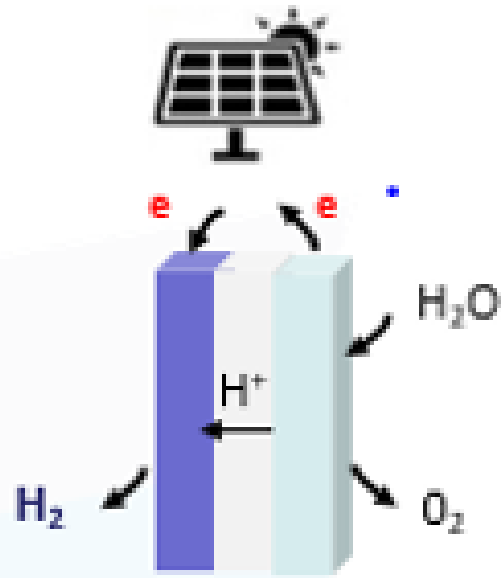


→ Production of non diluted hydrogen

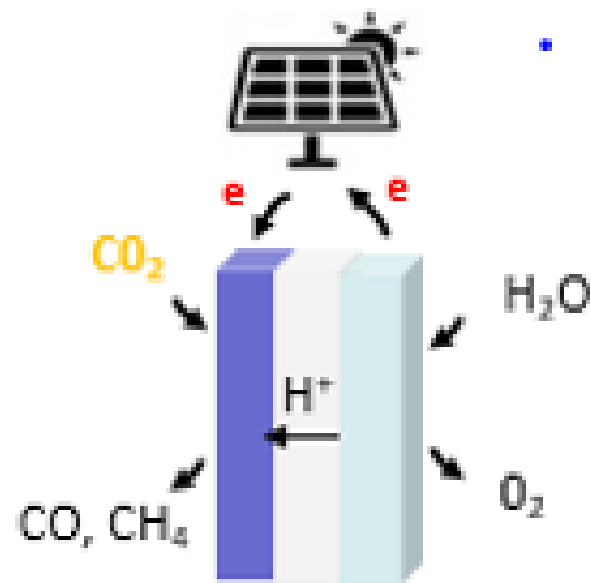
→ Protonic conduction efficient at lower temperature (lifetime)

1. Versatility of the PC-HTE

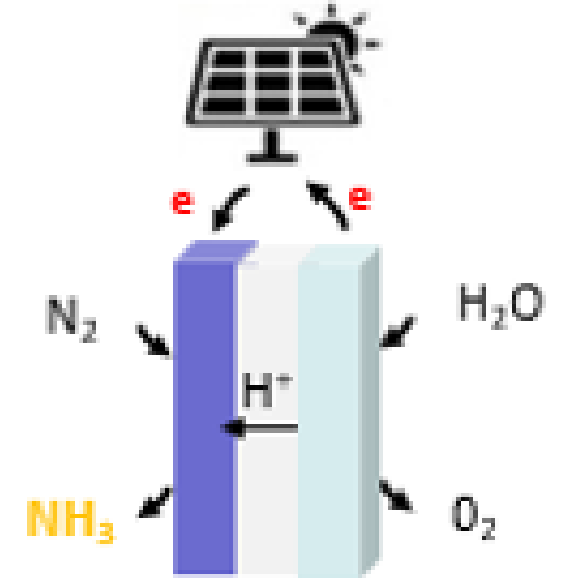
@ 600°C



H_2O Electrolysis



CO_2 Electrolysis

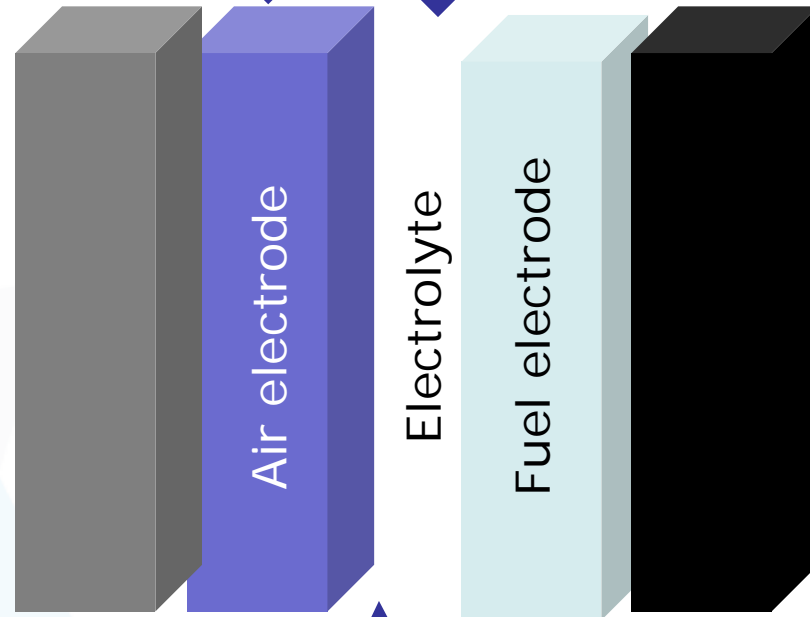


NH_3 Synthesis

1. How to improve PC-HTE

Electro-catalytic activity,
chemical stability,
architecture optimisation

Chemical stability, optimized conductivity



**Materials, architectures and
interfaces optimisation**

Cr diffusion

Delamination

Mechanical compatibility



PC PROTEC, G. Taillades et coll.

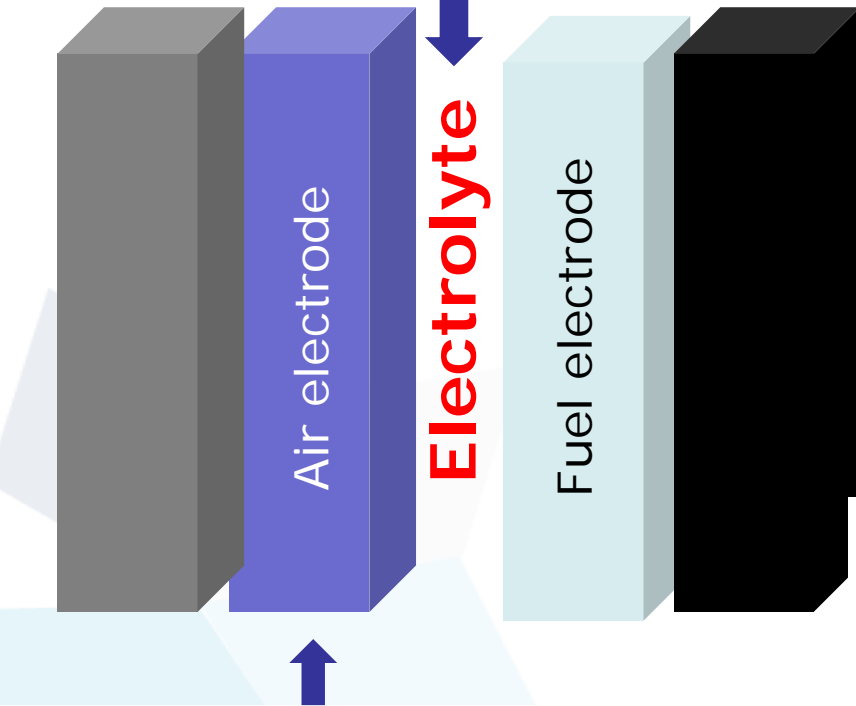
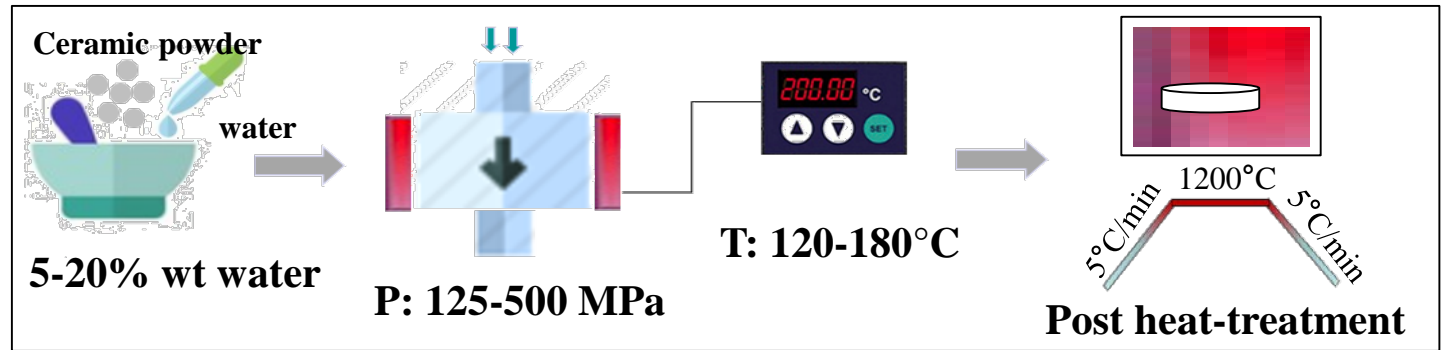


1. How to improve CP-HTE: electrolyte synthesis at IMN

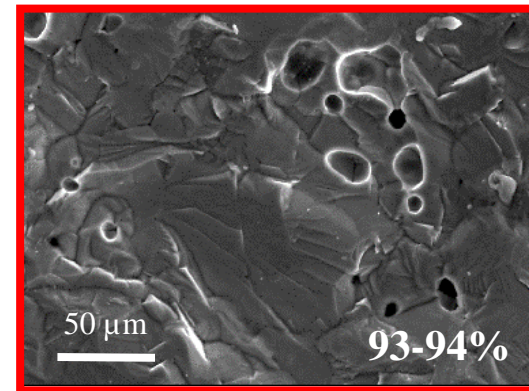
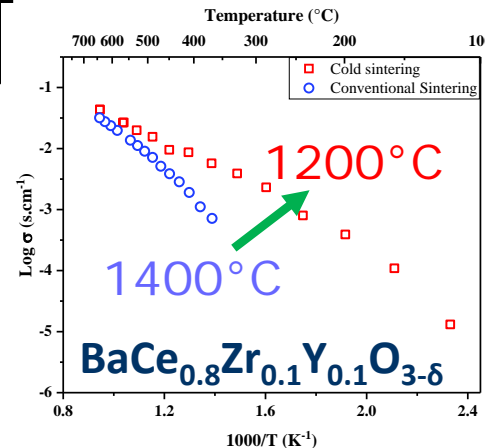
Chemical stability, optimized conductivity

1. $\text{BaCe}_{0.8}\text{Zr}_{0.1}\text{Y}_{0.1}\text{O}_{3-\delta}$ by Cold Sintering*

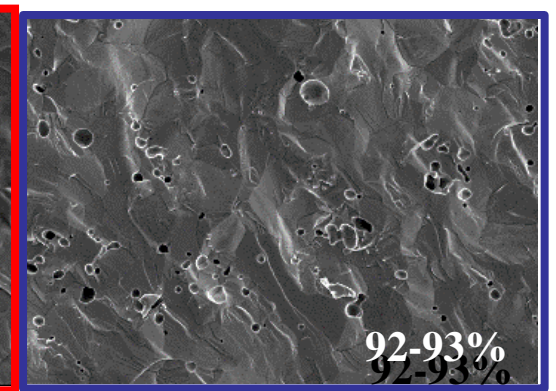
*Z. Zhao, J. Gao, Y. Meng, K. Brinkman, J. Tong, *Ceramics Int.* 2021



Electro-catalytic activity,,
chemical stability,
architecture optimisation



Cold sintering



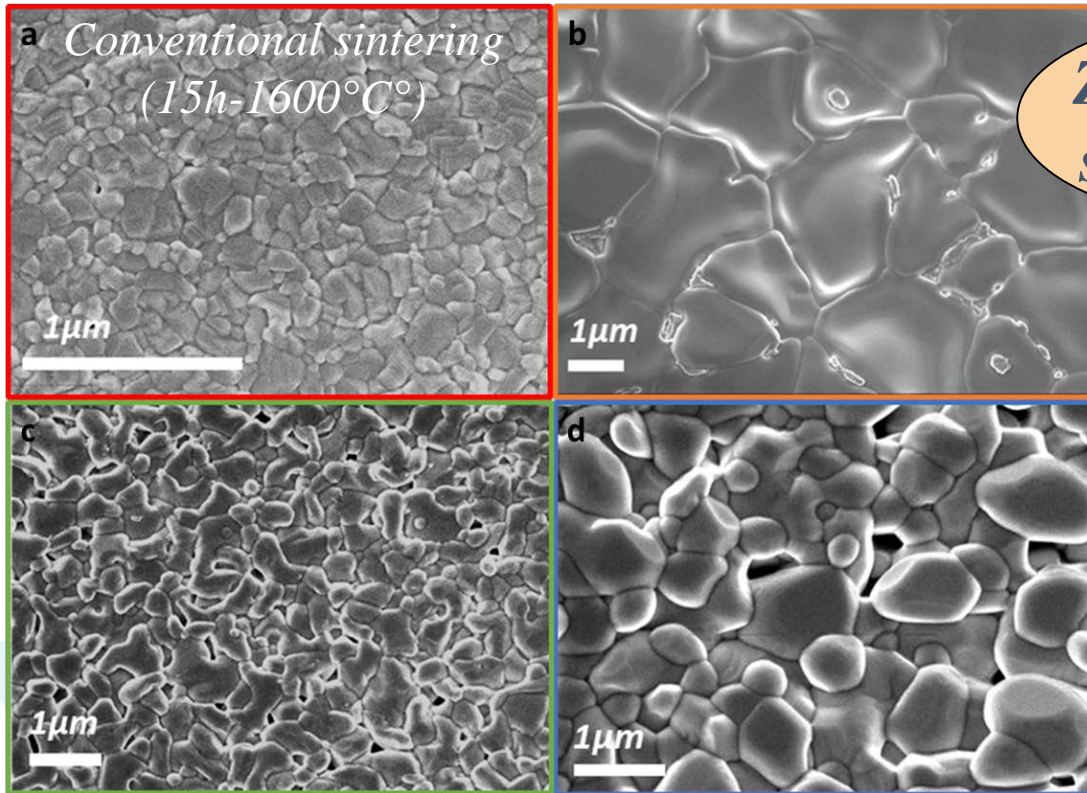
Conventional sintering

K. Thabet, A. Le Gal la Salle, E. Quarez, O. Joubert, *ECS Trans.* 91(1) 983-996, 2019

K. Thabet, E. Quarez, O. Joubert, A. Le Gal la Salle, *J. Eur. Ceram. Soc.* 2020

1. How to improve CP-HTE: electrolyte synthesis at IMN*

2. Another compound: $\text{BaCe}_{0.2}\text{Zr}_{0.7}\text{Y}_{0.1}\text{O}_{3-\delta}$ ** (CO₂/H₂O electrolysis) (↑ stability, ↓ sinterability)

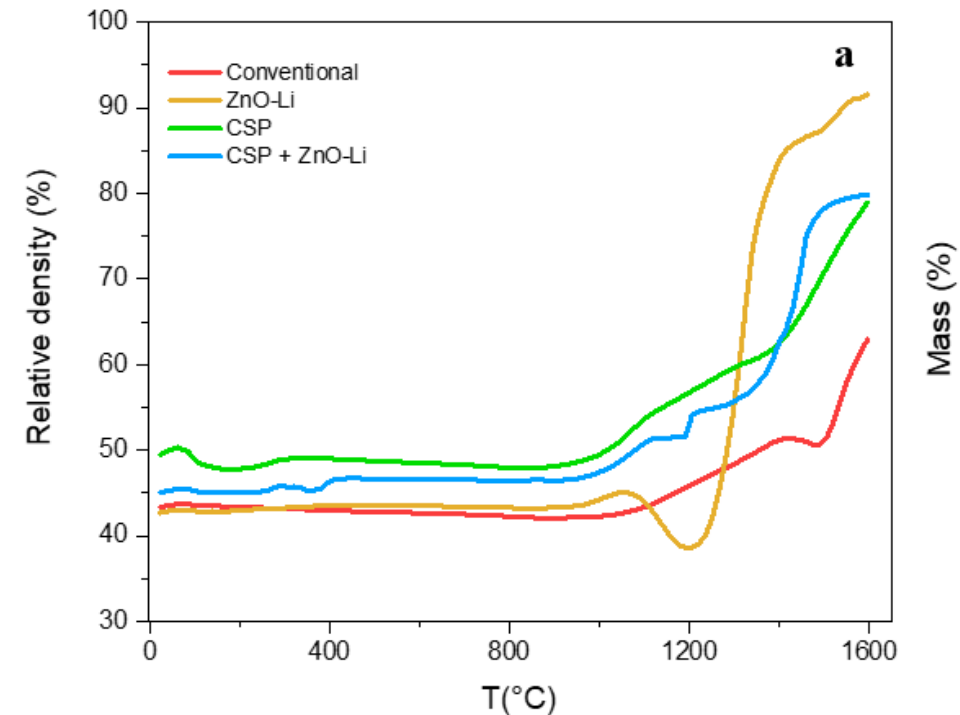


ZnO-Li 1wt% sintering aid

Cold-sintering process at 180°C before sintering

CSP with the addition of sintering aid

(↑ stability, ↓ sinterability)



Grain density values calculated by ImageJ from SEM images cross section:

Sintering protocol	Conventional	CSP	ZnO-Li	CSP + ZnO-Li
Grain count (grain)	50	86	6	74
Count Area (µm ²)	4.5	26.1	26.7	26.5
Grain Density (grain.µm ⁻²)	11	3.3	0.2	2.8

* P. Castellani thesis

** S. M. Babiniec et al. , *Int. J. Hydrogen Energy*, 2015

1. How to improve CP-HTE: synthesis of air electrode

Air electrode suited to electrolyte

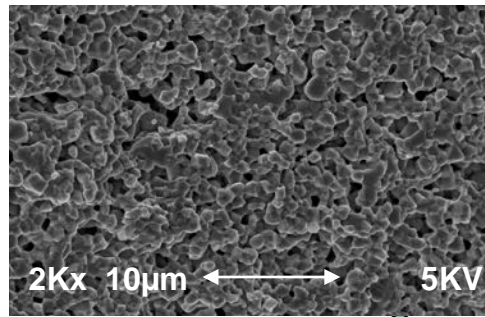
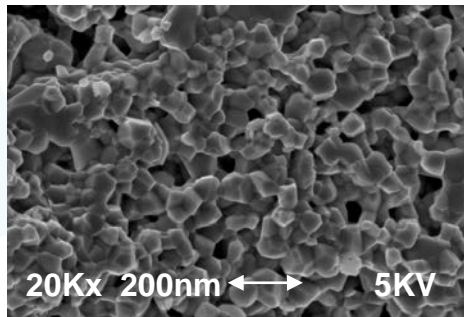
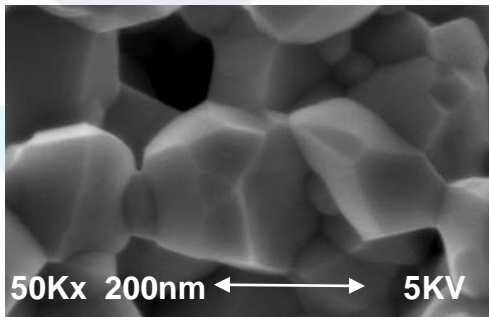
$\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$
• Commercial powder (Mariontech)

$\text{BaZr}_{0.7}\text{Ce}_{0.2}\text{Y}_{0.1}\text{O}_{3-\delta}$

- Preparation of two Inks for screen printing:
(powder + 95 wt% alpha terpineol (solvent) + 5 wt% ethyl-cellulose (binder))
- Single phase ink synthesis: $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$
- Composite ink synthesis : $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ + $\text{BaZr}_{0.7}\text{Ce}_{0.2}\text{Y}_{0.1}\text{O}_{3-\delta}$



- Screen printing on a $\text{BaZr}_{0.7}\text{Ce}_{0.2}\text{Y}_{0.1}\text{O}_{3-\delta}$ dense electrolyte
- 4 layers (3 Composite + BSCF) + drying at 120°C + treatment of the cell at 750°C for 6h



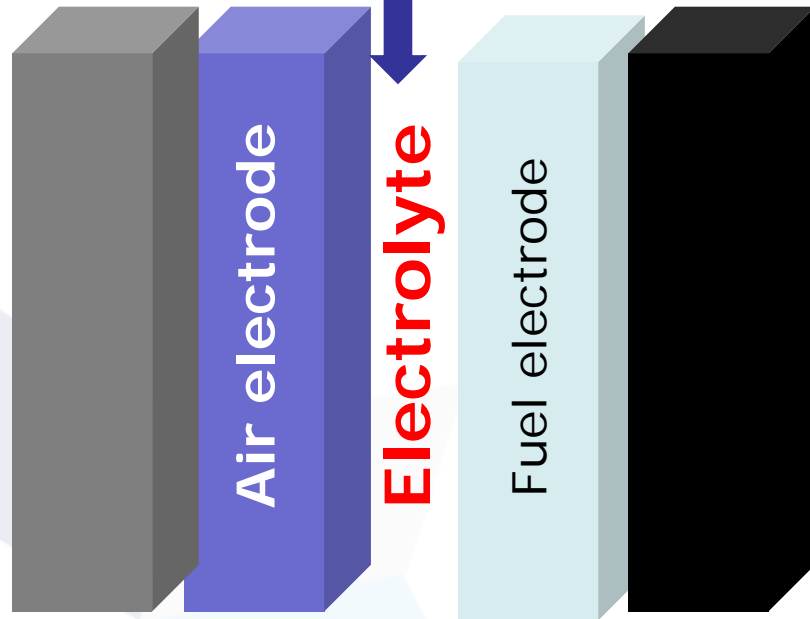
SEM images of the cathode

a) Porous structure of the air electrode
b) Homogeneous morphology of the electrode layer

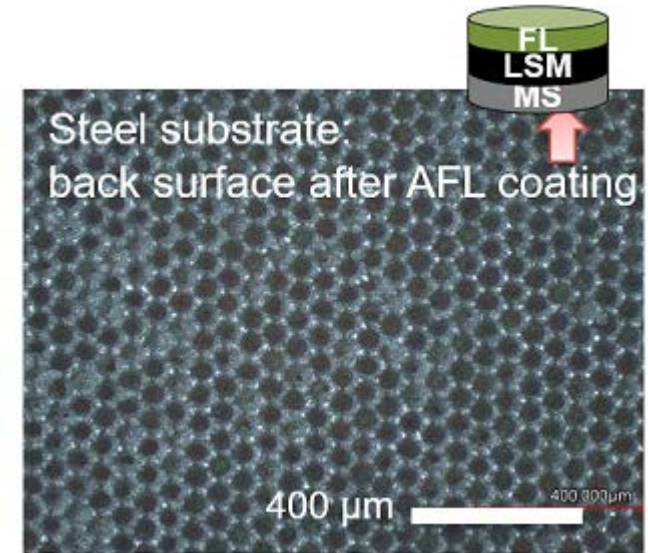
Complete cells...

1. How to improve CP-HTE: new designs

Chemical stability, optimized conductivity



3. New cells designs: metal supported cells:



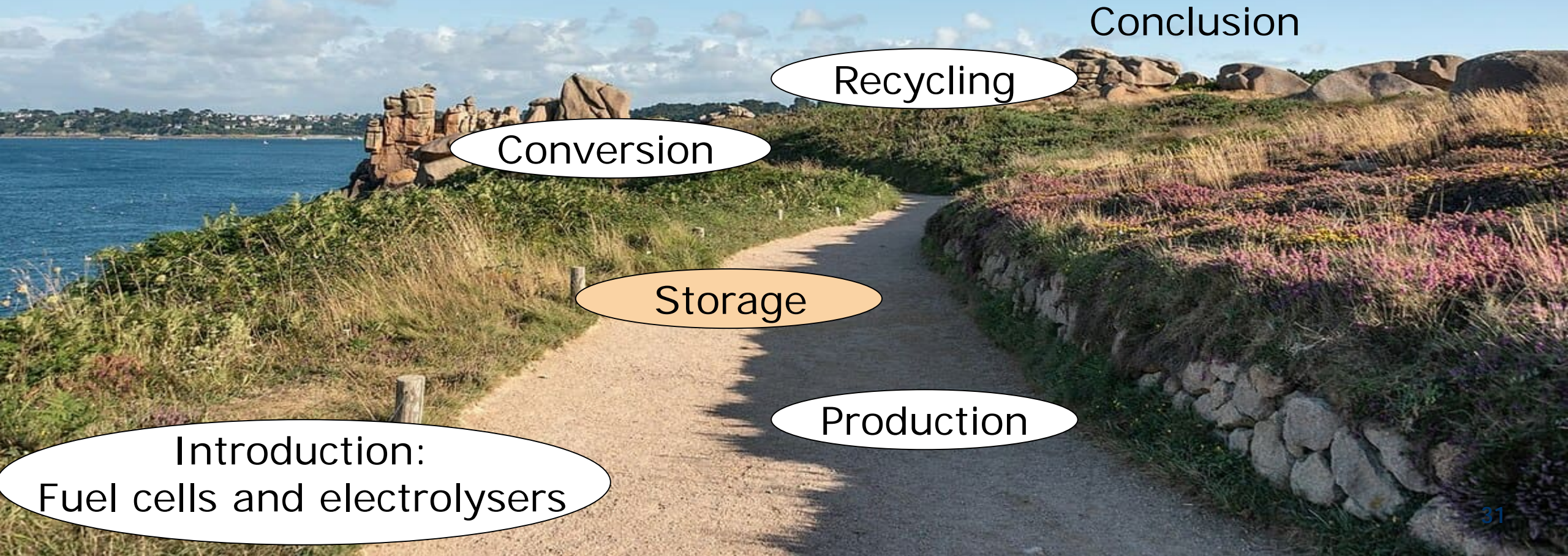
French-German ANR project "ARCADE" (2020-2023)
1 PhD (2020-23) – P. Castellani
Metal-supported SOEC cell based on $\text{BaCe}_x\text{Zr}_{1-x-y}\text{Y}_y\text{O}_{3-\delta}$ (BCZY)

Electro-catalytic activity,
chemical stability,
architecture optimisation

*Mechanical strength
assumed by the metallic
interconnect*

*Reduction of the amount of
active materials*

Outline



Introduction:

Fuel cells and electrolysers

Storage

Production

Recycling

Conversion

Conclusion

2. Another challenge: H₂ storage!



2g/mol

Light... BUT

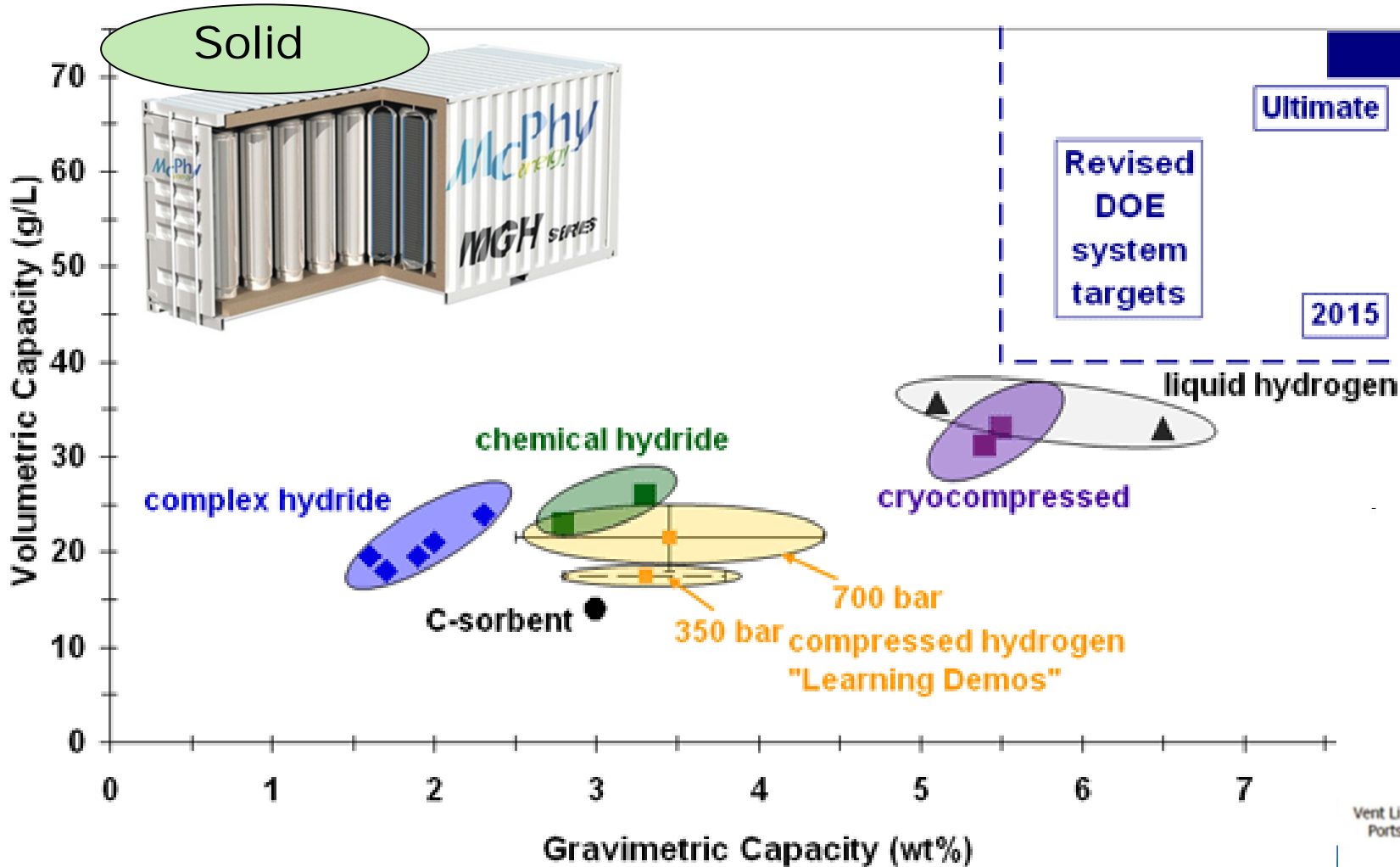


0.09 kg/m³

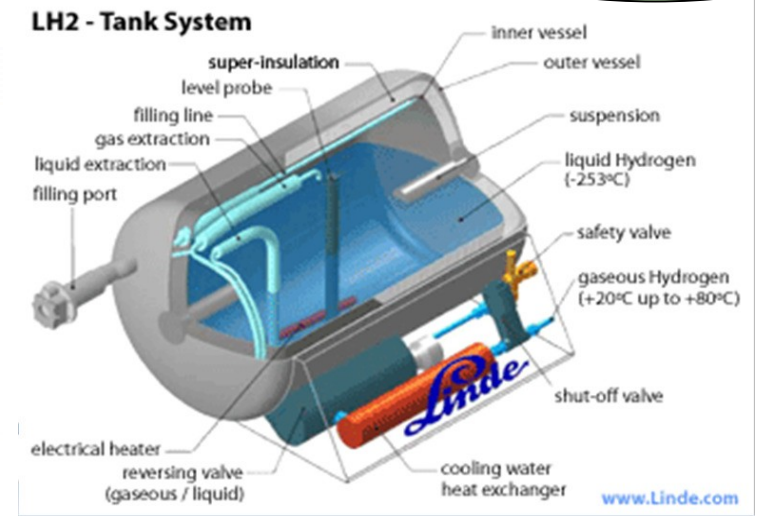
Voluminous!



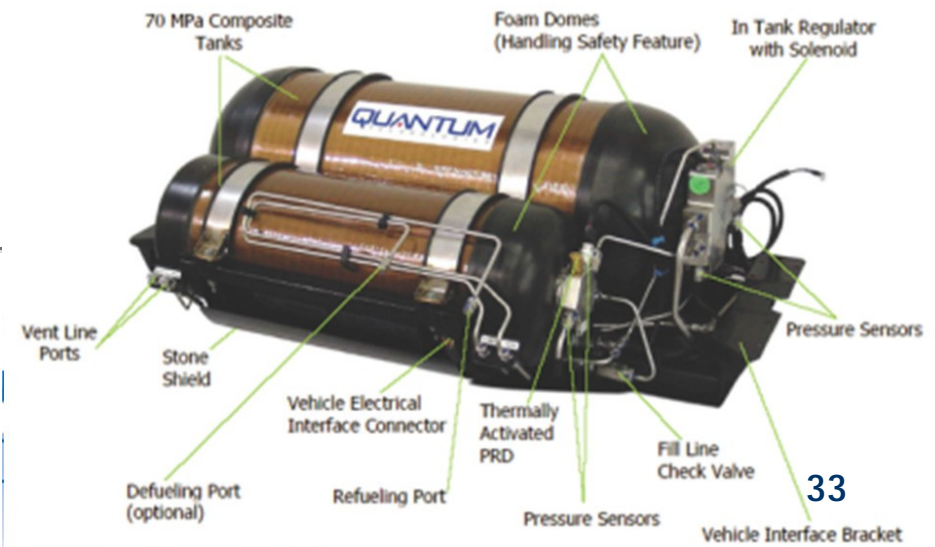
2. H₂ storage: existing solutions ...



Liquid



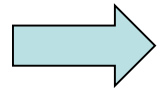
Compressed



2. Solid storage:

- compact, energy-efficient
- contributes to hydrogen social acceptability: safe, without pressure

2. Solid storage: current research ...



PC SOLHYD, *F. Cuevas et coll.*



...highly efficient...

Materials

Metal hydrides
(Mg_2FeH_6 , 150 kg H_2/m^3)

Regenerable hydrides
intermetallic: AB_5 ($\text{LaNi}_5\dots$), AB_2
(ZrV_2), A_2B (Mg_2Ni)...

Complex Hydrides and adsorption
materials (LiBH_4 (18%), but
200000 atm!)

*...costly, energy
consuming...*

Slow desorption
→ Improvement
of regeneration
processes

Development of
new compositions,
new materials

Improvement of synthesis
and regeneration
processes

2. Hyperbaric storage : remaining challenges

- ✓ Increasing its level of safety and confidence → better societal acceptability
- ✓ Reducing the carbon footprint of tanks (with life cycle analysis)

Zhenzhou Wang et al., *Int. J. Hydrogen Energy*, 2020
Xiulei Wang et al., *Int. J. Hydrogen Energy*, 2022
A. Laureys et al., *J. Natural Gas Science and Engineering*, 2023

2. Hyperbaric storage : remaining challenges

➔ PC HYPERSTOCK, *D. Chapelle et coll.*



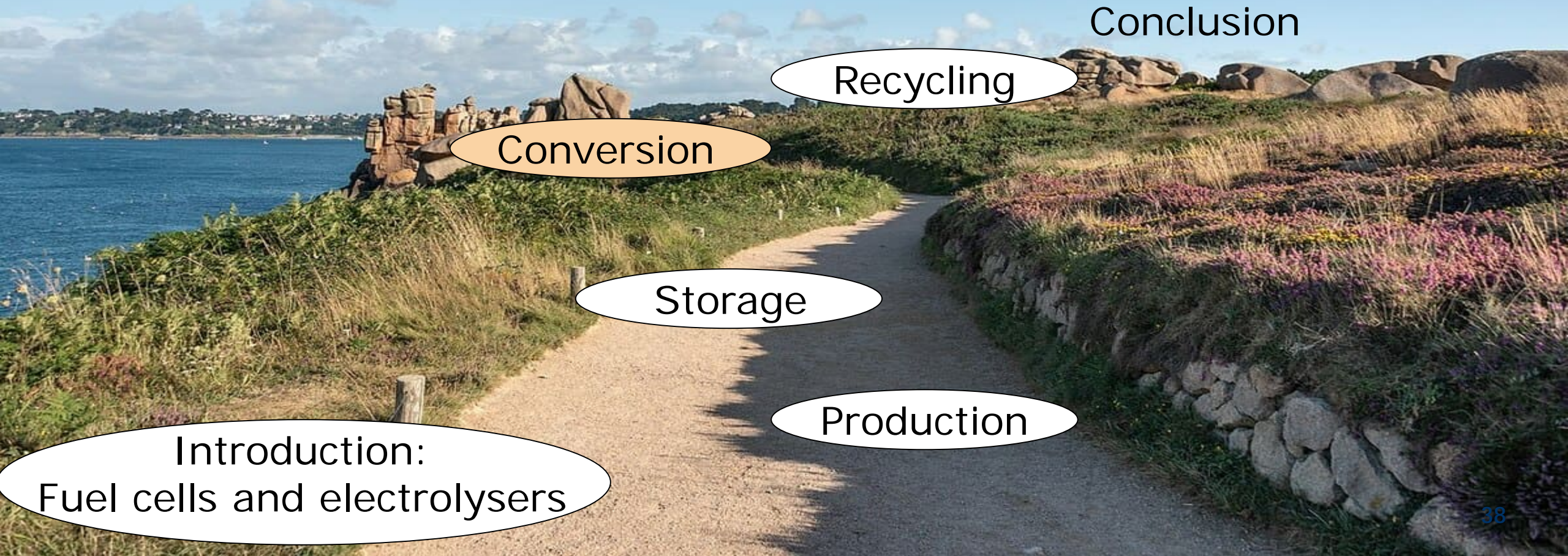
MAIN STUDIES:

- embrittlement of the different materials (metallic and non-metallic) with H_2 ,
- responses to mechanical stresses

Security,
Trust,
Acceptability

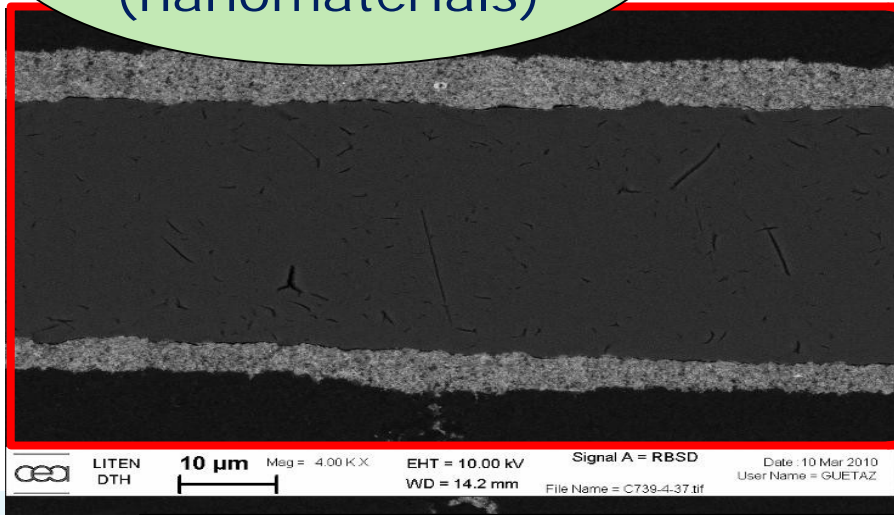
Carbon footprint

Outline



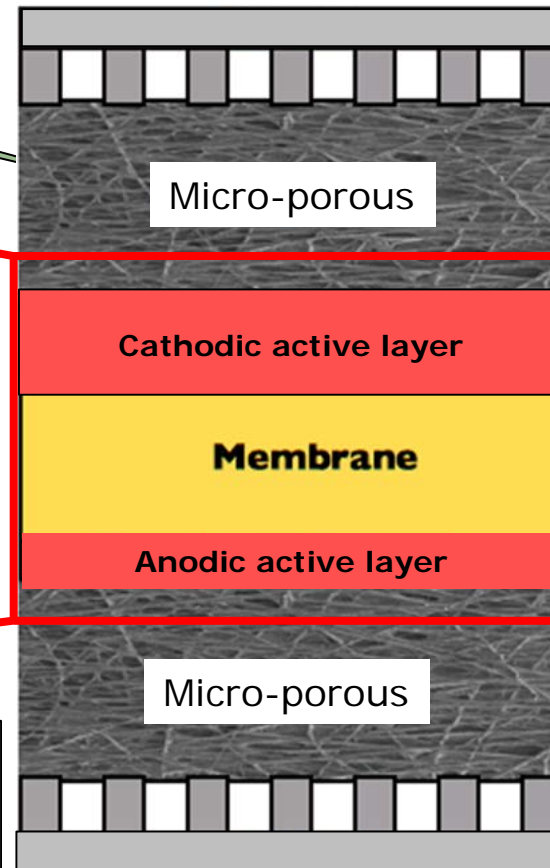
3. Low temperature fuel cells: remaining objectives

2. Decrease of the amount of catalyst (nanomaterials)

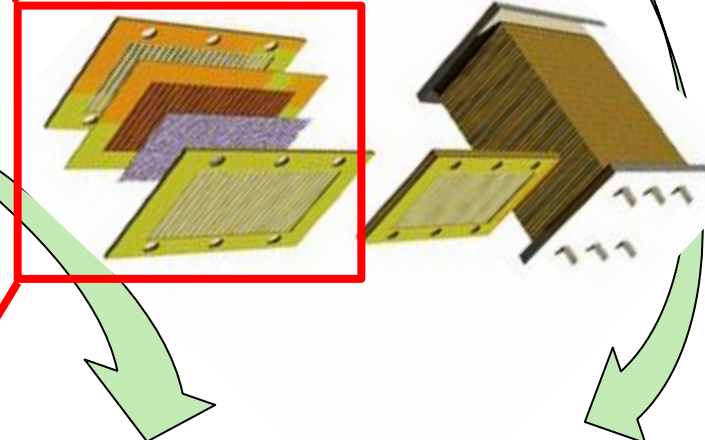


3. New materials, to increase activity, stability, robustness (impurities, stop and start,...) *

* (> 25000h)



1. System: temperature (H₂O) management

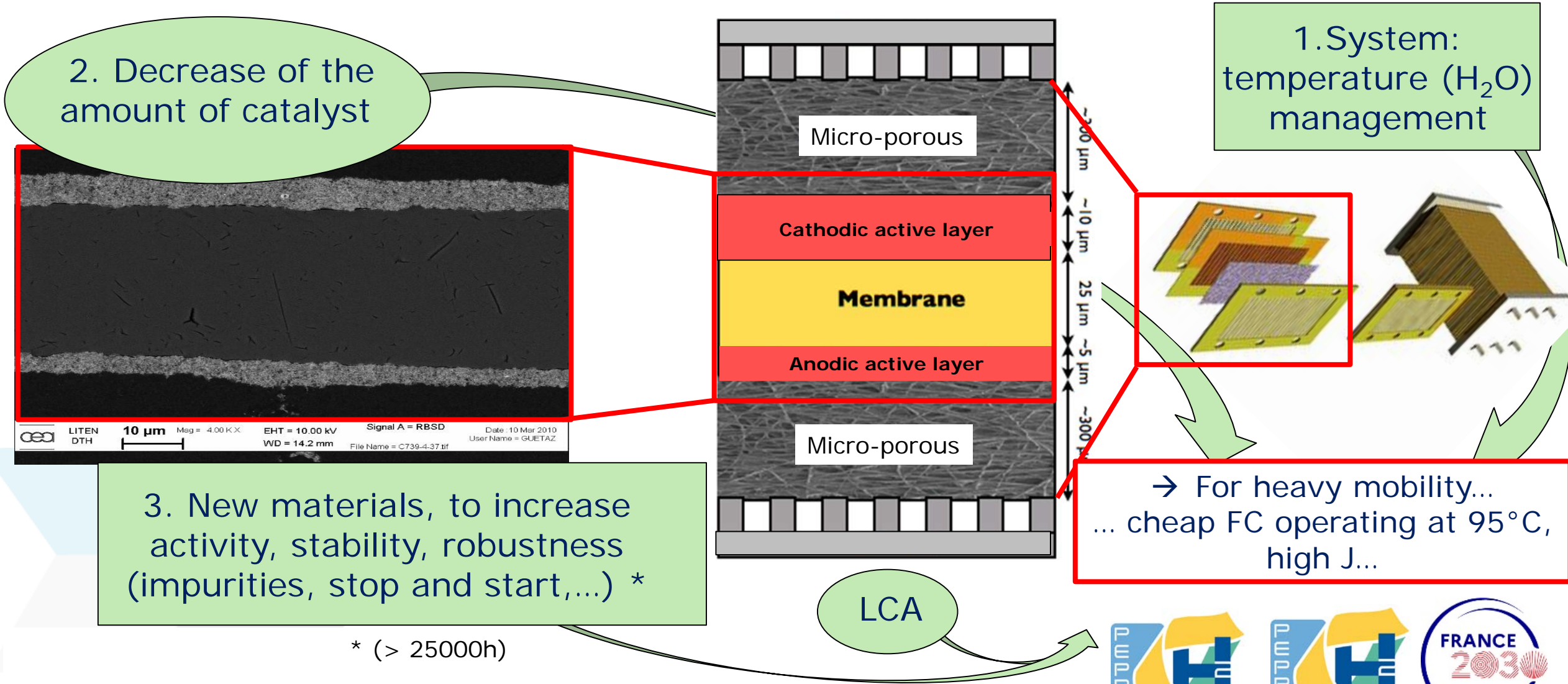


A. Parekh., Recent developments of proton exchange membranes for PEMFC: A review, *Frontiers in Energy Research*, 2022

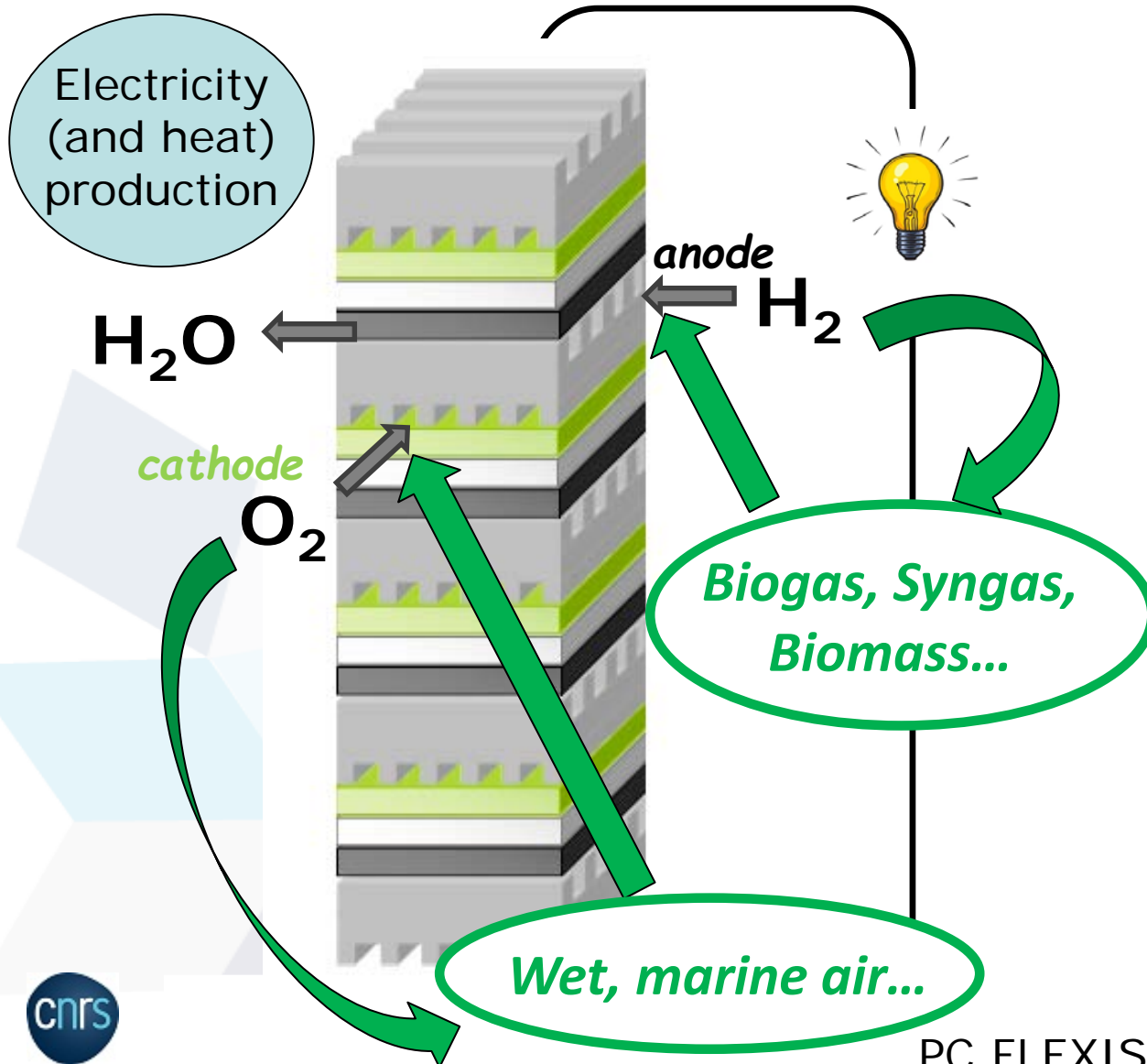
H. Su et al., A review of low temperature proton exchange membrane fuel cell degradation caused by repeated freezing start, *Int. J. Hydrogen Energy*, 2022

P.H. Affonso Nobrega et al., A review of physics-based low-temperature proton-exchange membrane fuel cell models for system-level water and thermal management studies, *J. Power Sources*, 2023

3. Low temperature fuel cells: remaining objectives



3. High temperature fuel cells



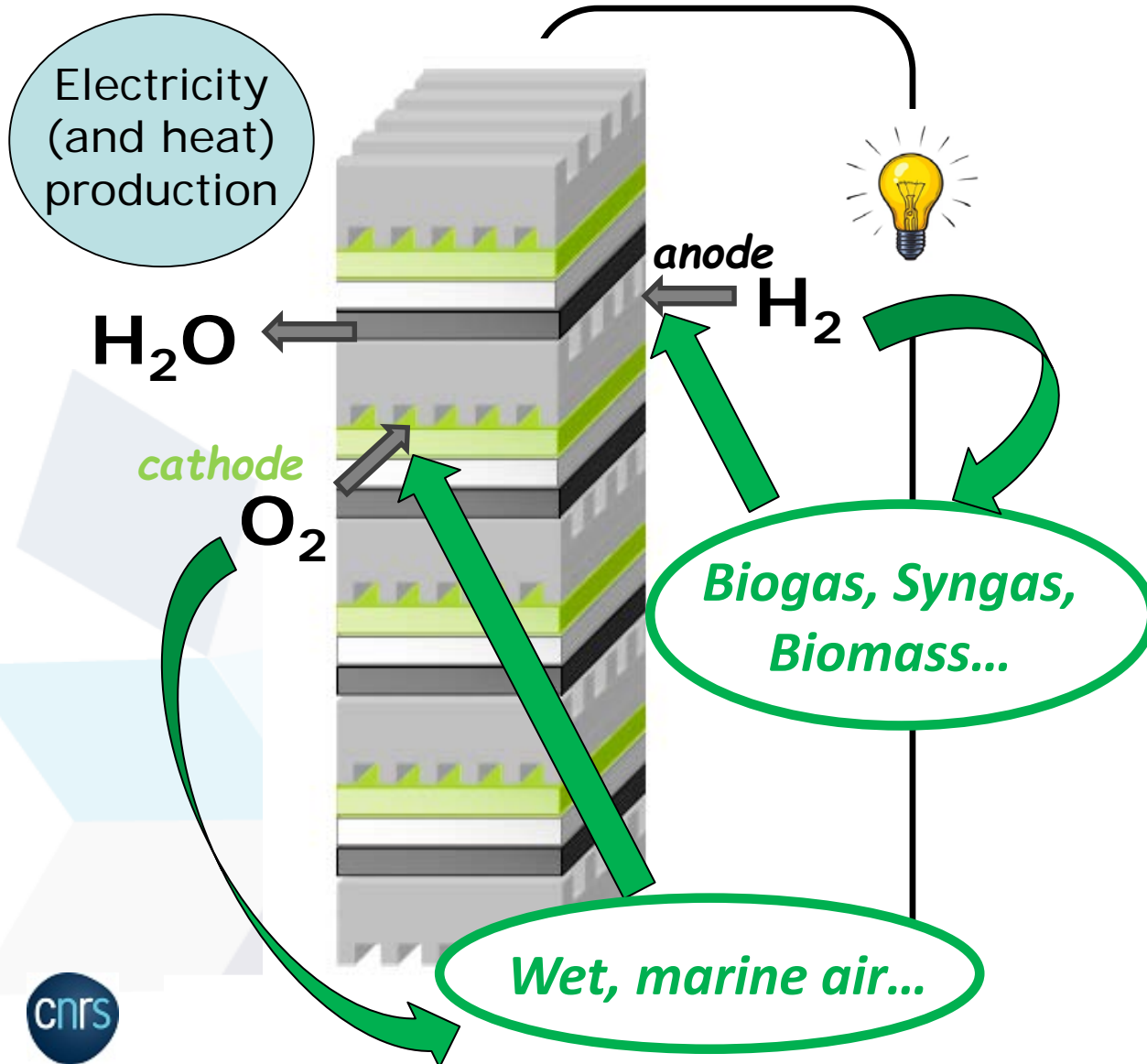
With these devices,

- High yields without costly catalysts
- Possible to use other fuels, such as various gaseous or liquid mixtures issued from biomass...
(≠ LTFC)

... Same materials as HTE, but:

- Increase their robustness towards pollutants present in different fuels

3. High temperature fuel cells



With these devices,

- High yields without costly catalysts
- Possible to use other fuels, such as various gaseous or liquid mixtures issued from biomass...
(≠ LTFC)

... Same materials as HTE, but:

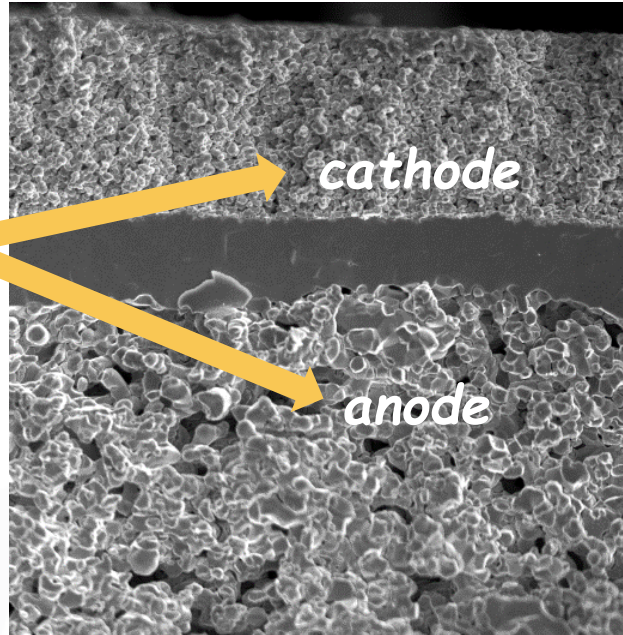
- Increase their robustness towards pollutants present in different fuels

To further increase their versatility:

- Use wet, marine, polluted air
- Decrease T

3. Versatile high temperature fuel cells

Development of convenient materials



PC FLEXISOC, A. Le Gal La Salle et coll.

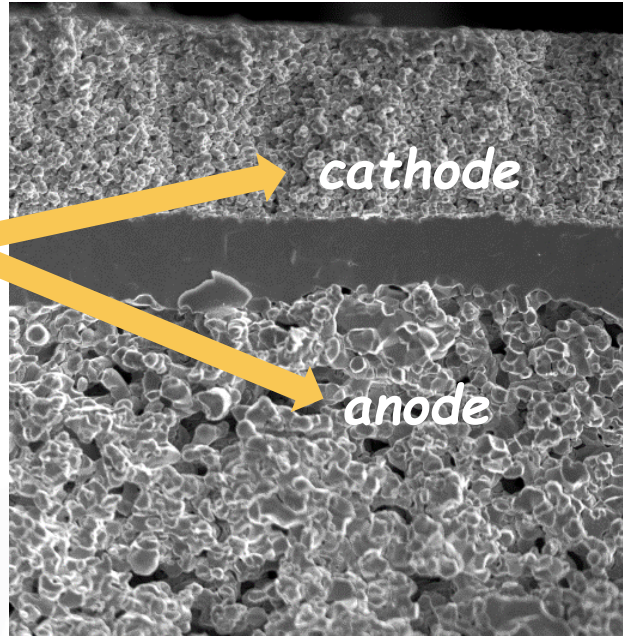


Precise objectives on fuel side:

- ✓ Carbon formation $< 0,5 \text{ mg}_{\text{carbone}} \text{ g}_{\text{cat}}^{-1} \text{ h}^{-1}$ à 600°C
- ✓ H_2S tolerance between 3 and 5 ppm

3. Versatile high temperature fuel cells

Development of convenient materials



After:

Materials and cells shaping:

Tests and optimisation, modélisations

✓ Power density (without reforming) of 1 W/cm² at 600°C

PC FLEXISOC, A. Le Gal La Salle et coll.

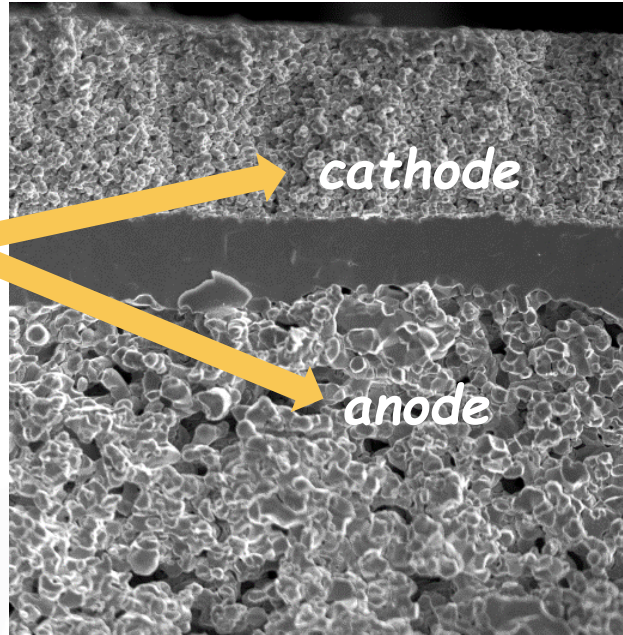


Precise objectives on fuel side:

- ✓ Carbon formation < 0,5 mg_{carbone} g_{cat}⁻¹ h⁻¹ à 600°C
- ✓ H₂S tolerance between 3 and 5 ppm

3. Versatile high temperature fuel cells

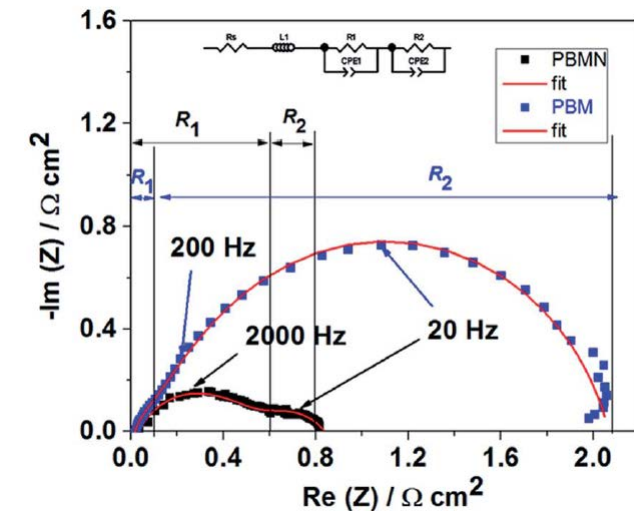
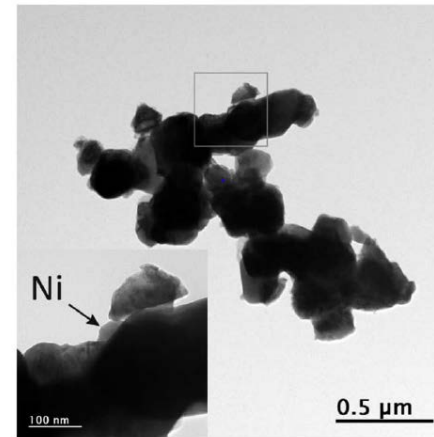
Development of convenient materials



Materials and cells shaping:

Tests and optimisation, modélisations

In situ exsolution of Ni particles from $Pr_{0.65}Ba_{0.35}Mn_{0.975}Ni_{0.025}O_3$



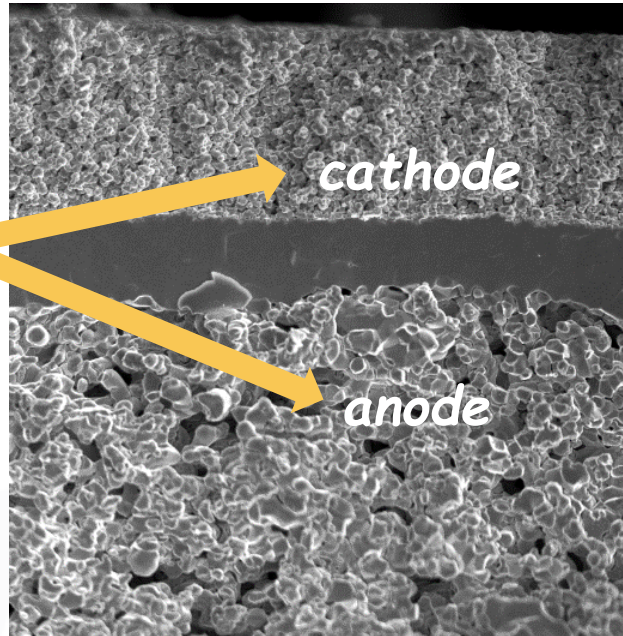
M. Bahout et al. J. Mater. Chem. A, 2020, 8, 3590–7

Precise objectives for fuel electrodes:

- ✓ Carbon formation $< 0,5 \text{ mg}_{\text{carbone}} \text{ g}_{\text{cat}}^{-1} \text{ h}^{-1}$ à 600°C
- ✓ H_2S tolerance between 3 and 5 ppm
- ✓ Power density (without reforming) of 1 W/cm^2 at 600°C

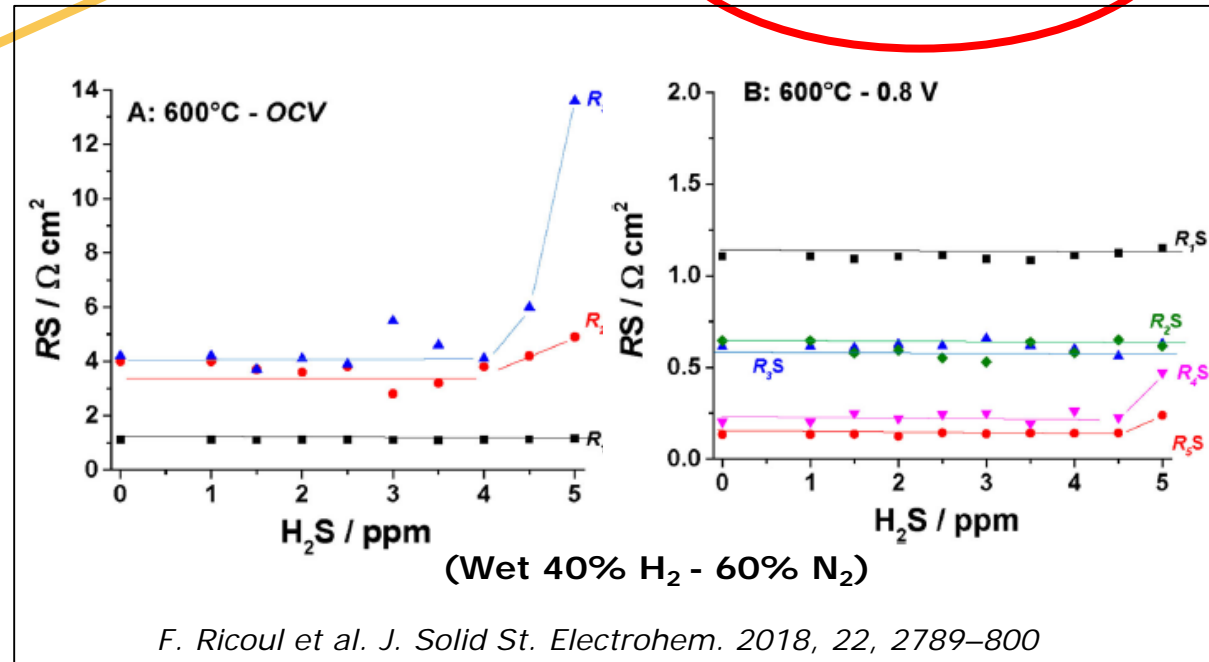
3. Versatile high temperature fuel cells

Développement of convenient materials



Materials and cells shaping:

Tests and optimisation, modélisations

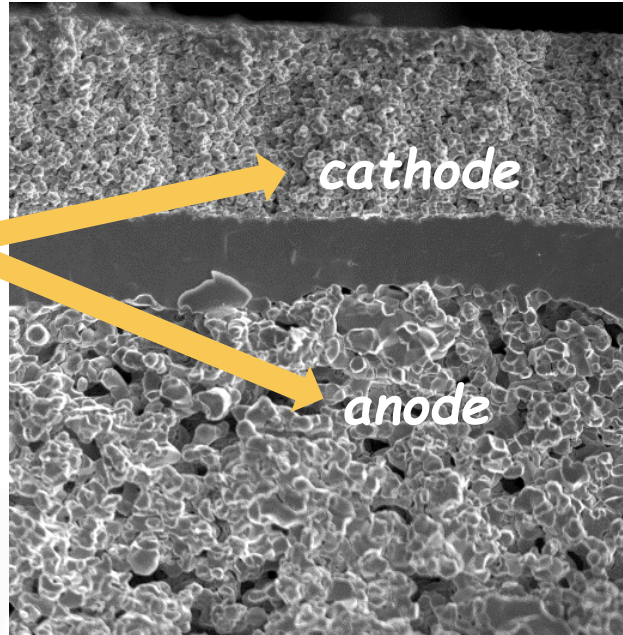


Precise objectives for fuel side electrodes :

- ✓ Carbon formation $< 0,5 \text{ mg}_{\text{carbone}} \text{ g}_{\text{cat}}^{-1} \text{ h}^{-1}$ à 600°C
- ✓ H_2S tolerance between 3 and 5 ppm
- ✓ Power density (without reforming) of 1 W/cm^2 at 600°C

3. Versatile high temperature fuel cells

Développement of convenient materials



Materials and cells shaping:

Tests and optimisation, modélisations

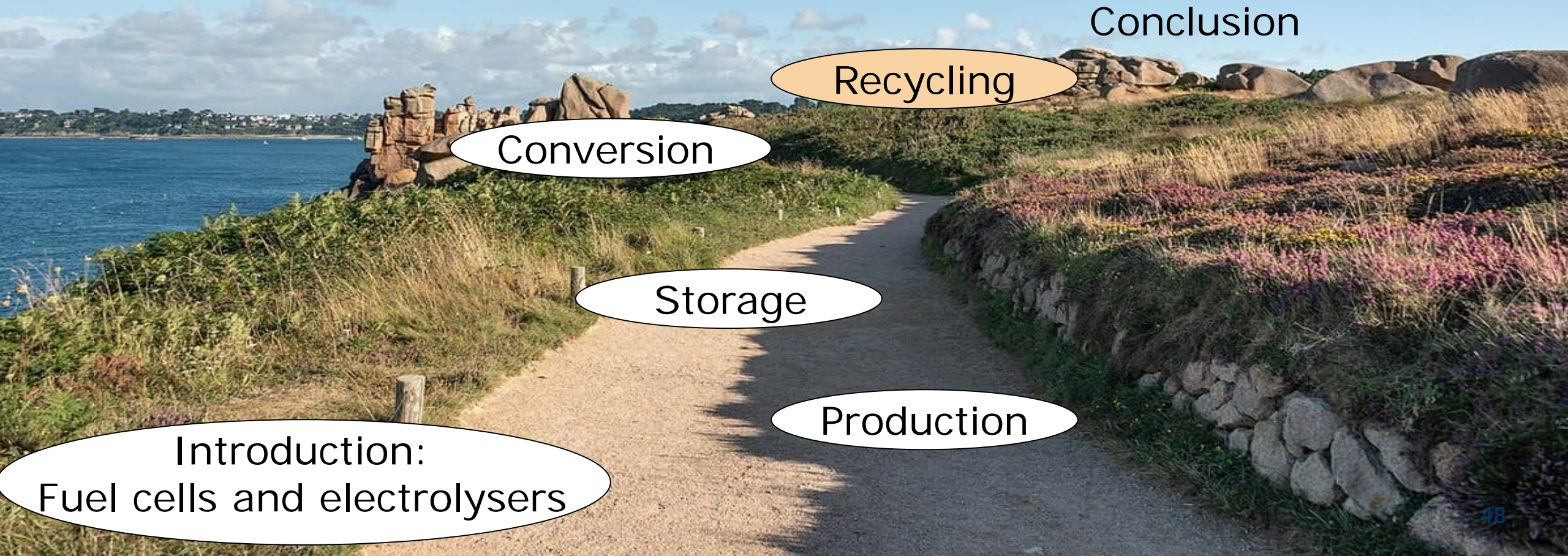
Precise objectives on the fuel side

- ✓ Carbon formation $< 0,5 \text{ mg}_{\text{carbone}} \text{ g}_{\text{cat}}^{-1} \text{ h}^{-1}$ à 600°C
- ✓ H_2S tolerance between 3 and 5 ppm
- ✓ Power density (without reforming) of 1 W/cm^2 at 600°C

... But also on the air side:

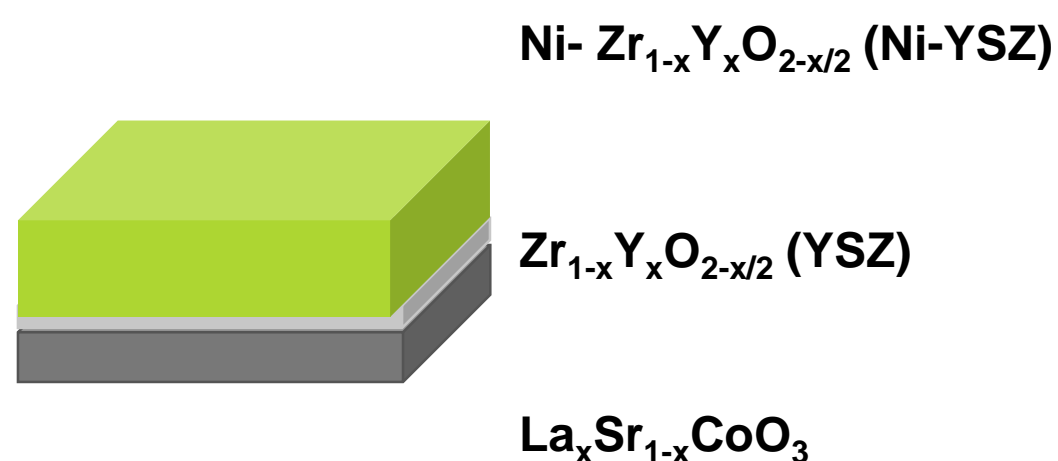
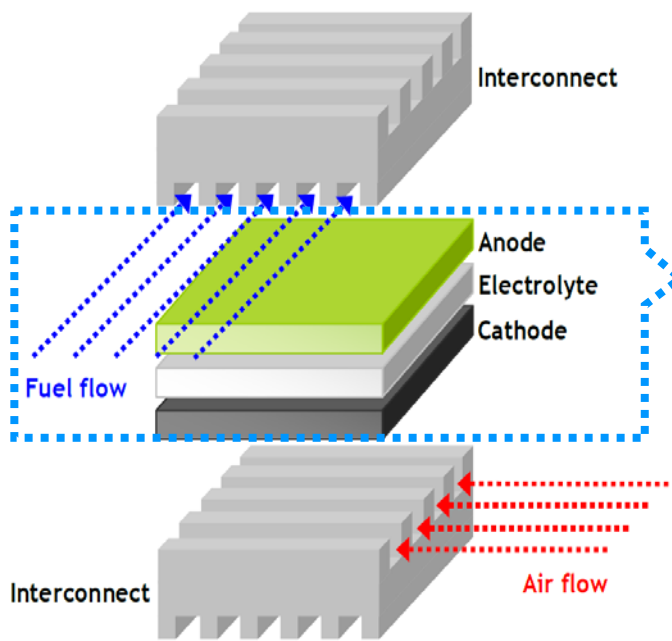
Increase of tolerance towards air impurities (NO_x)

Outline

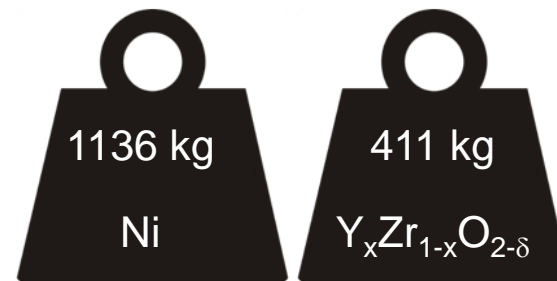


Recycling... Why?

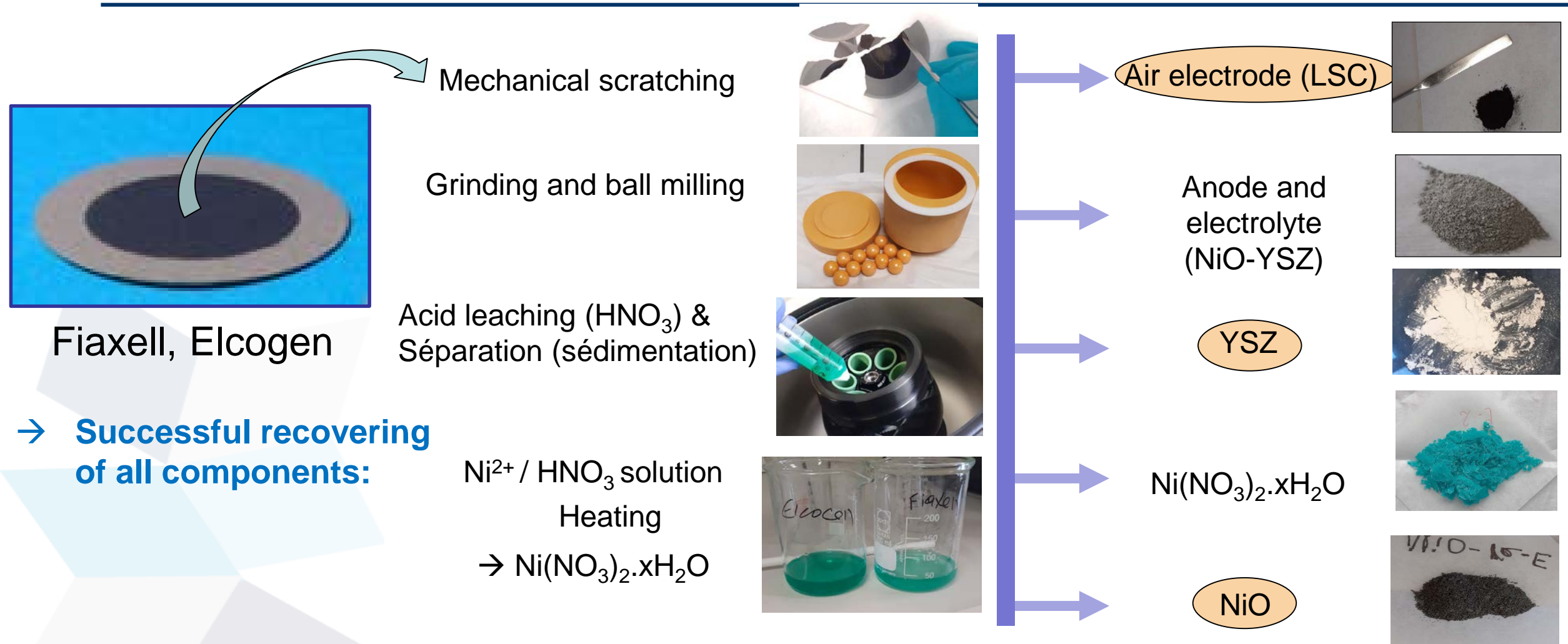
Aim:
Recycling and re-use of oxides entering the composition of commercial cells



Interest: 1MW electrolysis*:

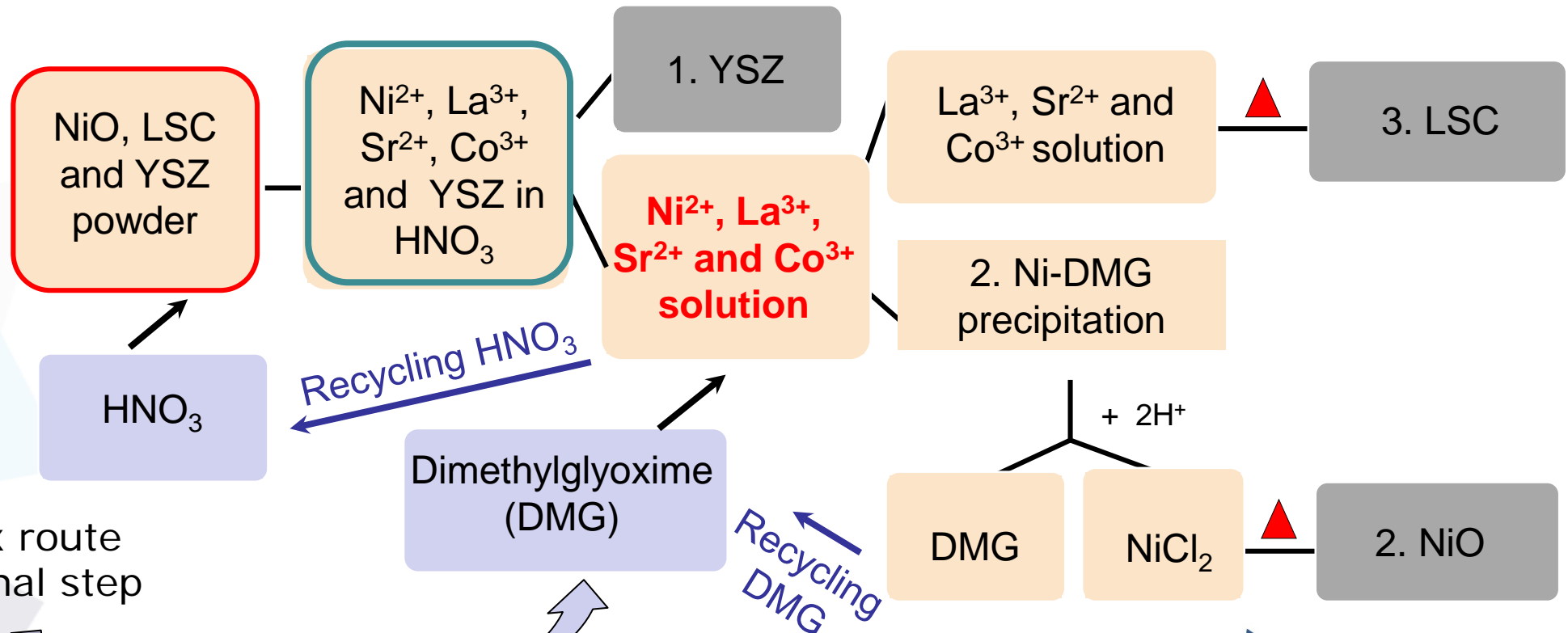


PhD, 80|PRIME CNRS program : 1st route



PhD, 80IPRIME CNRS program : 2nd route

Broken cells???
→ Grinding of the entire cell



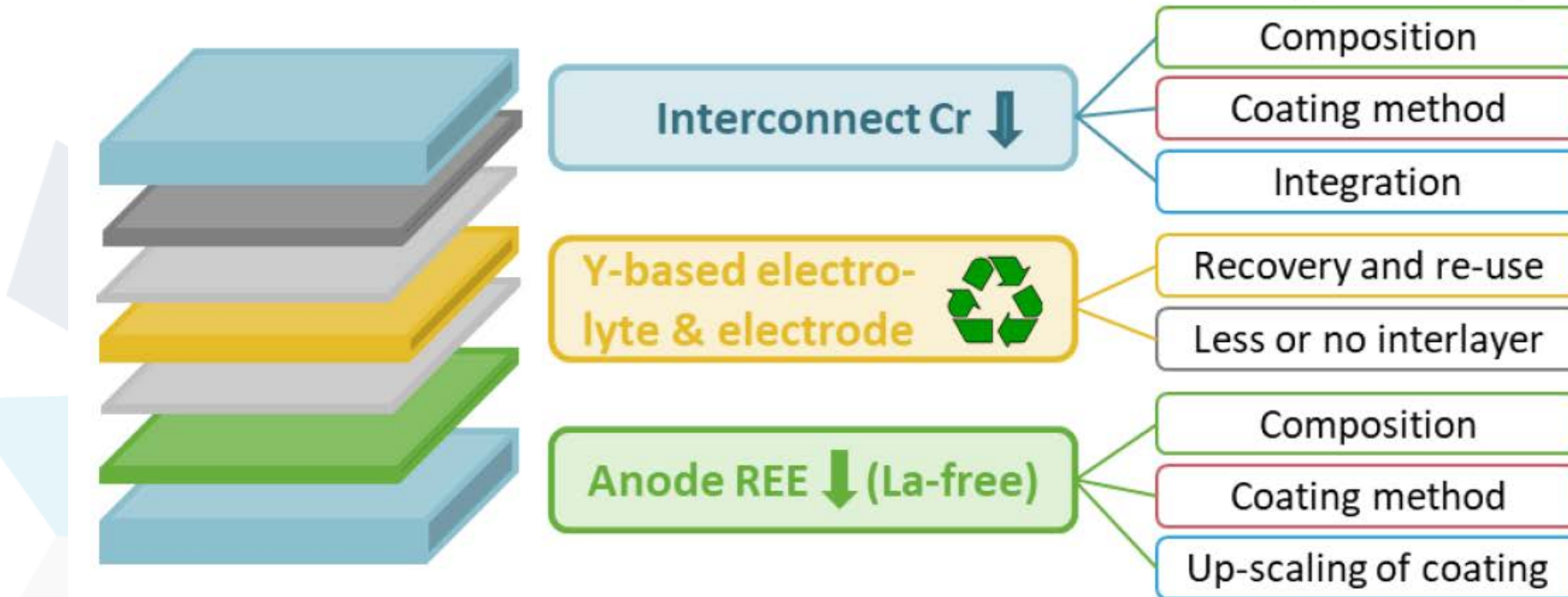
More complex route
→ One additional step

European project NOUVEAU (2022-2025)

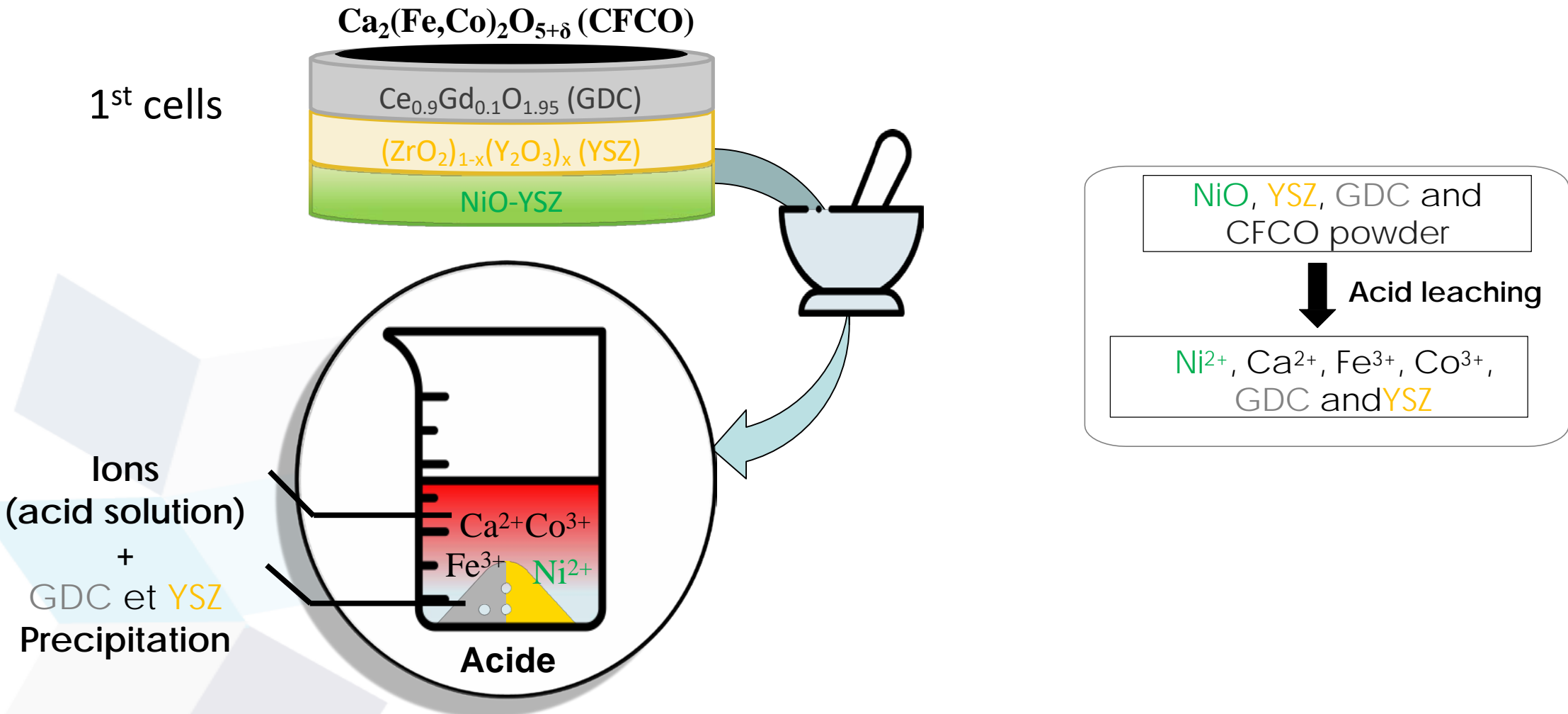


NOVEL ELECTRODE COATINGS AND INTERCONNECT FOR SUSTAINABLE AND REUSABLE SOLID OXIDE ELECTROLYSIS CELLS

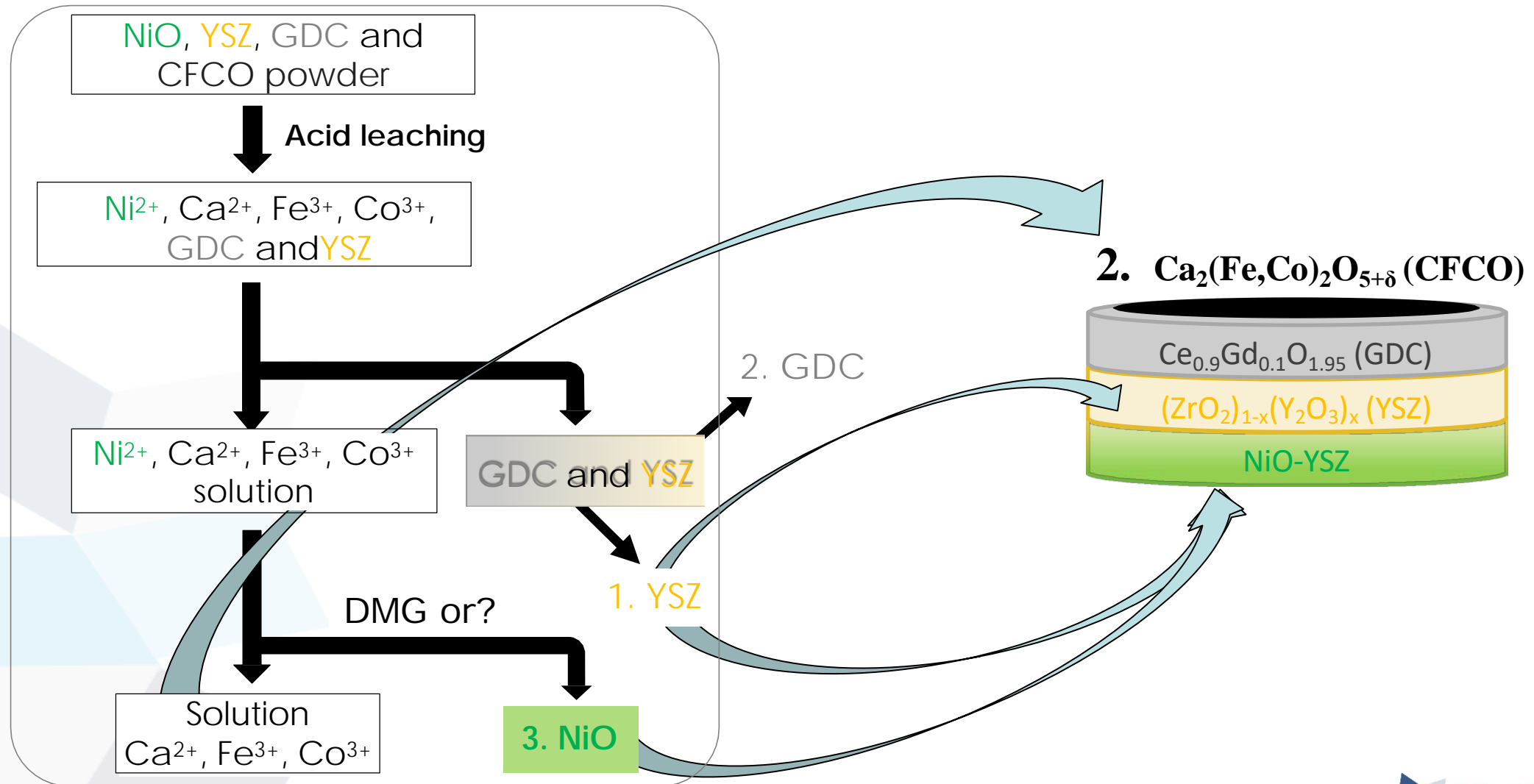
EU Grants: Application form (HE RIA/IA): V1.2 – 25.05.2021



European project NOUVEAU (2022-2025)



European project NOUVEAU (2022-2025)



Outline

Introduction:
Fuel cells and electrolysers

Storage

Conversion

Production

Recycling

Conclusion

Conclusion

Hydrogen sector to be developed (with other storage technologies) in order to limit CO₂ emissions and global warming

→ Technical limitations to overcome for fuel cells/electrolysers :

↗ Durability : Targets: 40 000 h to 60 000h (stationary, HT systems)
5 000h (transport)
+ robustness (temperature, ...)

↗ Versatility : Increase tolerance to pollutants to use industrial H₂ or coming from biomass

↘ Costs : use of rare and expensive materials (Pt)

→ Technical limitations *for the whole sector (FC/Electrolysers/Storage)*

↘ Environmental impact of the synthesis and use, Life Cycle Analysis

To conclude... evolution of our research topics...

**New materials:
electrolyte, electrodes
Synthesis → Recycling**

**Cell Shaping: New
and/or optimized
methods**

**Diagnosis by EIS: Application to materials
and complete cells**

**Enlarging cell operating conditions, other fuels,
and other conditions of electrolysis
(seawater electrolysis, marine atmosphere,...)**

... non-toxic and cheap
reagents, and involving less
energy consuming reactions

... Recyclable
materials

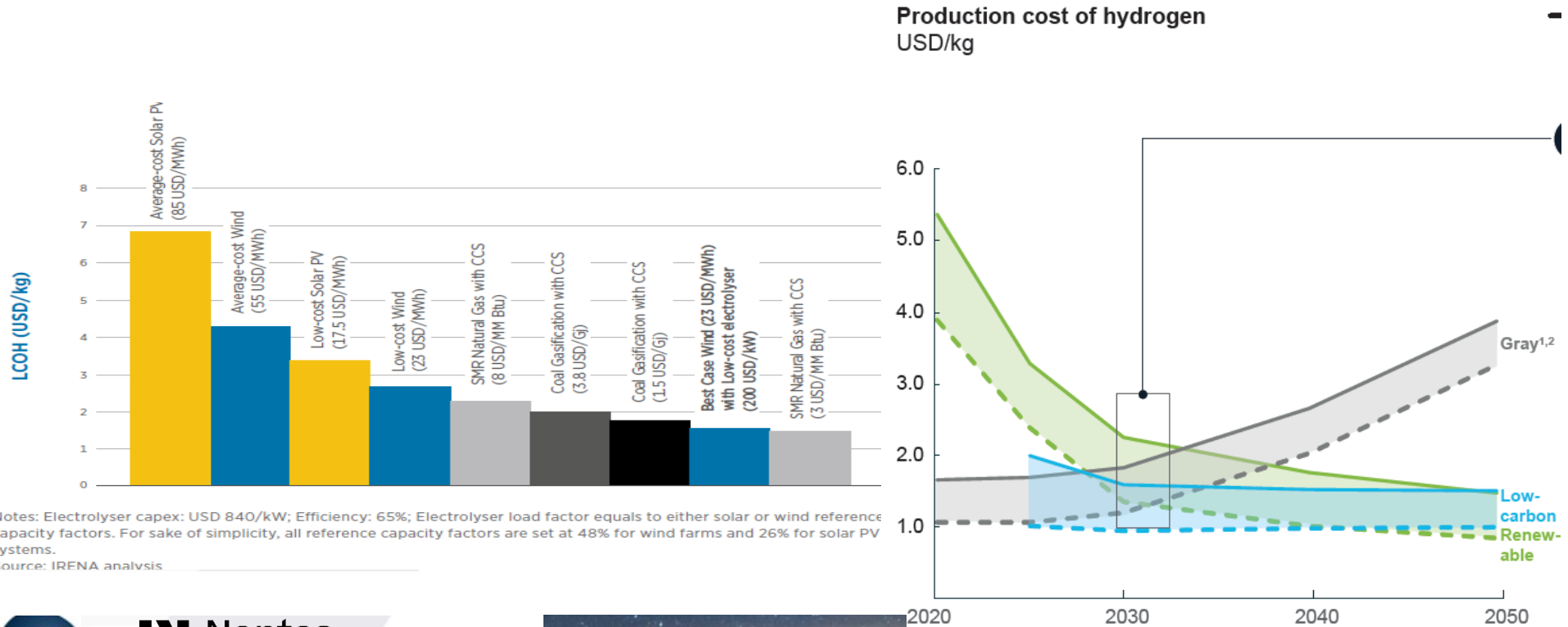
...recyclable cells

Outlooks

Besides technical objectives:

- Enlarge H₂ infrastructures deployment
- Create and harmonize hydrogen regulations between countries

... depends on political wills...



Notes: Electrolyser capex: USD 840/kW; Efficiency: 65%; Electrolyser load factor equals to either solar or wind reference capacity factors. For sake of simplicity, all reference capacity factors are set at 48% for wind farms and 26% for solar PV systems. Source: IRENA analysis

- Chile : 2028?
- Germany: 2032?
- US (some states) 2034?

And finally...

A lot of technical exciting challenges

But none technical solution will prevent our earth to be limited...

**We need a real
energy saving policy
all around the world!**



Aknowledgments



ARCADE



OPHARM

DEBHAT

FLEXISOC

CELCER-HT



MODTESTER



PROTEC

NOUVEAU

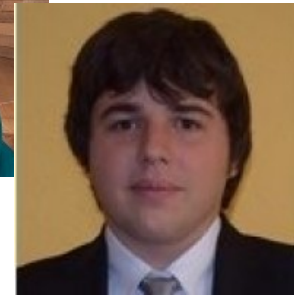
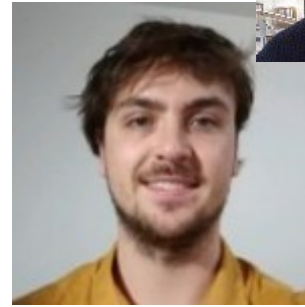
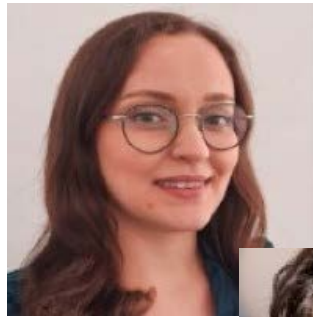


Aknowledgments

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Annie LE GAL LA SALLE
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Thanks for your attention!

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