INTERNATIONAL IBERIAN NANOTECHNOLOGY LABORATORY

NOA Nanofabrication for Optoelectronic Applications

High performing Photoelectrochemical (PEC) systems based on hematite

Café com Física :: 2021-06-02

António Vilanova

antonio.vilanova@inl.int

NOA GROUP :: Nanofabrication for Optoelectronic Applications

- Overview on green-H_2 production
- Basic principles of PEC water splitting
- Hematite photoelectrodes for PEC water splitting
- Challenges for developing new PEC devices
- The future of PEC-H_2 production

But first, just a short presentation about myself…

From **Santo Tirso**
Currently living in **Póvoa de Varzim**

MSc in Environmental Engineering at FEUP :: 2009-2014

Dissertation with the title “Preparation and optimization of hematite photoanodes for hydrogen production from photoelectrochemical cells”

Member of the UPorto team in the EU Project PECDEMO :: 2014-2017

Research fellow at LEPABE (Laboratory for Process Engineering, Environment, Biotechnology and Energy)

PhD on Chemical and Biological engineering :: 2017- Feb 2021

LEPABE (Laboratory for Process Engineering, Environment, Biotechnology and Energy), Dissertation with the title “Photoelectrochemical devices for solar hydrogen production”

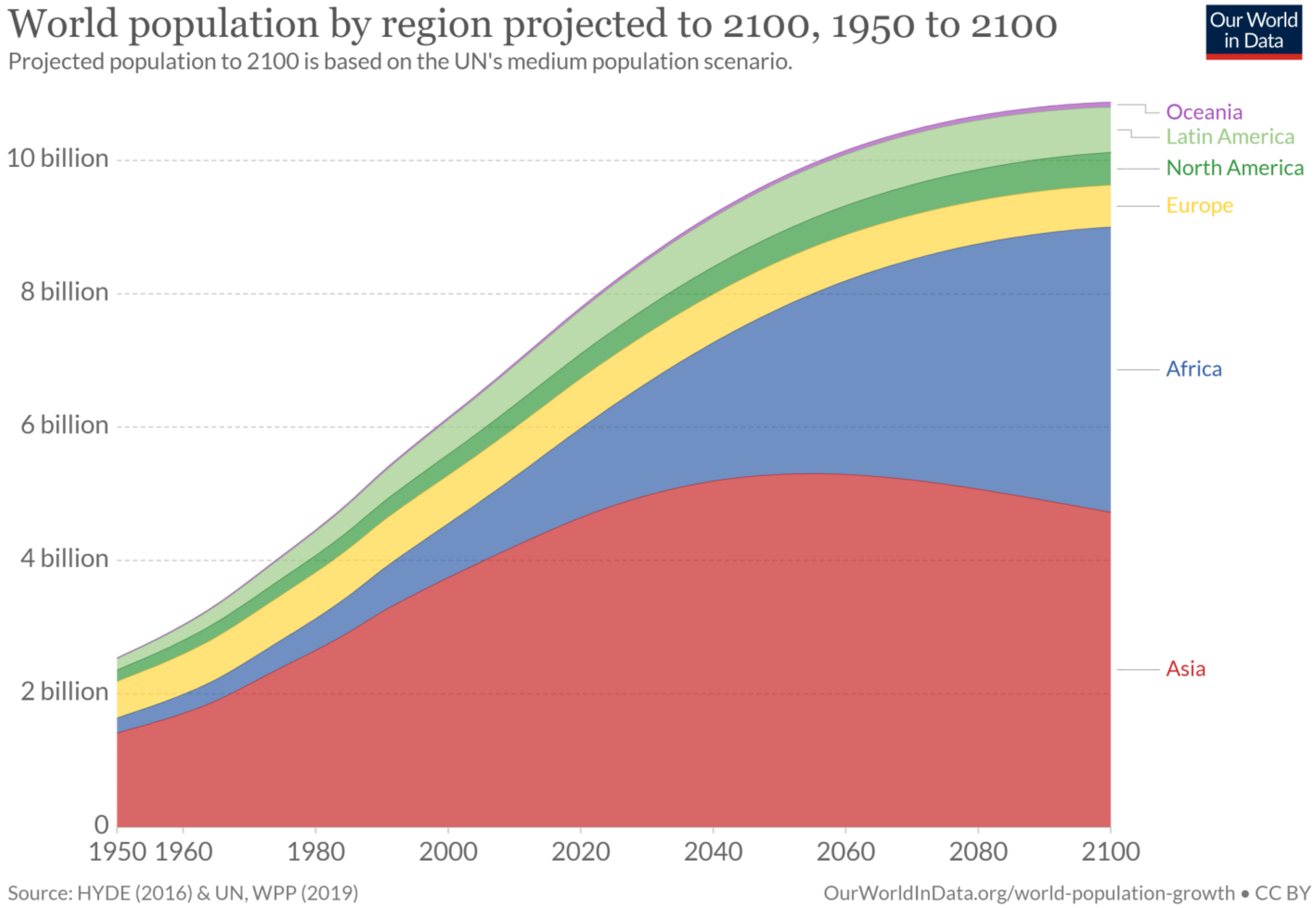
Research Fellow at INL:: Apr 2021-present

NOA group (Nanofabrication for Optoelectronic Applications)

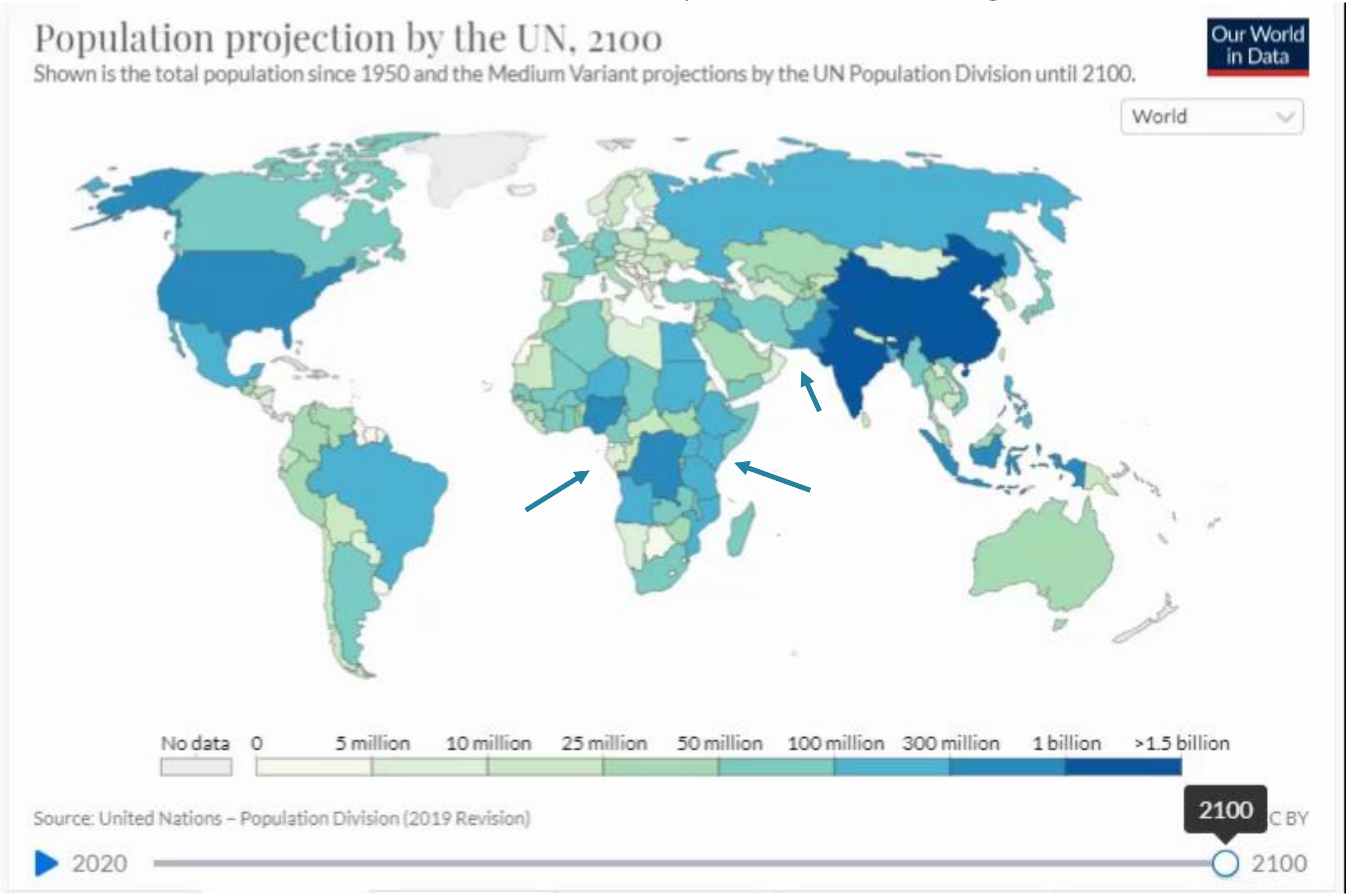
And now, lets move on with it…

Population growth and the energy dilemma

Energy challenges have always been related with the world **population growth**, which is experiencing an **exponential growth**.

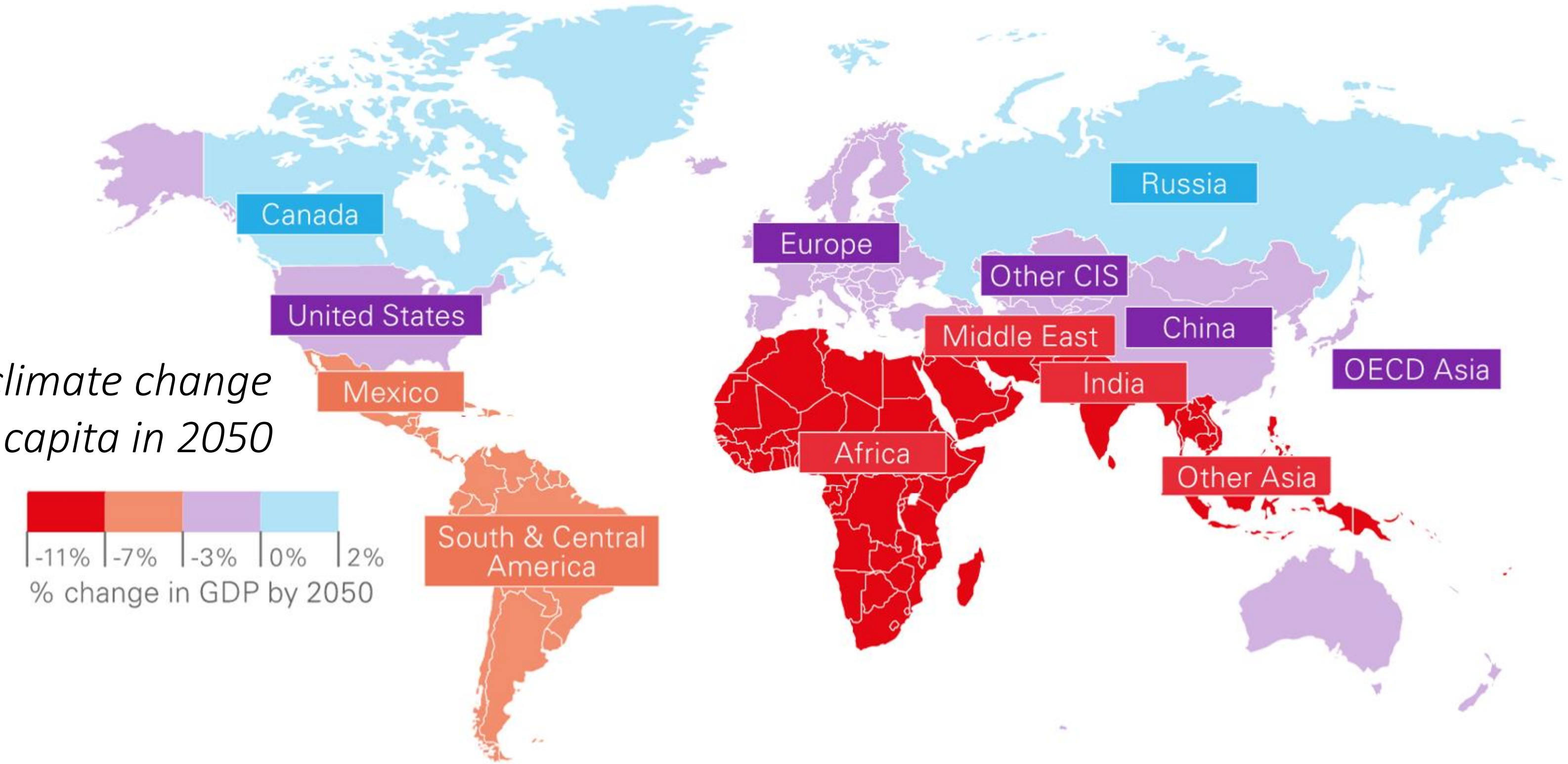


The world population growth is projected to reach a peak by 2100.
However, **not all countries will experience the same growth rate**.



Poorer countries will be the most affected by climate change, which will create **millions of climate refugees**.

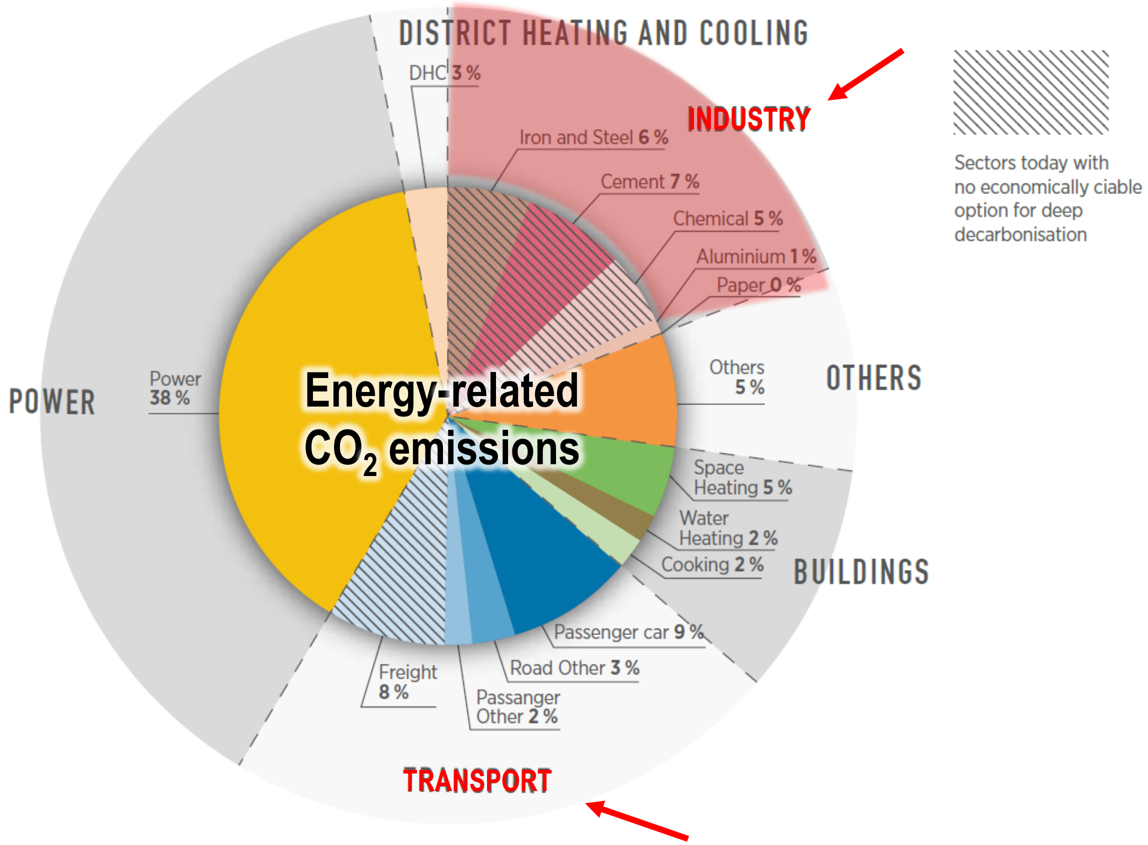
Impact of climate change in GDP per capita in 2050



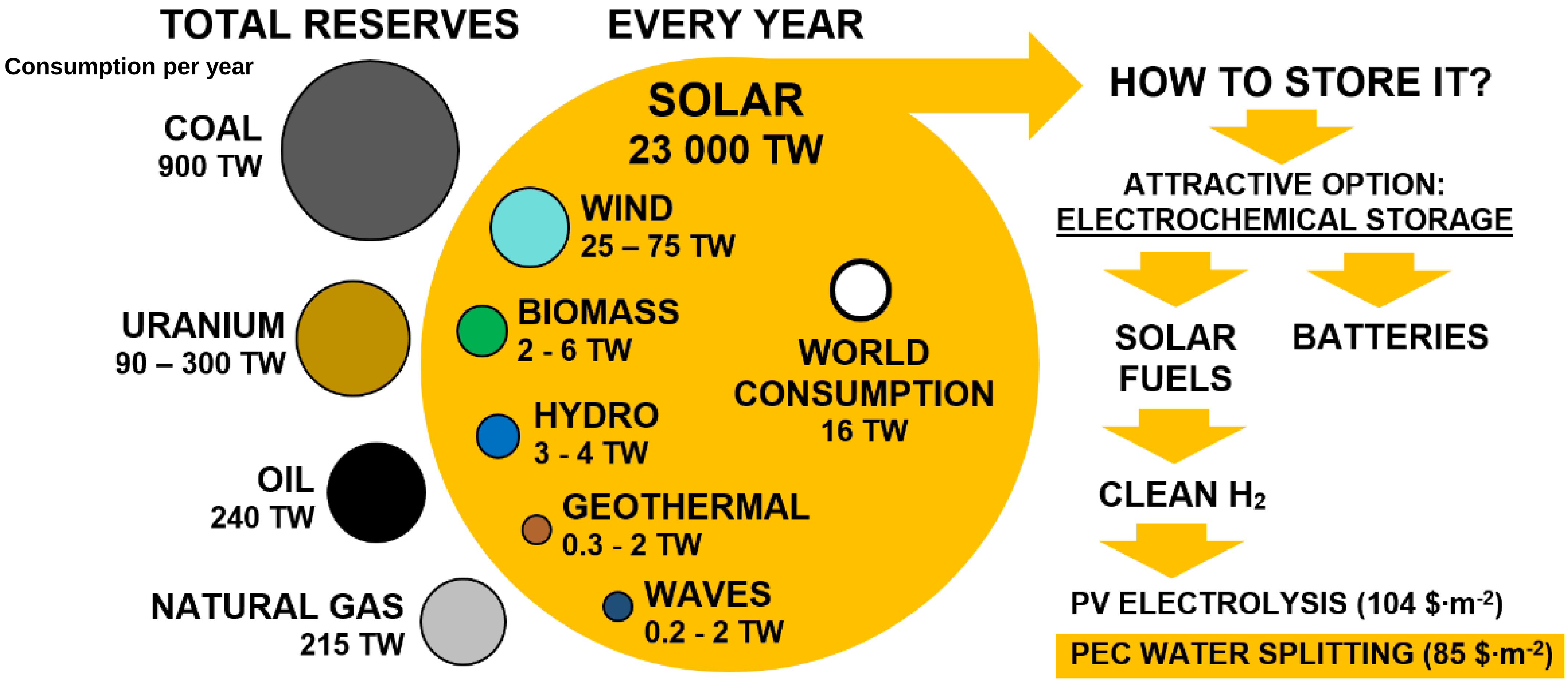
Impact of climate change in GDP per capita in 2050. Source: BP energy outlook 2020 ©

The world needs **practical technological solutions** that enable a **rapid transition** to an economy based on **renewable energy sources**.

The **industry** and **transportation** sectors require the use of liquid fuels, where electricity and batteries are not an option; **hydrogen** could be an interesting alternative.

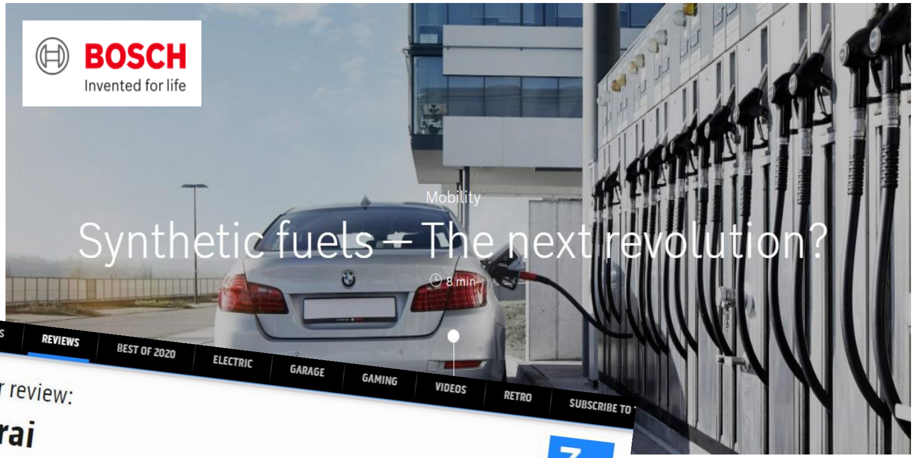


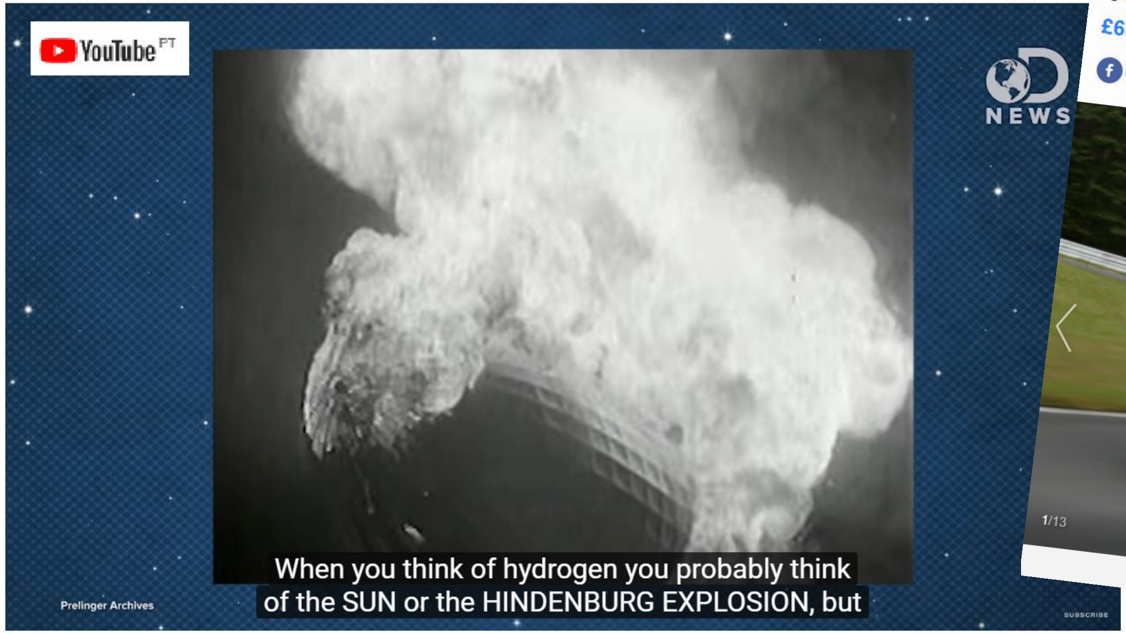
Breakdown of global energy-related CO_2 emissions by sector in 2015. Source: IRENA © 2017



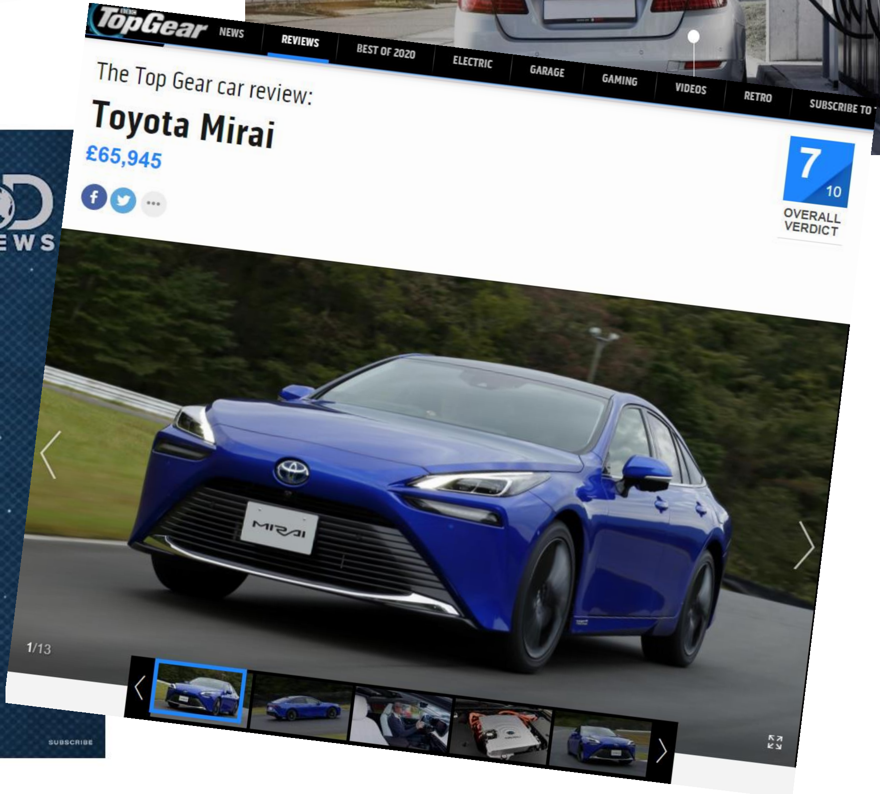
Shaner, M.R., et al., Energy & Environmental Science, 2016.

HYDROGEN always surrounded by myths, doubts and fears...



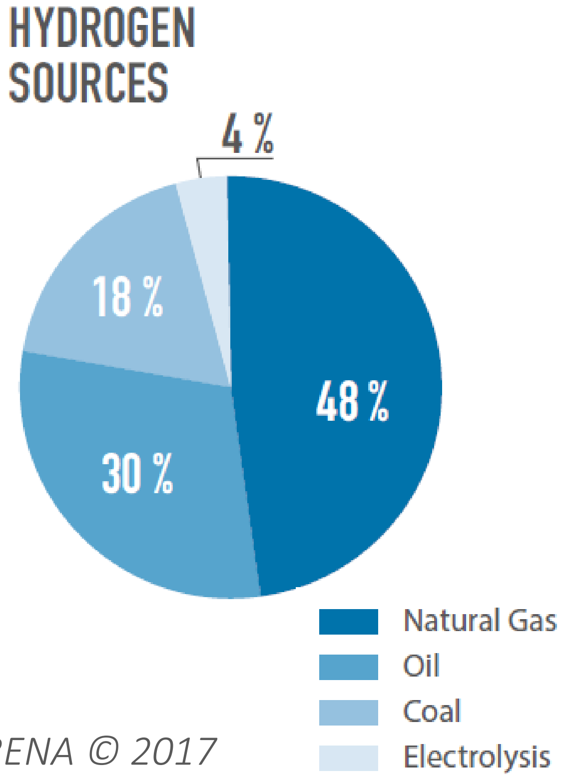


Will Your Hydrogen Car Explode?



Hydrogen is considered a promising option for the upcoming decades, mainly due to its advantages as an **energy carrier** and as **industrial feedstock**.

But **where does hydrogen come from**?



Source: IRENA © 2017

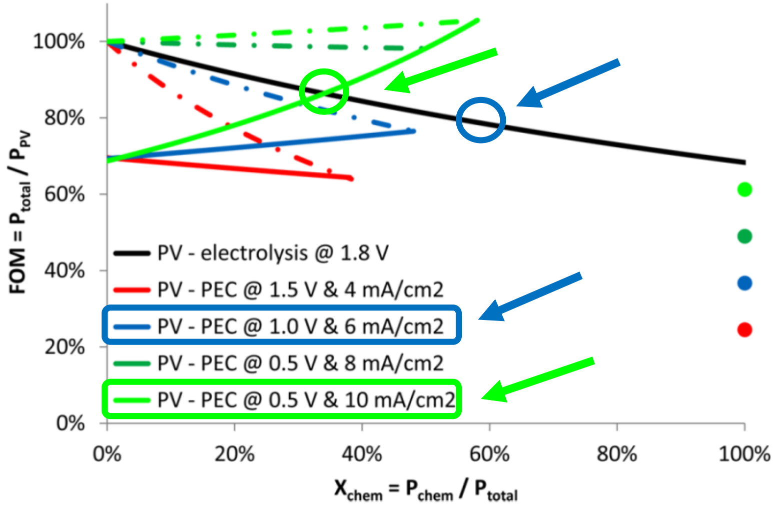
To be considered a proper **green alternative,** H_2 must be produced from renewable sources in a **cost-competitive, emission-free, and efficient way**.

Hydrogen produced from water electrolysis has always been pointed quite promising for the **transportation and industry sectors**, alternatively to fossil fuels.

… and is a well-known process, **optimized over two centuries.**

Presently, clean **water electrolysis** can be made using highly **efficient PV cells**.

So, where does photoelectrochemical hydrogen takes part?



Calculated FOM (figure of merit) as a function of the fraction of the power that goes toward chemical generation (X_{chem}) for hypothetical PV-electrolysis (black) and PV–PEC tandem cells (color) that co-generate chemical (i.e., hydrogen) and electrical power.

Solid lines: PV cells are covered by PEC cells in front, with 30% reduction of their power due to light absorption.

Broken lines: the reduction in PV power production scales with the chemical power production by the PEC cells.

Filled circles: conventional PV–PEC tandem cells that produce only hydrogen and no electrical power.

ACS Energy Letters
ACS Publications
© 2016 American Chemical Society
http://pubs.acs.org/journal/aelccp

Beating the Efficiency of Photovoltaics-Powered Electrolysis with Tandem Cell Photoelectrolysis

DOI: 10.1021/acsenergylett.6b00610
ACS Energy Lett. 2017, 2, 45−51

The basic configuration of a PEC system includes a <u>photo-sensitive electrode</u> and a <u>counter-electrode</u>, both immersed in an aqueous <u>electrolyte solution</u>.

Main component of the PEC cell:
<u>photoelectrode</u> ⟶ converts incident photons to <u>electron-hole pairs</u>.

Key requirements for a <u>semiconductor photoelectrode</u>:

(1) Efficient absorption of visible light;

(2) Good charge transport.

Ability of absorbing light → determined by the <u>bandgap</u> (E_g)

Most of PEC devices achieve very low efficiencies since most of the semiconductors <u>have a large energy bandgap</u>.

⇩

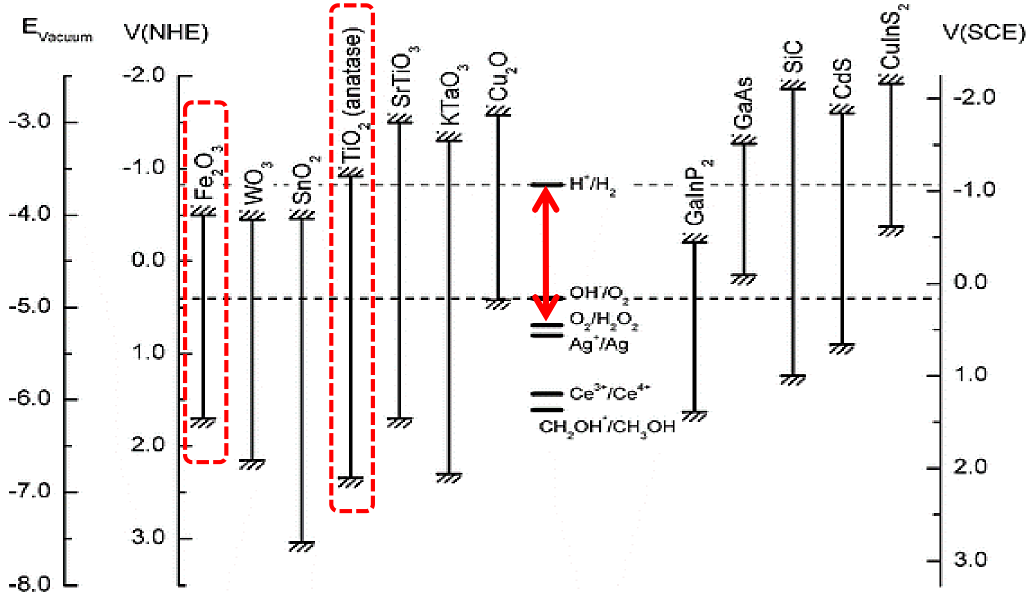
The band edge potentials are not suitable for oxygen and hydrogen evolution and the water splitting reaction cannot take place.

What should be the semiconductor requirements for water splitting?

1. Stability - resistant to chemical, mechanical and photo corrosion degradation;
2. Ability to absorb a large portion of the solar spectrum;
3. Energy difference between h^+ and e^- higher than 1.23 eV → bandgap of 1.6 – 2.0 eV;
4. The valence band shall be below the redox potential of O_2 formation;
5. The conduction band shall be above the redox potential of H_2 formation.

1971
Fujishima and Honda

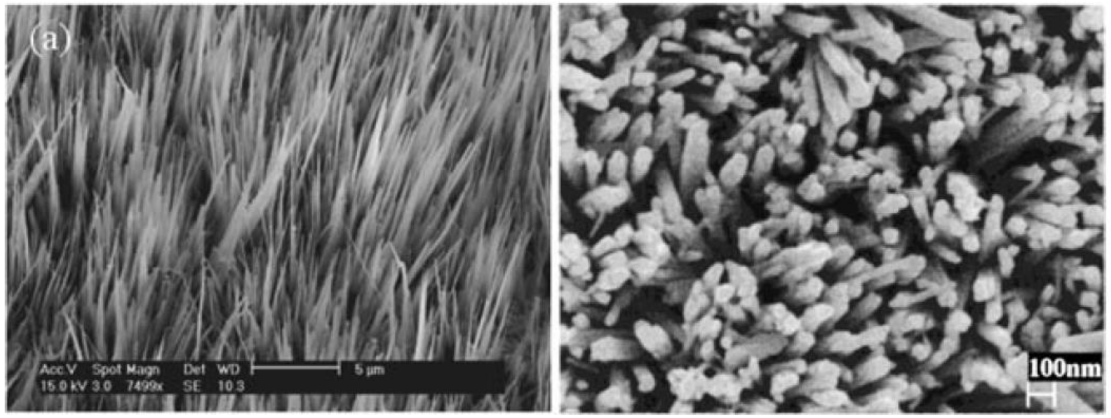
1976
Hardee and Bard



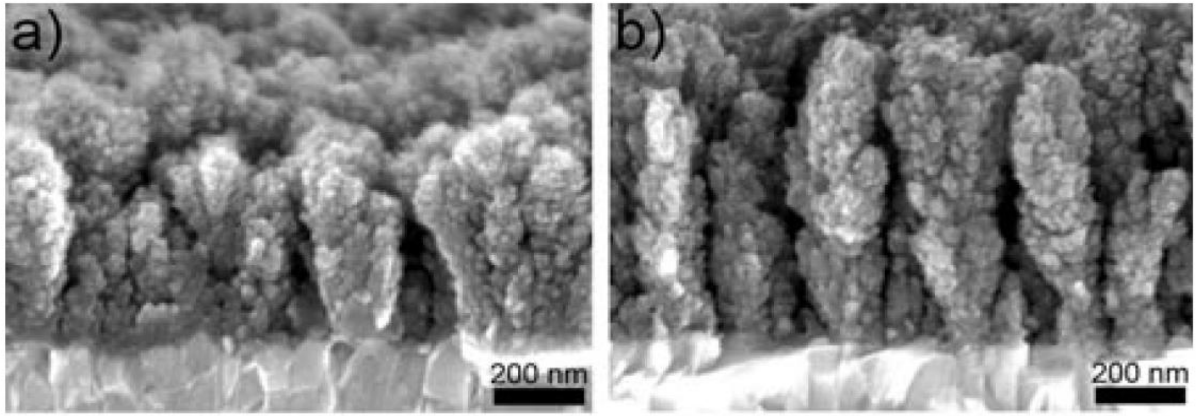
Band edge positions for some semiconductors at pH 14 and some important redox potentials.

(Adapted from van de Krol, R., Springer© 2012)

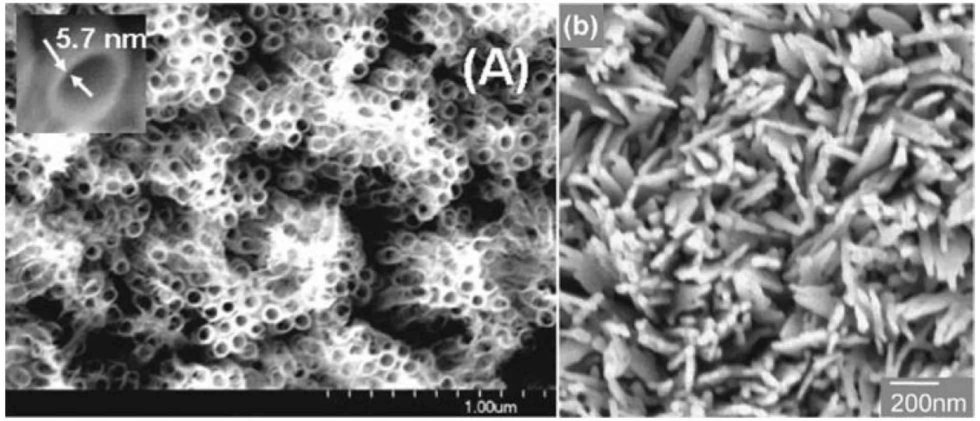
… and hematite photoelectrodes are quite versatile.



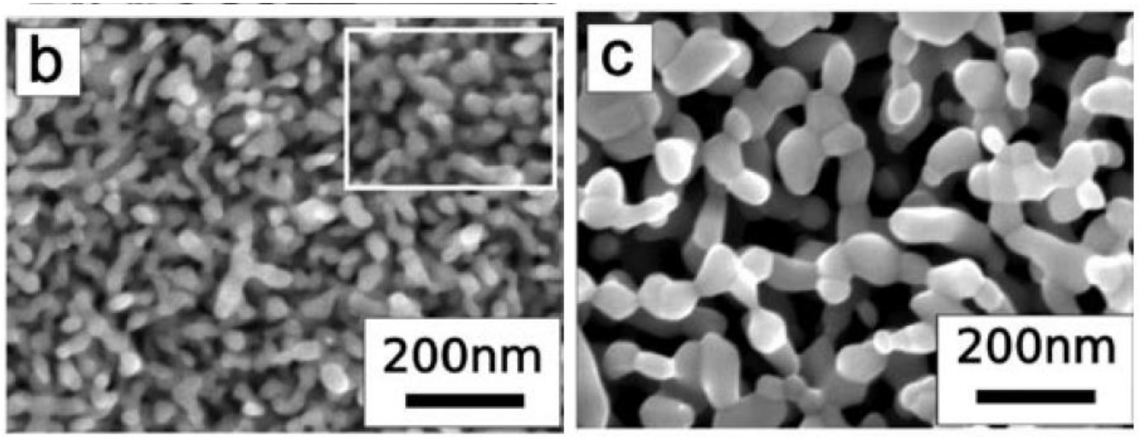
Thermal oxidation



APCVD



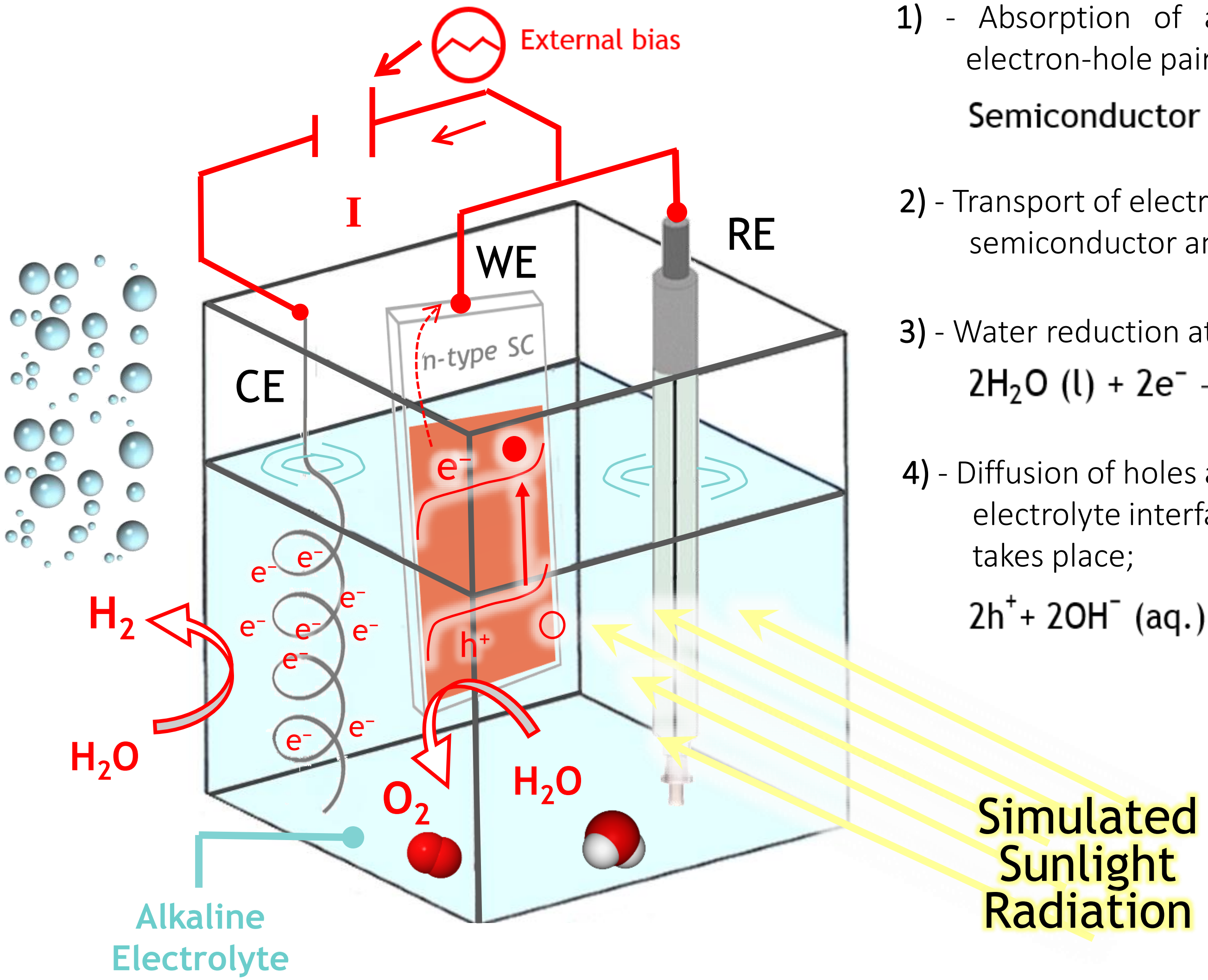
Electrochemical anodization



Hydrothermal method

Images from Sivula *et al*. ChemSusChem 2011, 4, 432 – 449

BASIC PRINCIPLES OF SOLAR WATER SPLITTING USING A α-Fe_2O_3 PHOTOELECTRODE



1) - Absorption of a photon, generating an electron-hole pair;

$$\text{Semiconductor} + h\nu \rightarrow (e^-_{CB} + h^+_{VB})$$

2) - Transport of electrons through the semiconductor and the external circuit;

3) - Water reduction at the cathode surface;

$$2H_2O\ (l) + 2e^- \rightarrow 2OH^-(aq.) + H_2\ (g)$$

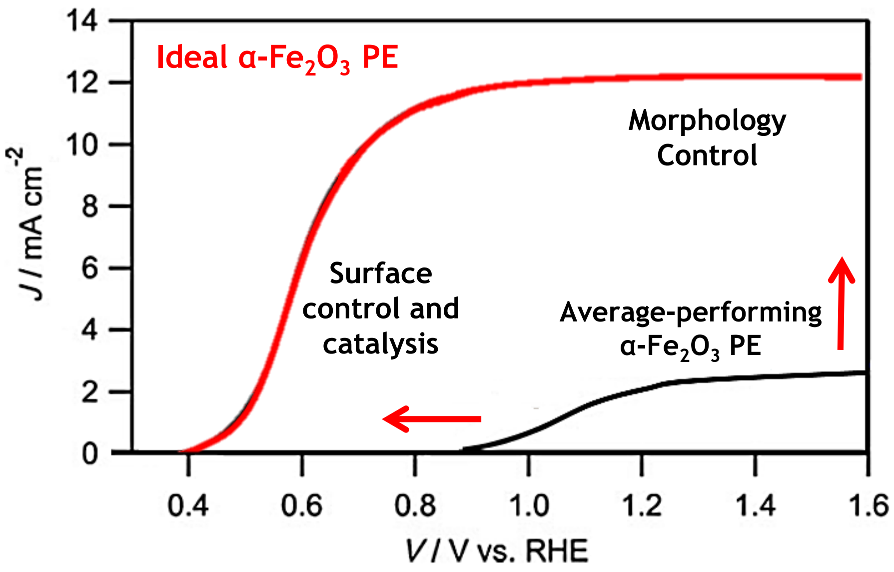
4) - Diffusion of holes at the semiconductor-electrolyte interface, where water oxidation takes place;

$$2h^+ + 2OH^-\ (aq.) \rightarrow H_2O\ (l) + {}^1/_2\, O_2\ (g)$$

Standard conditions:
1-sun illumination
(1000 W·m^{-2}),
25 ºC
and AM1.5G

KEY CHALLENGES FOR PREPARING EFFICIENT AND STABLE α-FE_2O_3 PES

- Increase the surface area;
- Structural integrity (chemical and mechanical stability);
- Application of co-catalysts without hindering the transmittance;
- Reproducible performance;
- Use scalable and low-cost preparation techniques;



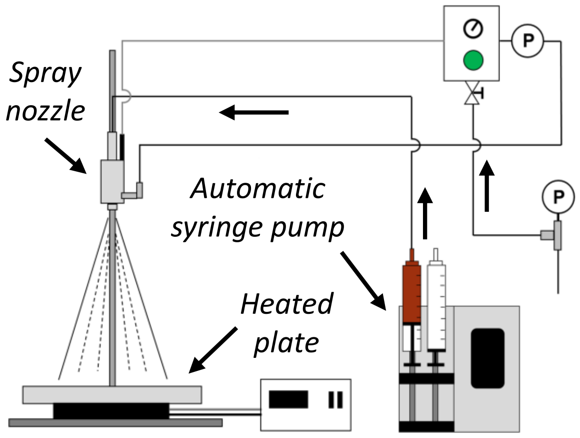
Spray pyrolysis and hydrothermal methods: two different tecnhiques for preparing upscaled hematite photoelectrodes

SPRAY PYROLYSIS TECHNIQUE

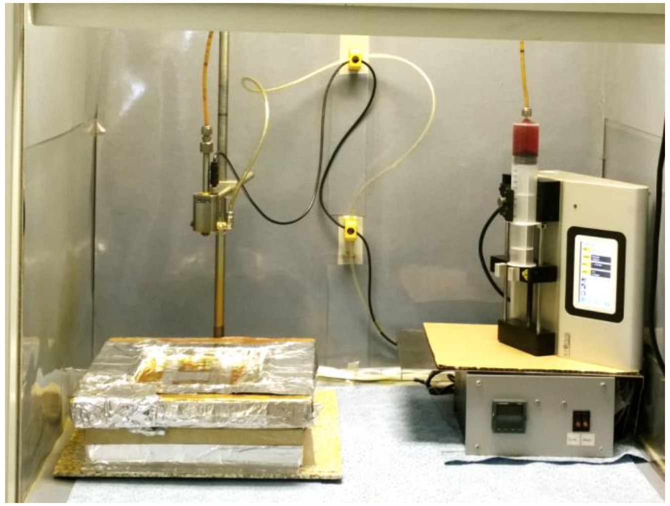
Consists of spraying a Fe^{3+} aqueous or ethanolic solution onto a hot substrate (400–600 ºC).

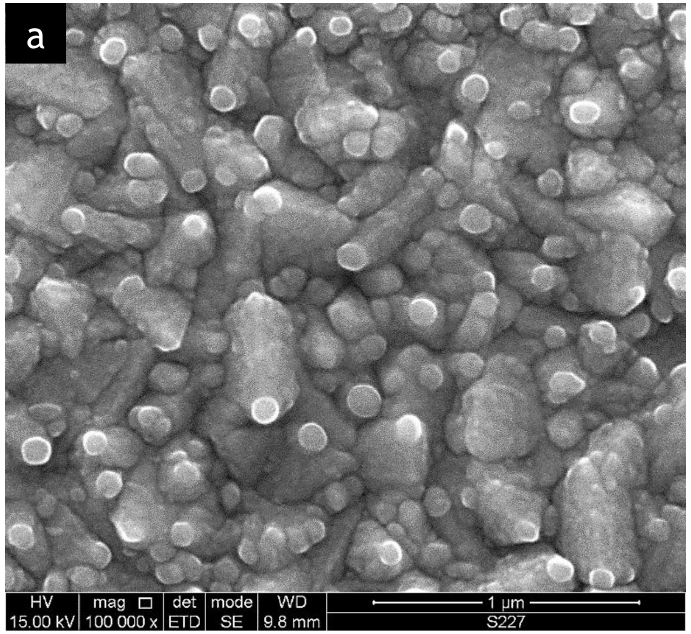
Main advantages:

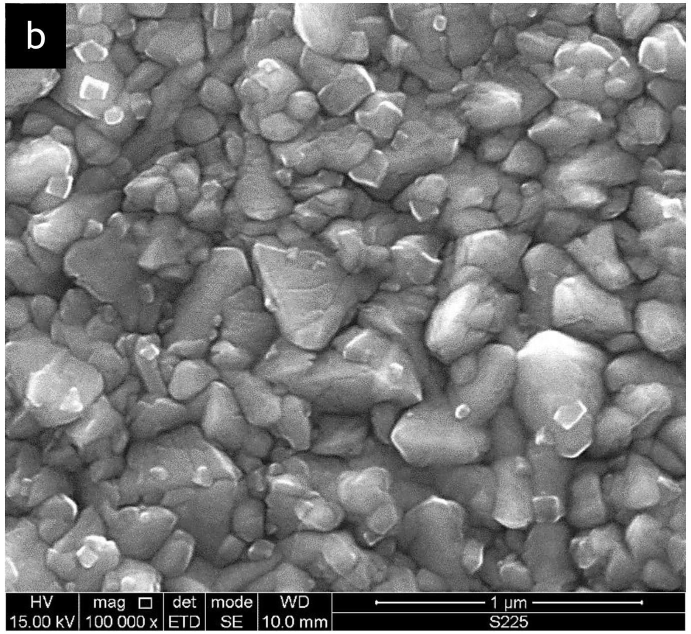
1. Does not require the use of very expensive equipment;
2. Easy operation steps;
3. Allows high reproducibility of stable samples.



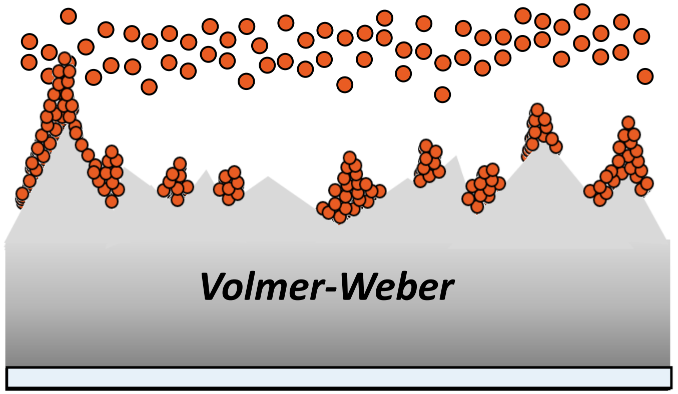
P. Dias, et al., Nano Energy, 23 (2016) 70-79

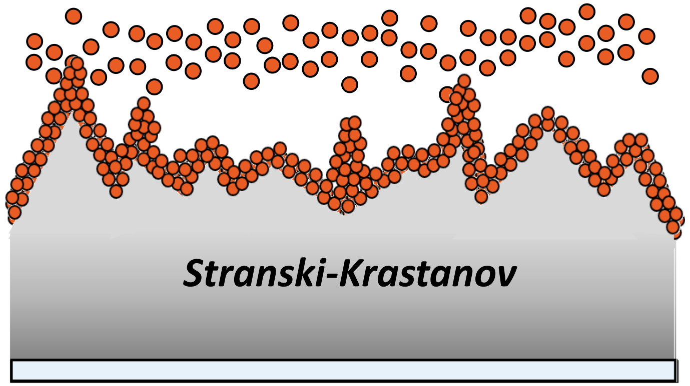


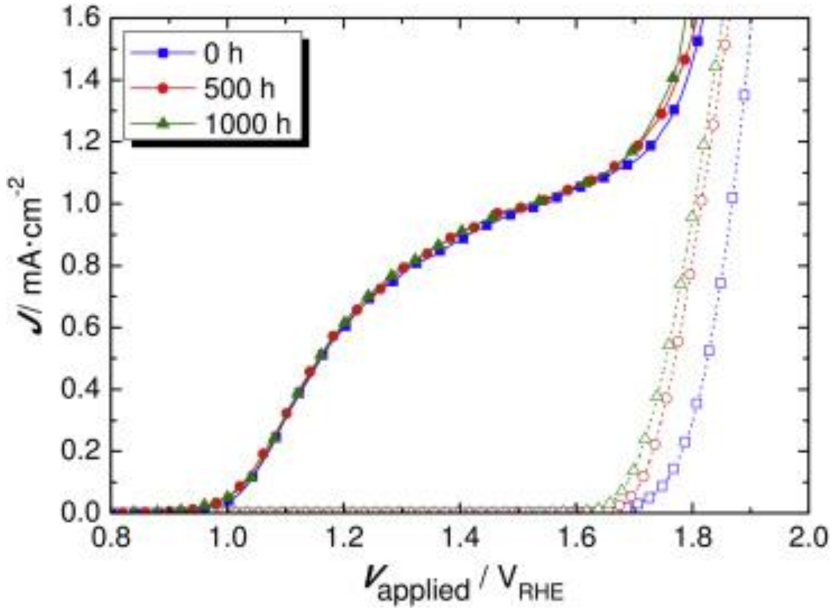


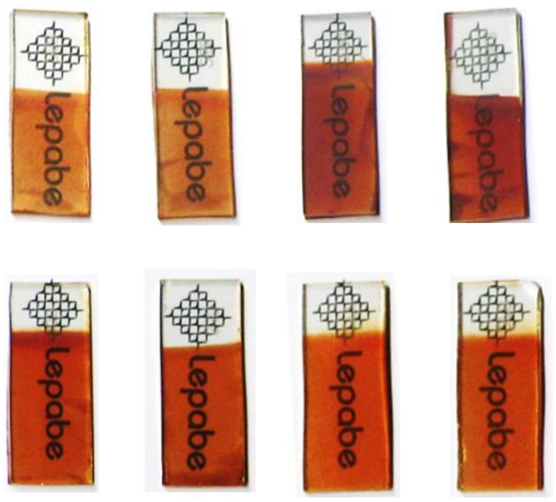


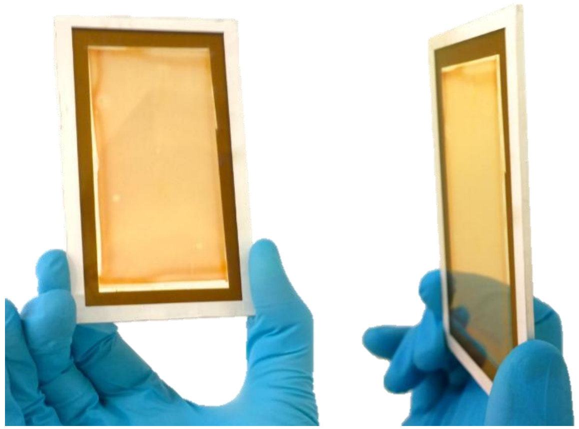
Top view SEM images of hematite films produced with the optimal conditions obtained by the DoE study: a) without TEOS pre-treatment; and b) with TEOS pre-treatment.











Hematite photoelectrodes prepared by spray pyrolysis (SP)

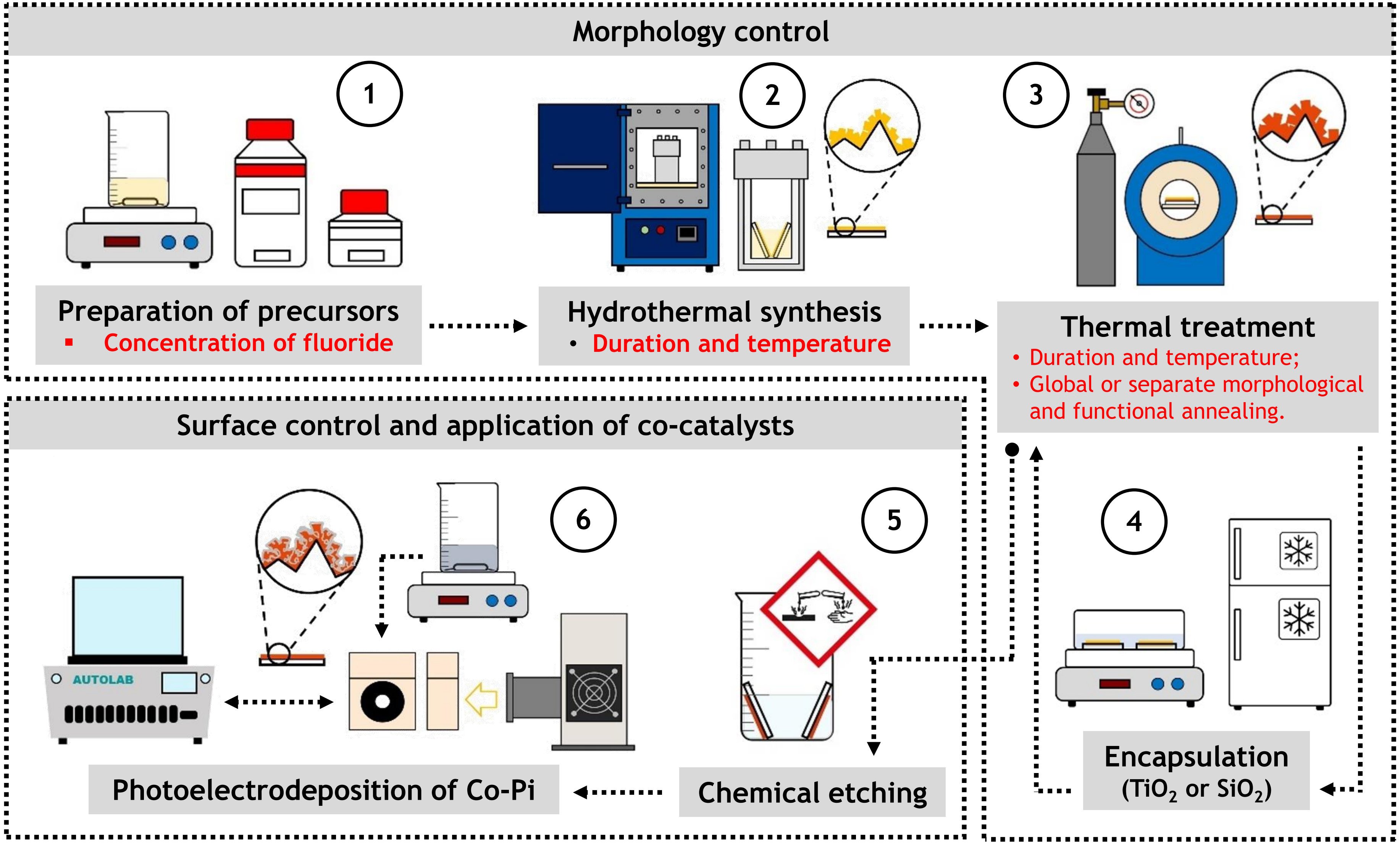
Pros

- Easy to prepare
- Easy to install
- Reproducibility
- Great stability
- High transmittance

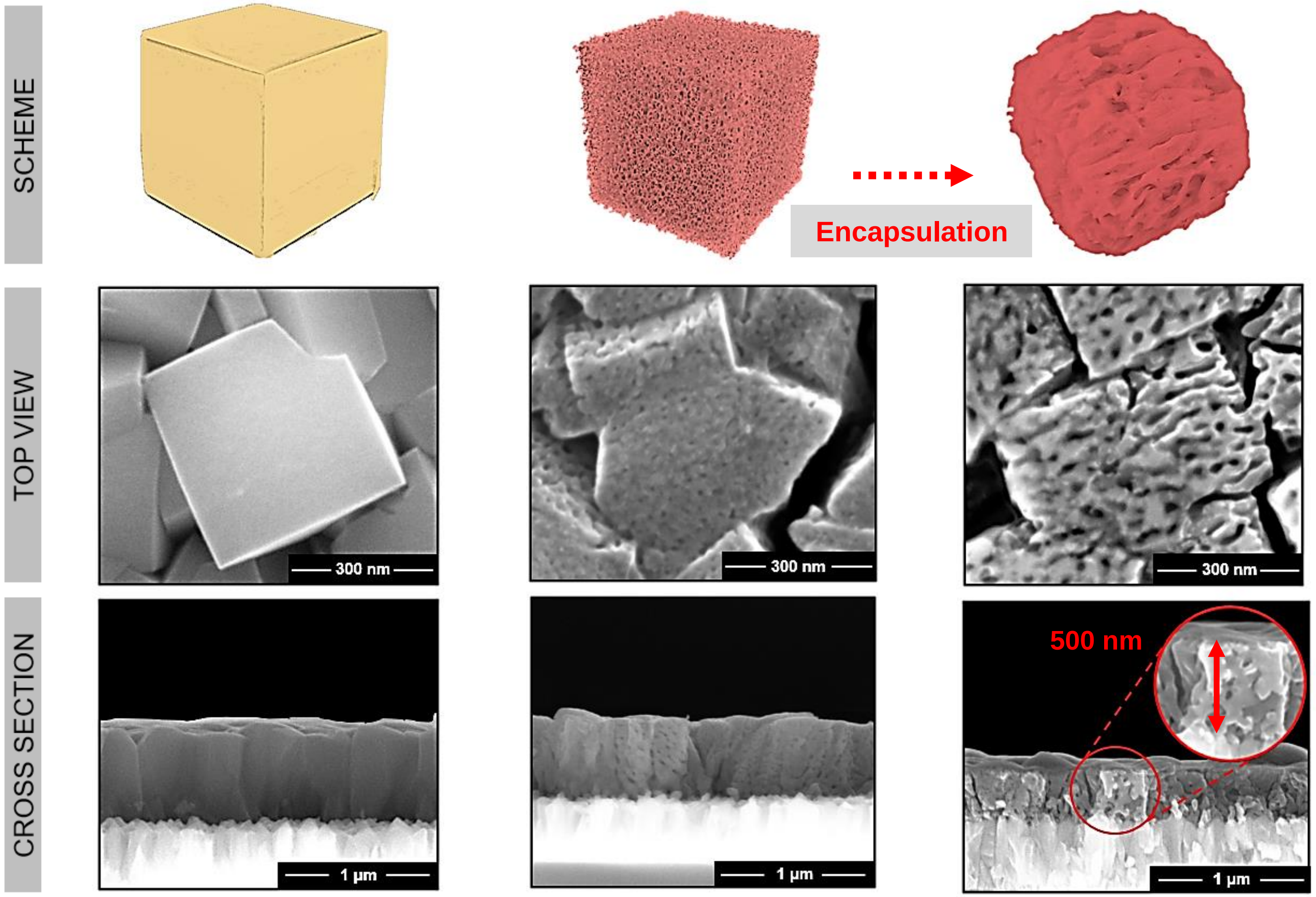
Cons

- Compact planar film
- Poor efficiency
- No room for further improvement

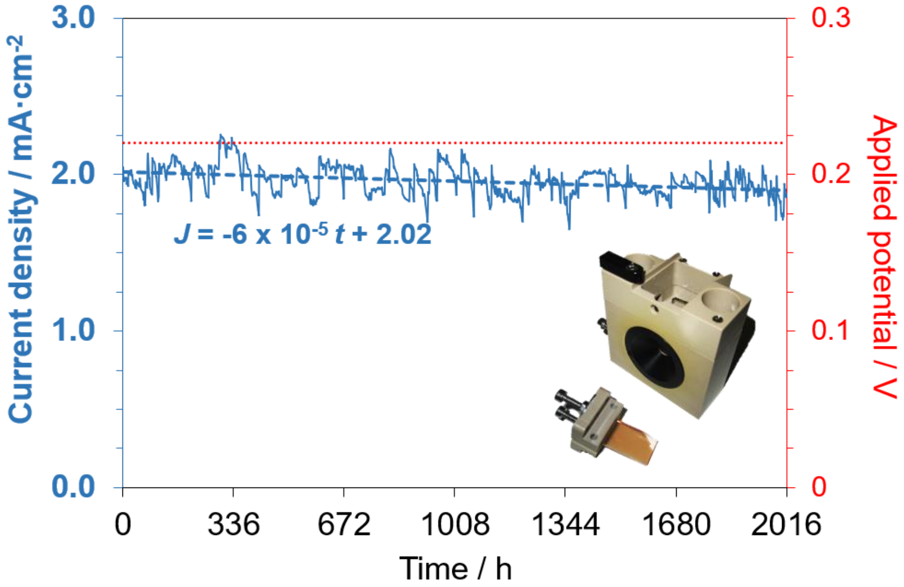
and that’s where hydrothermal methods become interesting

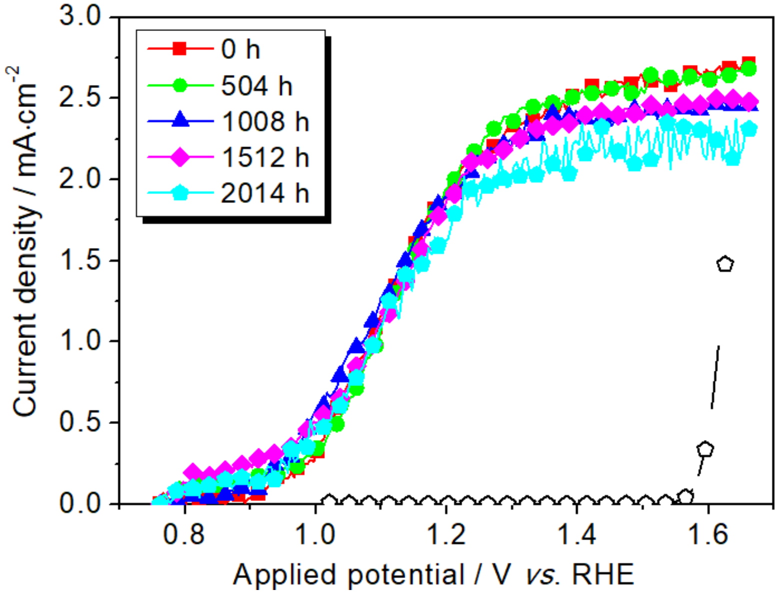

Morphology control
1
2
3
Preparation of precursors
Concentration of fluoride
Hydrothermal synthesis
Duration and temperature
Thermal treatment
Duration and temperature;
Global or separate morphological and functional annealing.
Surface control and application of co-catalysts
6
5
4
AUTOLAB
Photoelectrodeposition of Co-Pi
Chemical etching
Encapsulation
(TiO_2 or SiO_2)

Hydrothermal synthesis NH_4F 0.05 M 6 h at 100 °C	Morphological annealing 2 h at 550 °C	Functional annealing 20 min at 800 °C



A **top-performing nanostructured hematite PE** was subjected to a **long-term stability** test (1000 W·m^{-2}, AM 1.5 G) in a **small PEC cell filled with KOH 1.0 M**.





The sponge-like α-Fe_2O_3 PE remained stable over **2014 h**, generating *ca*. 2.01 mA·cm^{-2} at 1.23 V_{RHE}.

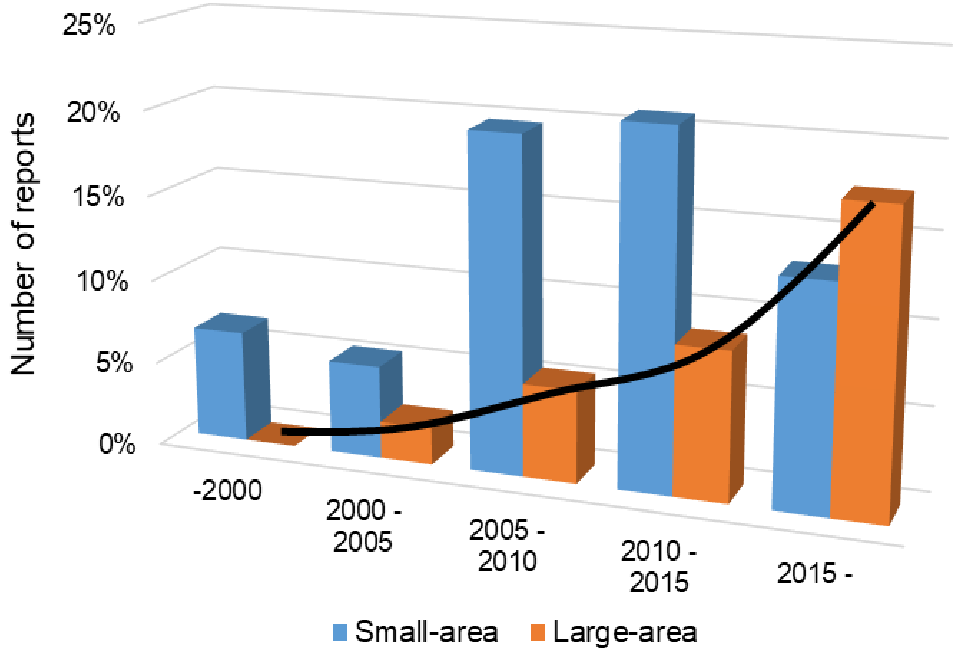
This record-breaking result more than doubles the state-of-art.

Everything looks so promising… So, why is PEC water splitting not commercial yet?

Over the last decades, the **upscaling of efficient materials** and the development of **large-area PEC devices** have been neglected.

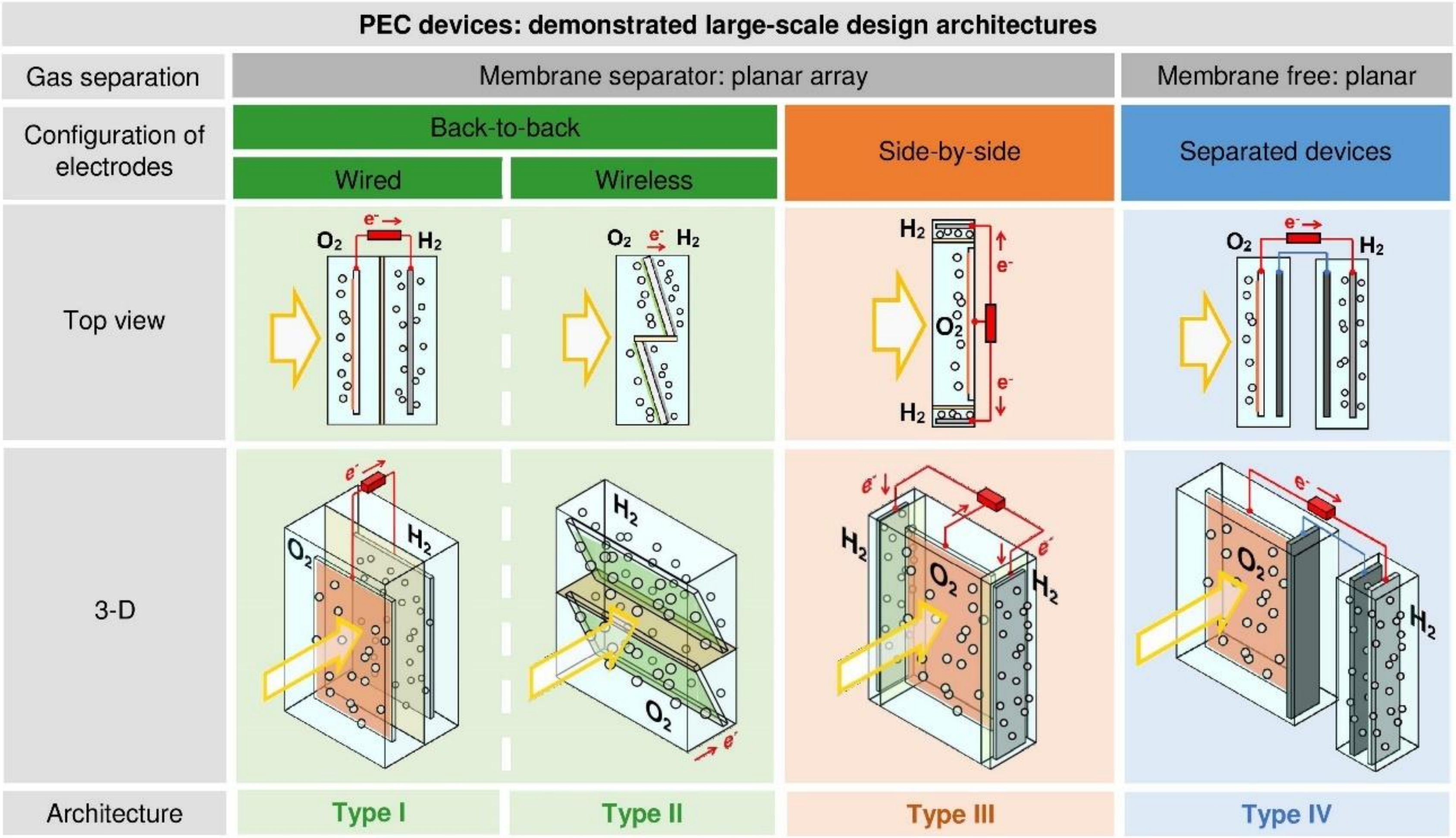
The **lack of a commercial prototype** has been considered the **main obstacle** for the integration of this technology in the energy market.

Luckily, a **change in paradigm** is now on-going.



Reported PEC reactors over the last 20 years: small-area (blue) and devices with an illuminated area ≥ 50 cm^2 (orange); (searched keywords: "photoelectrochemical" + "water splitting" + "small area" + "large area" + "device"); database: Google Scholar and Scopus.

Considering the **configuration of the electrodes** and the **strategy for gas separation** it is possible to categorize PEC devices into **four main types**.

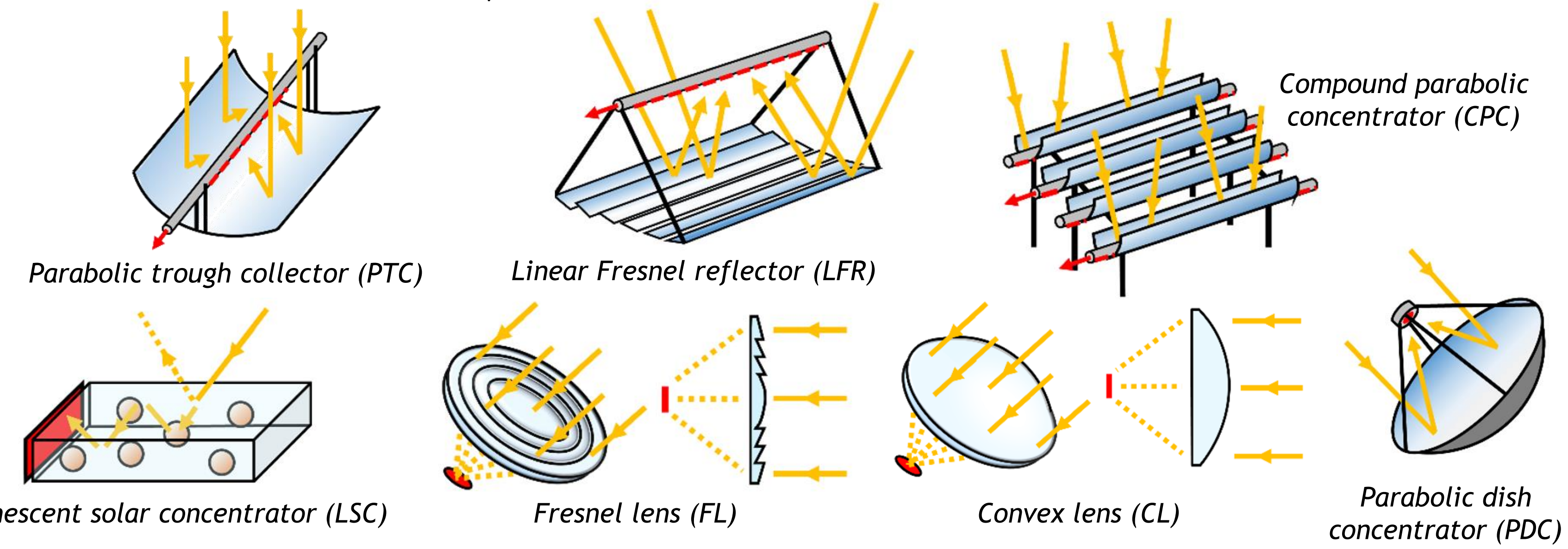


Independently from the device architecture, using **concentrated sunlight** is mandatory for achieving the efficiency targets at an industrial scale.

Symbiotic optimization process

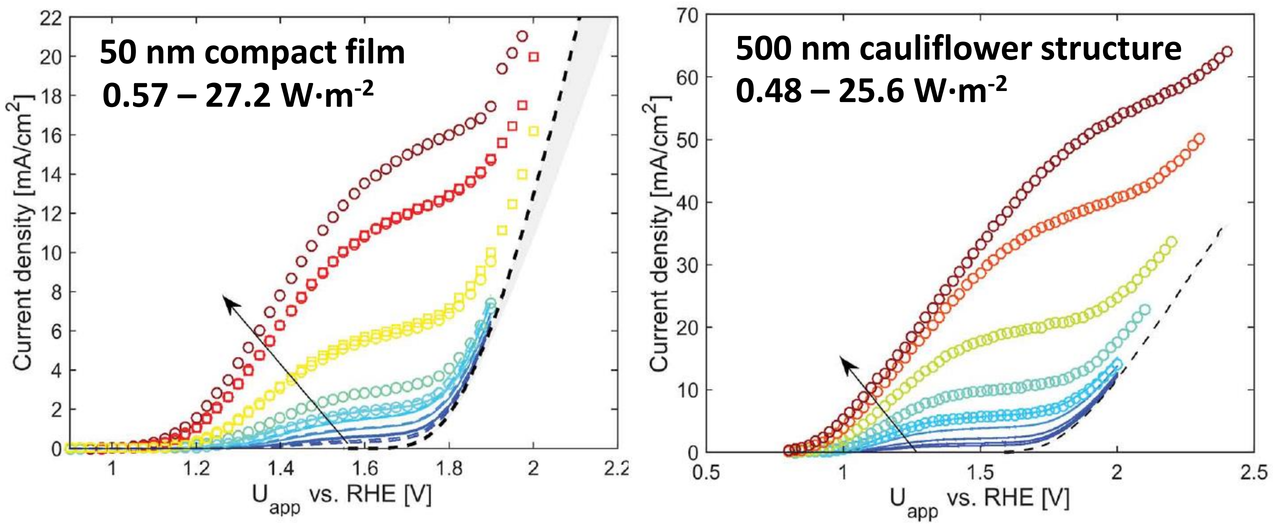
Solar concentrators compatible with PEC device restrictions

PEC devices compatible with the specifications of solar concentrators.



These technologies can be **coupled externally**, in separate structures, or they can be **integrated in a single device.**

In a pioneer work by Segev *et al.* two **0.28 cm^2 hematite PEs** (50 nm film and 500 nm mesoporous cauliflower), were subjected to **concentrated simulated sunlight** (1 to 25 suns).



G. Segev, et al., High Solar Flux Concentration Water Splitting with Hematite (α-Fe2O3) Photoanodes, Advanced Energy Materials, 6 (2016)

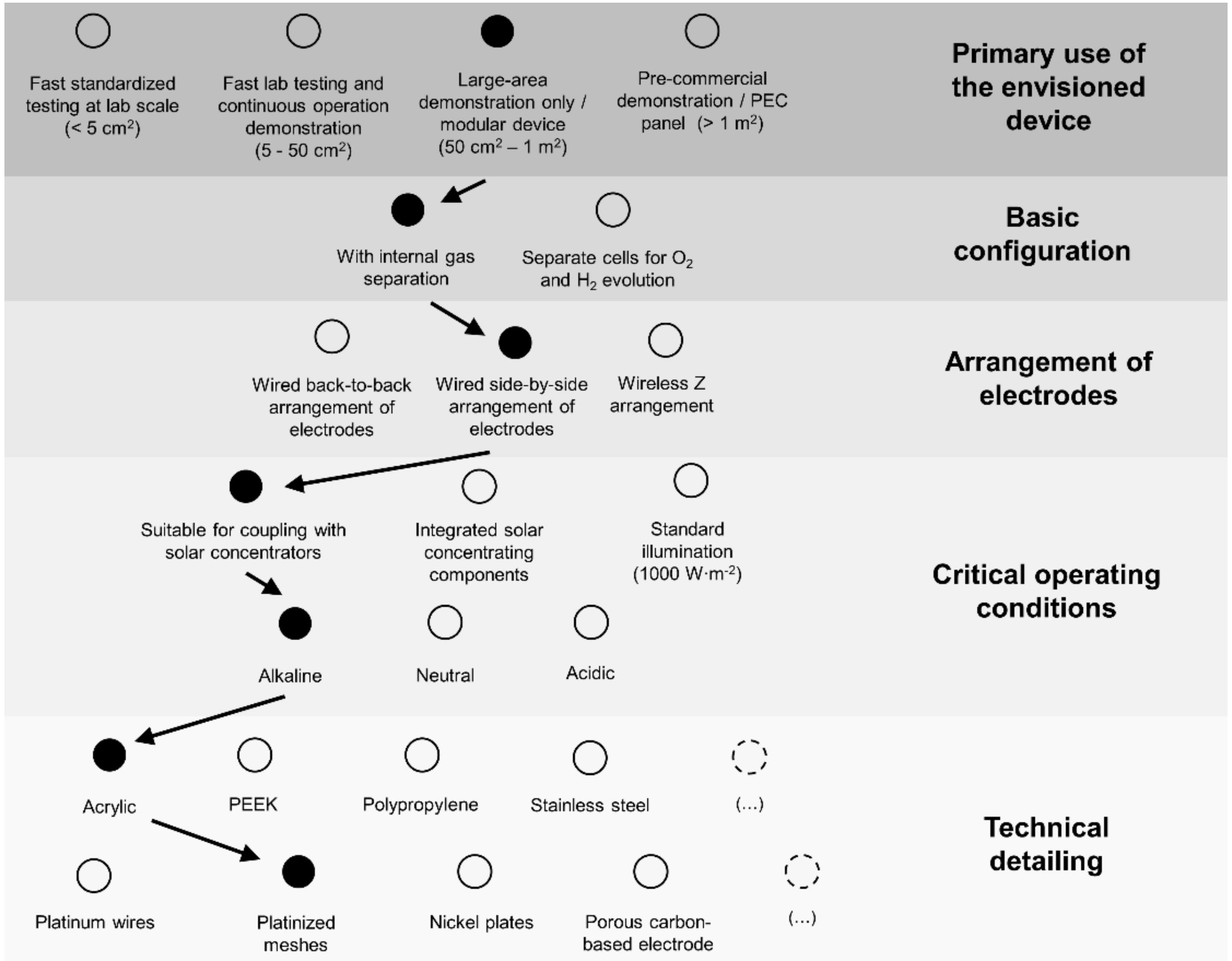
The **photocurrent** generated by both samples **increased linearly with the solar flux**.

Still…

The use of **concentrated sunlight** for continuous solar-H_2 generation requires **efficient thermal management solutions** integrated in the PEC device.

Quick overview on the development of efficient PEC devices for solar water splitting

DEVELOPMENT OF A NEW PEC CELL DESIGN: DECISION TREE

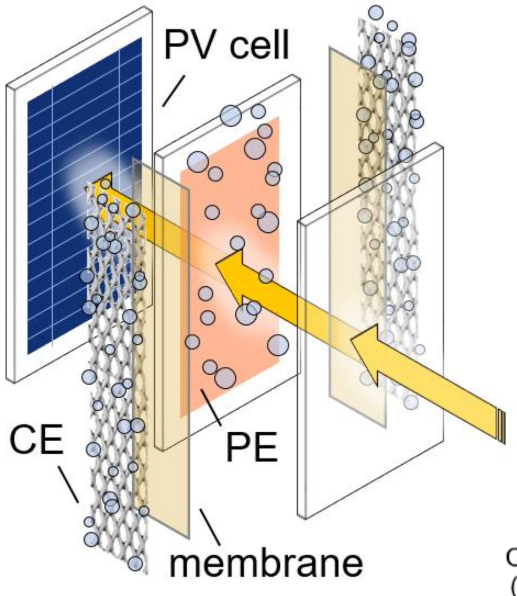


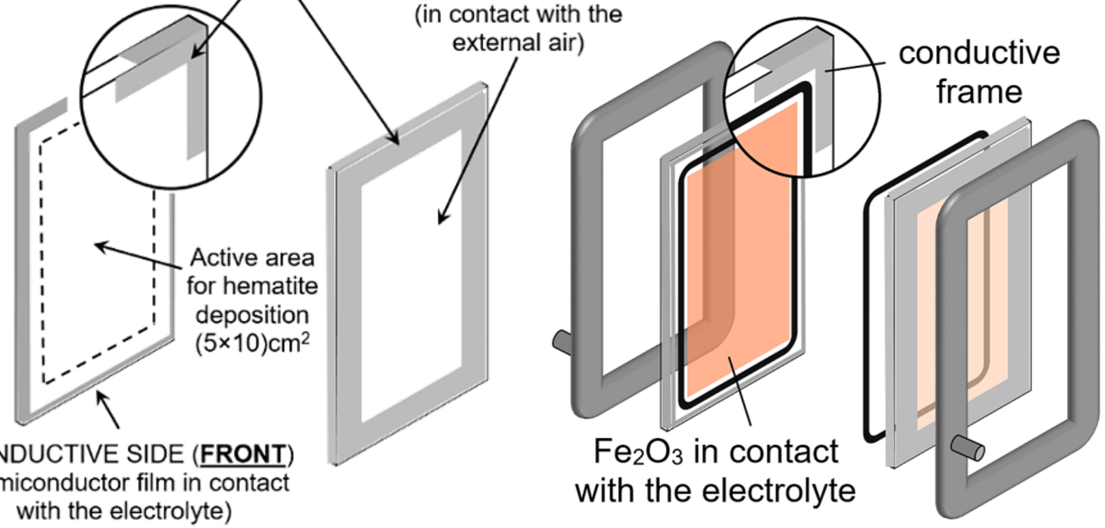
Requirements

- Active area of 50 cm^2;
- Narrow embodiment;
- Suitable for tandem arrangements.

Implemented solutions

- Type III architecture → CEs placed side-by-side to the PE, separated by a membrane;
- Development of a PE that is simultaneously one window of the cell.



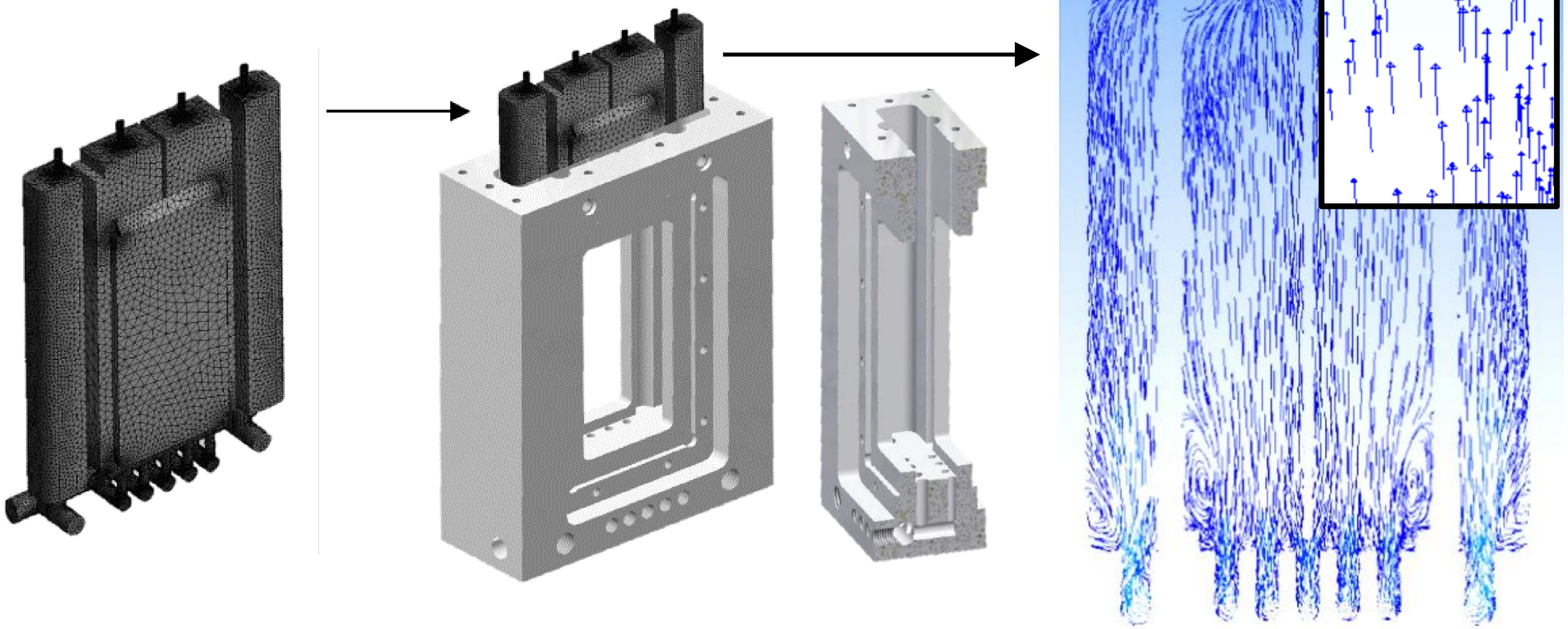


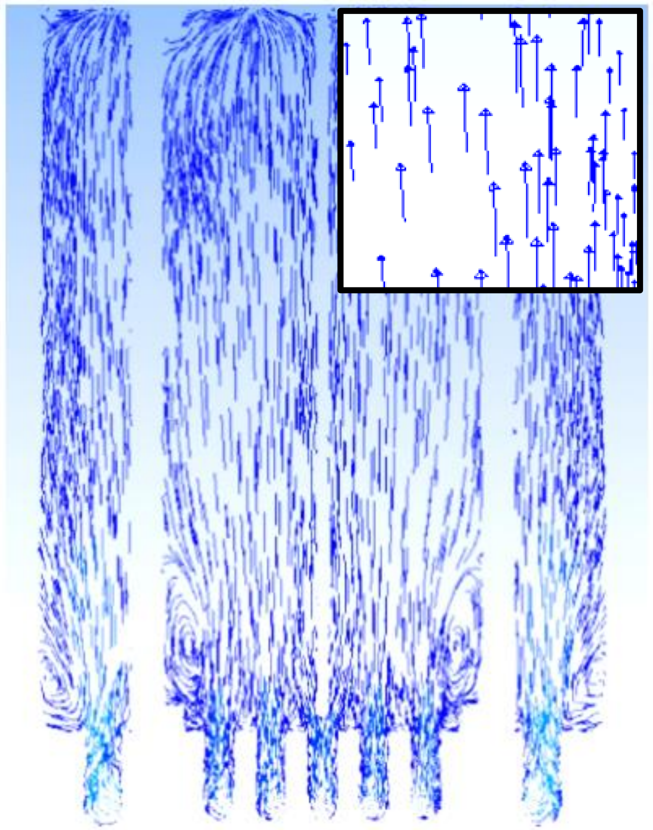
Requirements

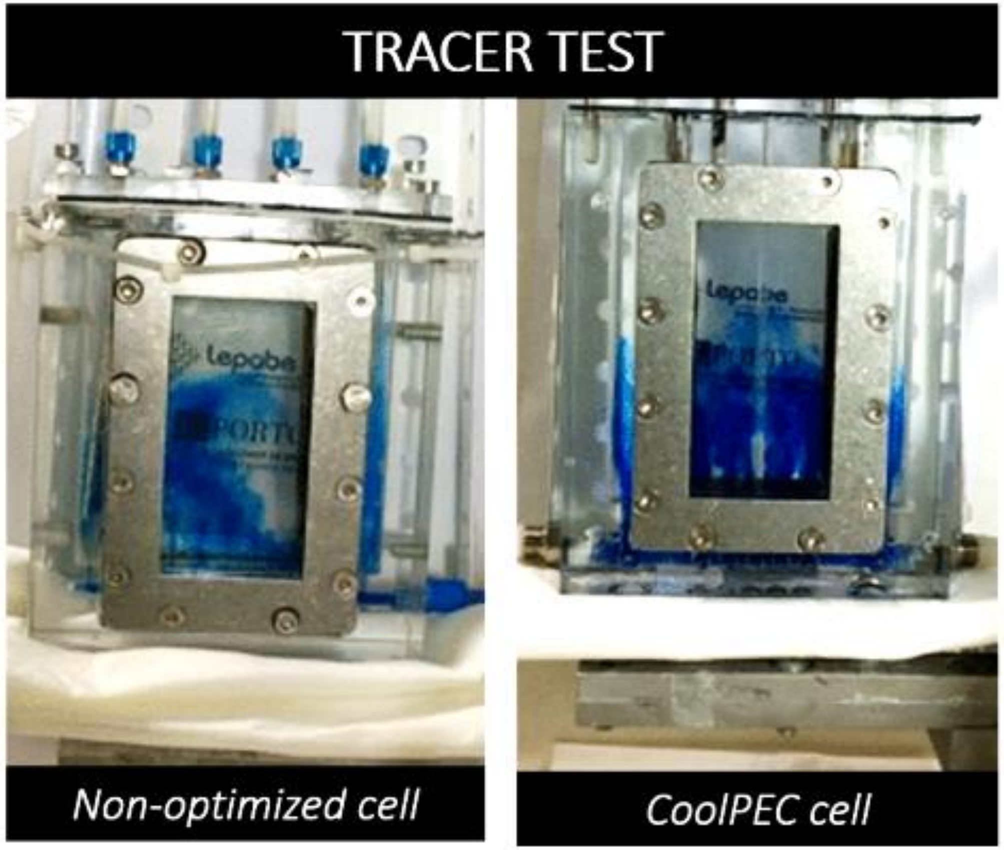
- Electrolyte recirculation;
- Separate collection of H_2 and O_2;
- Efficient heat dissipation.

Implemented solutions

- Optimized electrolyte flowpath inside the cell with **CFD simulations;**
- Manifold incorporating several diffusers to promote electrolyte feeding.





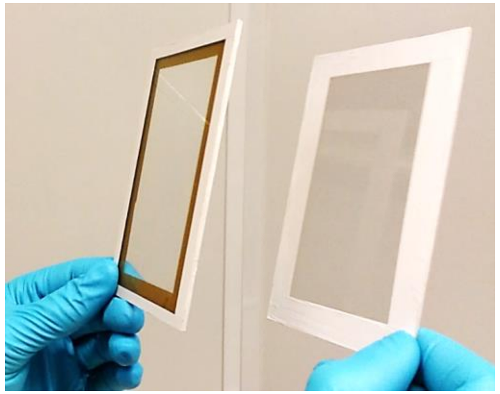

TRACER TEST
Non-optimized cell
CoolPEC cell

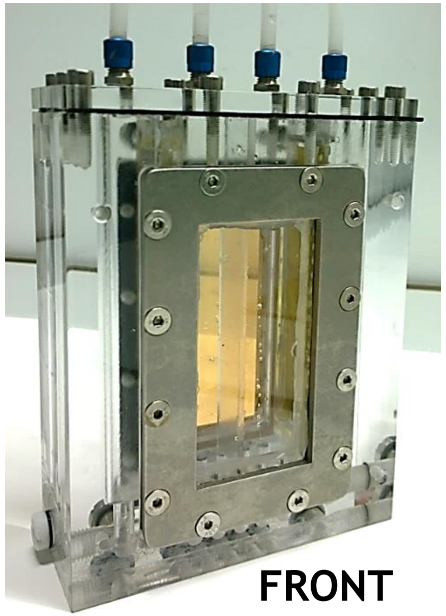
Requirements

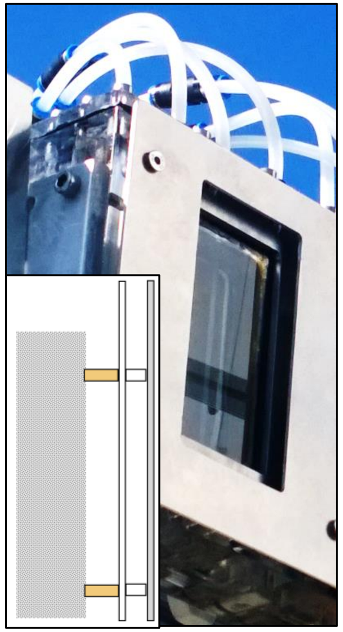
- Suitable for different electrolytes;
- Suitable for operation under concentrated sunlight.

Implemented solutions

- Acrylic embodiment;
- Protective shield assembled at the front.







CoolPEC cell → Compact Optimized Open Light PEC cell

THE CHALLENGE: UPSCALING OF EFFICIENT PEs

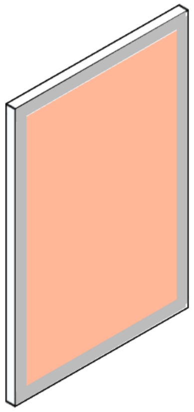
Transparent conducting oxides (TCOs) such as fluorine doped tin oxide (FTO) are the most commonly used substrates for making PEs for PEC water splitting.

⇩

Main advantages:
Resistant to different liquid electrolytes and suitable for tandem arrangements.

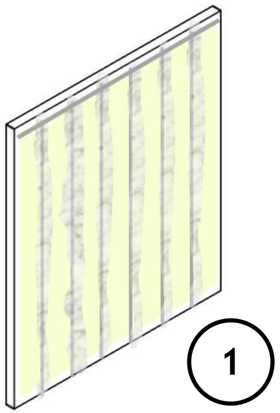
⇩

Critical drawback:
High ohmic losses in large-area PEs due to the electronic resistance.

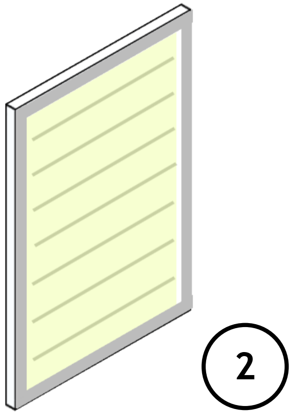


50 cm^2 previously developed for the CoolPEC cell

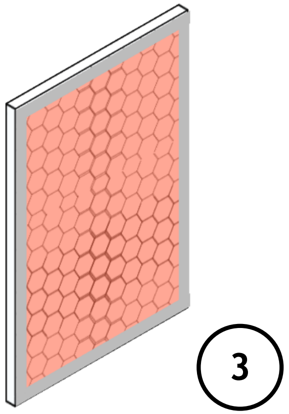
⇨ Available solutions



TCO-glass with metal lines protected by epoxy resin (demonstrated by Lee *et al.* 2011)



TCO-glass with metal lines protected by the semiconductor (demonstrated by Ahmet *et al.* 2019)

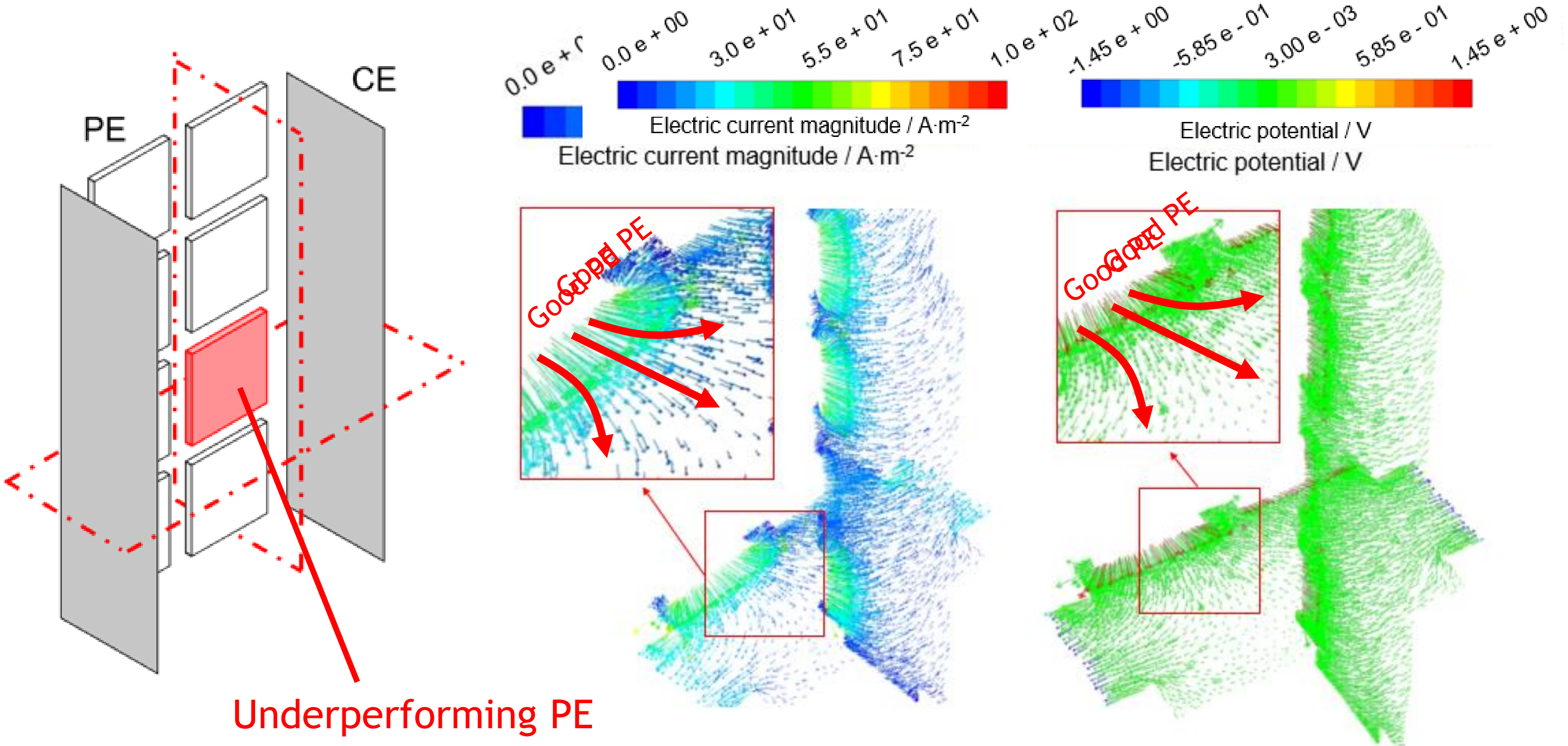


Embedded TCO (ETCO) covered by the semiconductor (ongoing work at UPorto)

Why not connecting multiple small PEs in parallel, fulfilling large-area requirements?

Challenge: assuring full reproducibility between multiple small PEs.

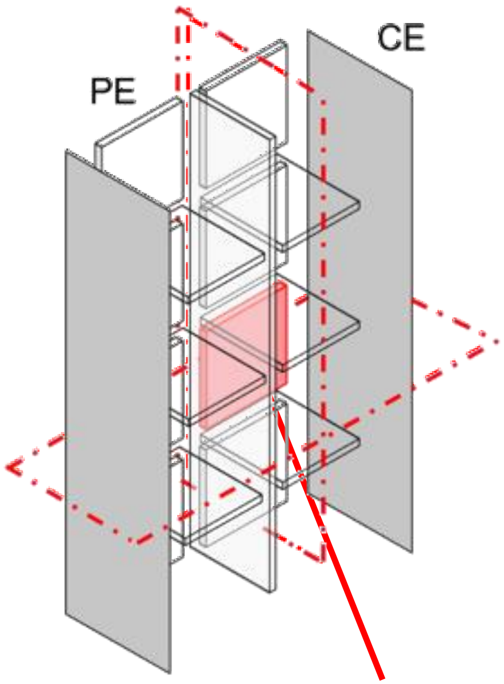
Solution: using internal separators between PEs.

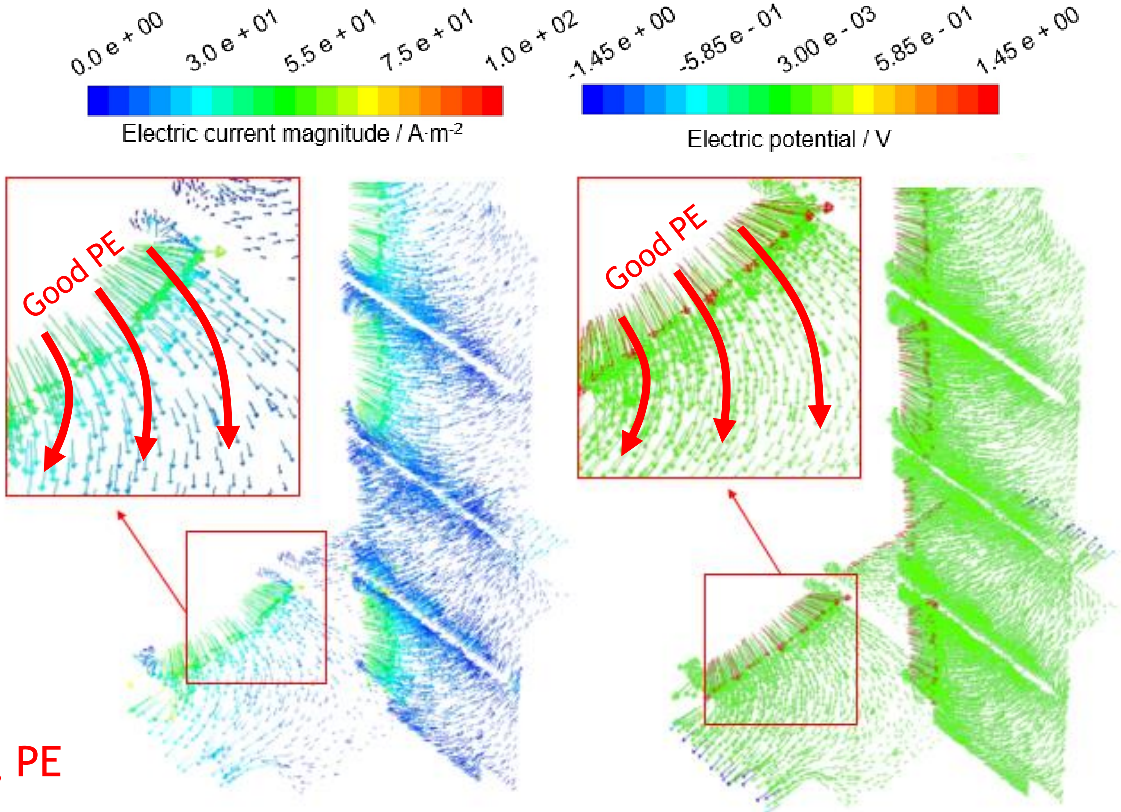


Why not connecting multiple small PEs in parallel, fulfilling large-area requirements?

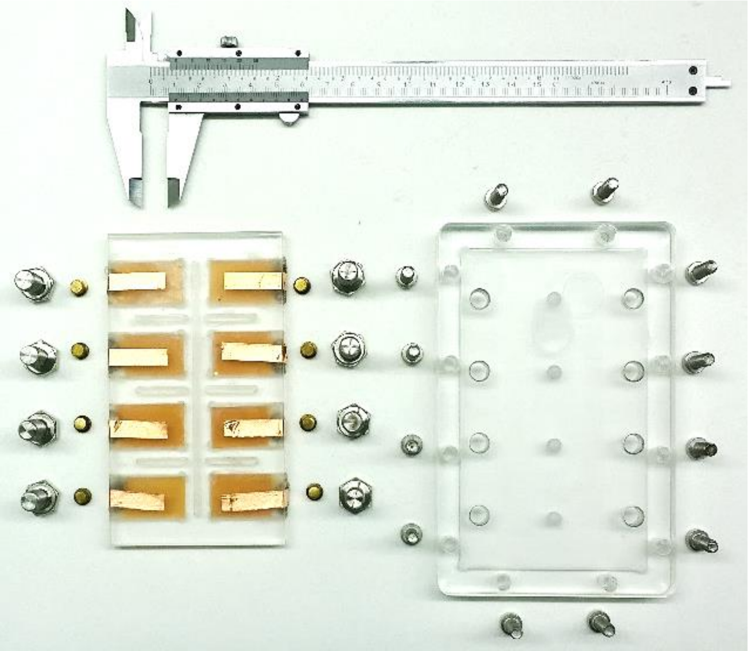
Challenge: assuring full reproducibility between multiple small PEs.

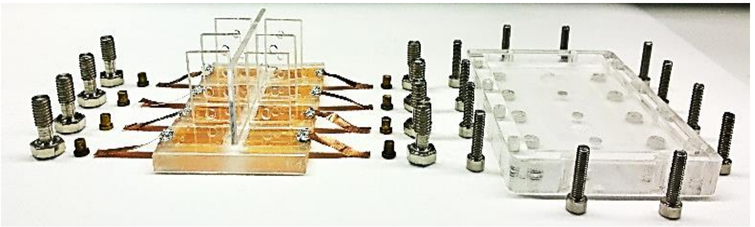
Solution: using internal separators between PEs.



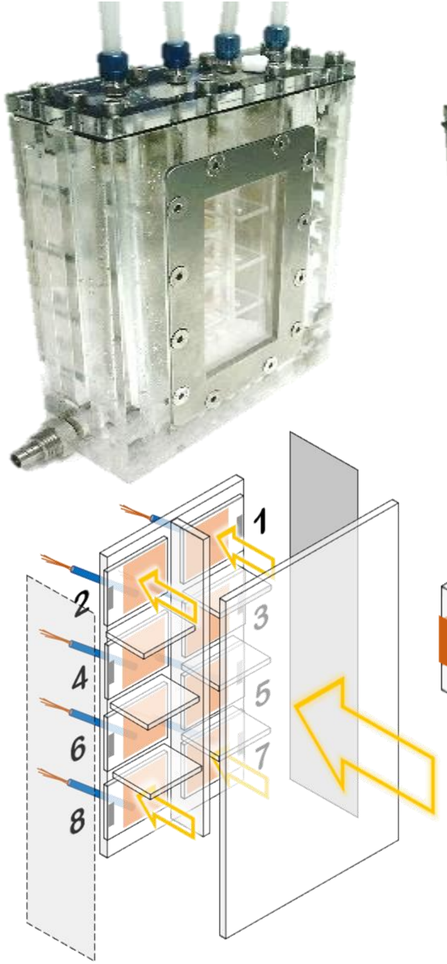


Main components of the multi-PE window

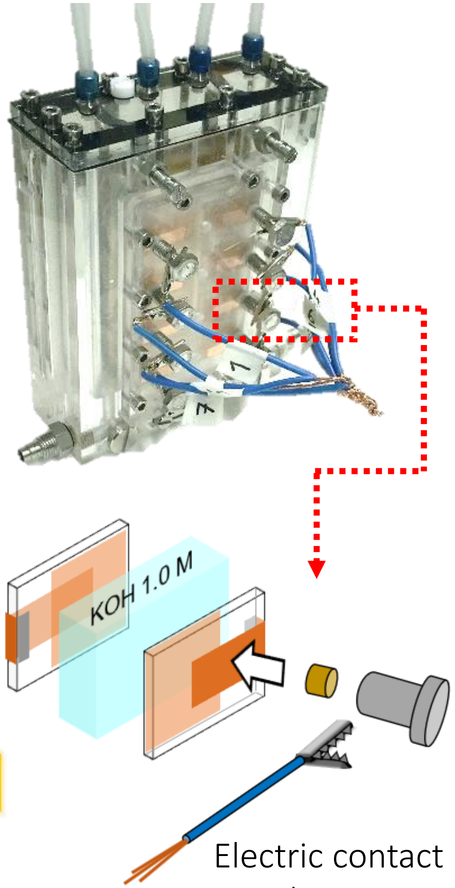




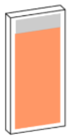
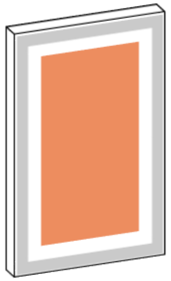
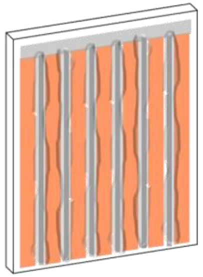
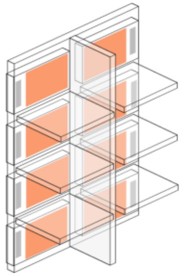
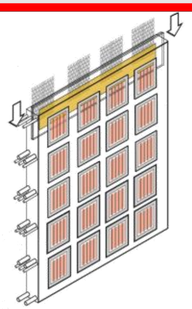
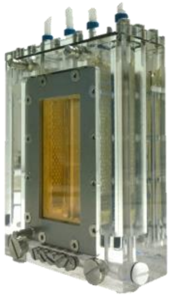
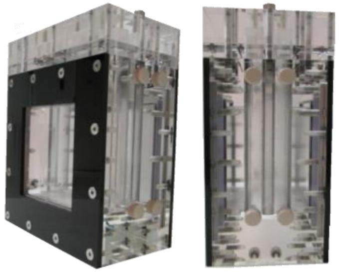
Front view



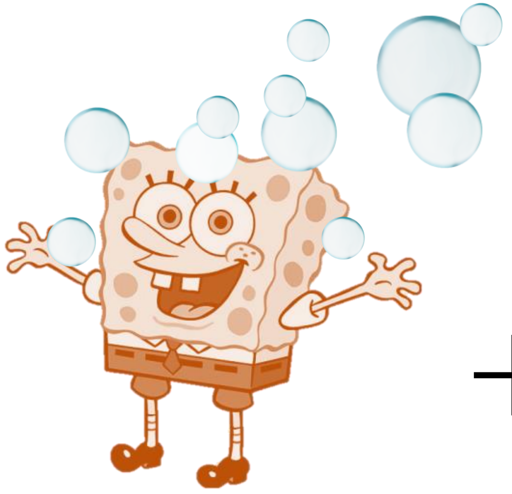
Rear view



Electric contact and current collectors

Type of PE (size)		Large PEs (≥ 50 cm^2)	Large PEs with metal lines (≥ 50 cm^2)	Multi-PE window (≥ 50 cm^2)	PEC panel (≥ 1 m^2)
3-D scheme of the photoelectrode					
Preparation	✓	⚠	⚠	✓	⚠
Testing	✓	⚠	✗	⚠	⚠
Efficiency	✓	✗	⚠	✓	✗
Stability	✓	⚠	✗	✓	✗
Active area	✗	✓	✓	✓	✓
Published device for demonstration (example)	 Cappuccino Cell **[2007]**	 CoolPEC cell **[2018]**	 PortoCell **[2014]**	 CoolPEC cell **[2018]**	 Artiphyction **[2015]**

In short…

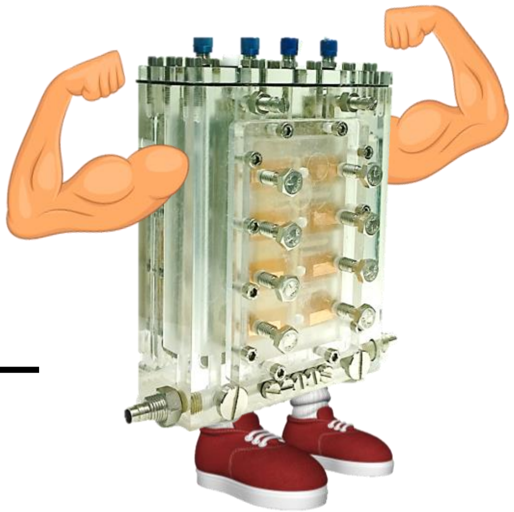


Efficient and stable sponge-like α-Fe_2O_3 PEs

+

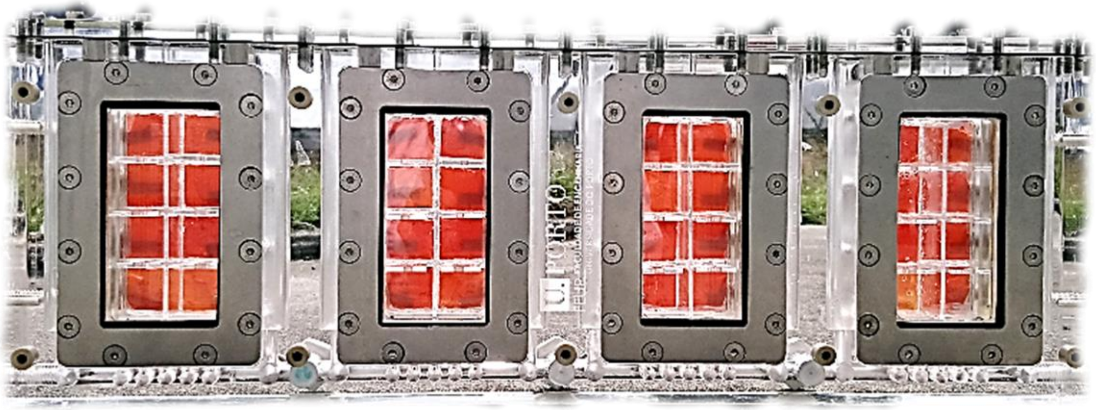
The CoolPEC cell

+

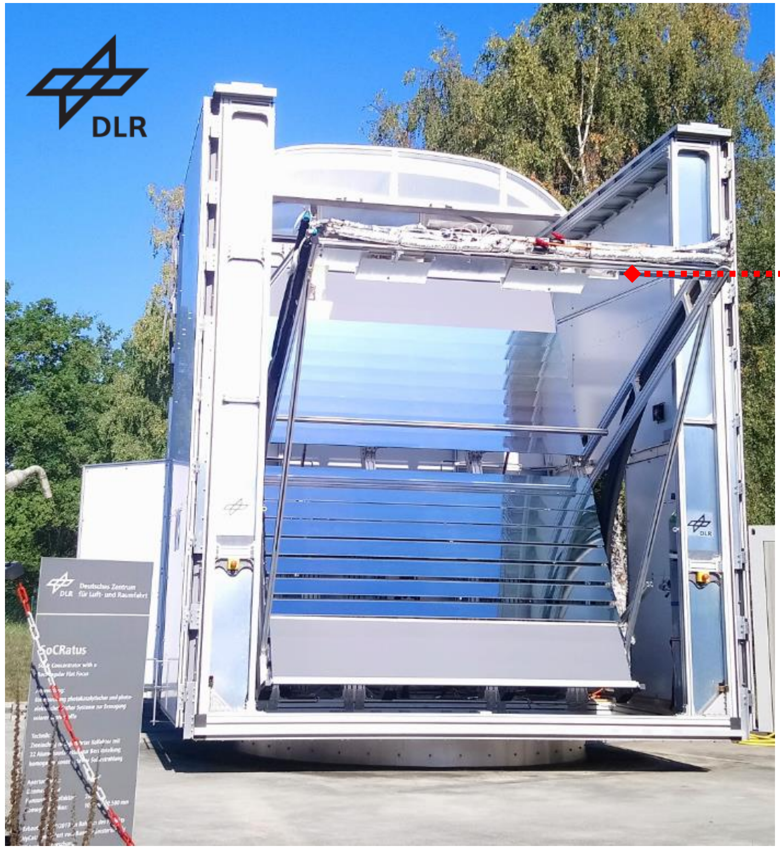


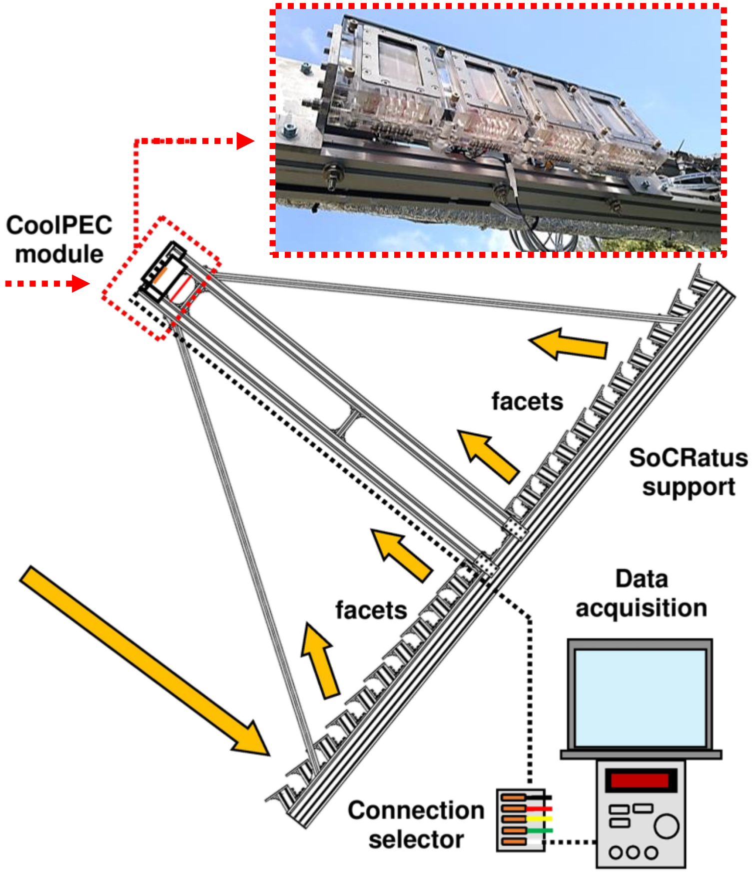
Multi-PE window

⇩

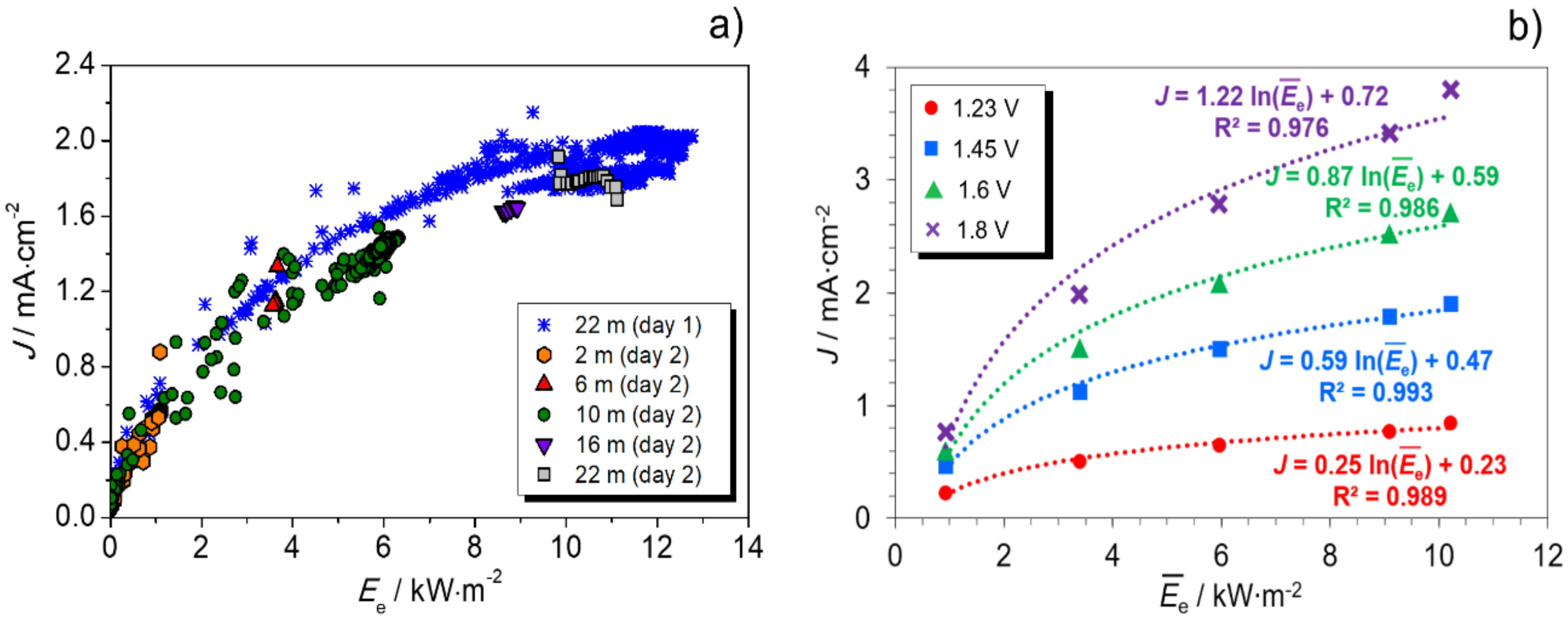


The developed PEC device was tested in the **SoCRatus**, a solar concentrator developed by the Institute of Solar Research (DLR, Köln) equipped with **22 linear mirrors** and a **two-axis tracking system,** comprising a rectangular flat focus of 250 × 10 cm^2.





The **current density did not follow a linear increase with the solar irradiance**...



The photocurrent density (J) generated by α-Fe_2O_3 PEs connected in parallel, subjected to a linear increase in solar irradiance (E_e), exhibited a logarithmic saturation behavior, which can be written as:

$$J = k \ln(E_e)$$

where k is related to the applied potential

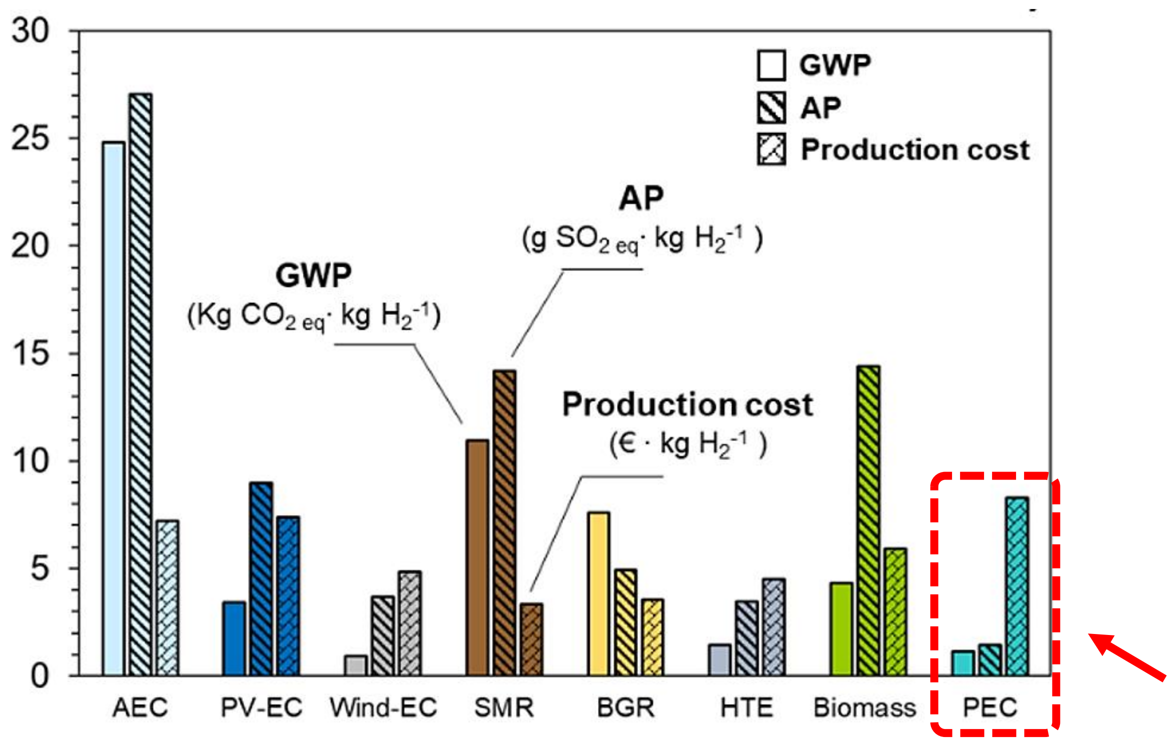
Surface recombination 🤔 Bulk recombination 🤔 Specific recombination sites 🤷‍♂️ Current collection 🤷‍♂️

So, give me a good reason to keep investigating PEC-H_2 production.

NOA Nanofabrication for Optoelectronic Applications

INL International Iberian Nanotechnology Laboratory

Life-cycle assessment of different hydrogen production methods



And how should we move forward? What are the main challenges in the field?

The direct competitor of PEC-H_2 production is **PV-based alkaline electrolysis**.

Viable PEC devices must deliver **H_2 at a lower cost than PV-EC systems**.

During this decade research efforts should be directed to:

1. Develop clever design features and optimize promising materials;
2. Prepare large PEs with an active area $\geq 1\ m^2$;
3. Optimize preparation techniques for industrial applications;
4. Enhance the stability of large PEs targeting tens of thousands of hours;
5. Develop modular PEC panels with thermal and power management;
6. Investigate new approaches for coupling solar concentrators;
7. Reach consensual standards for evaluating PEC devices.

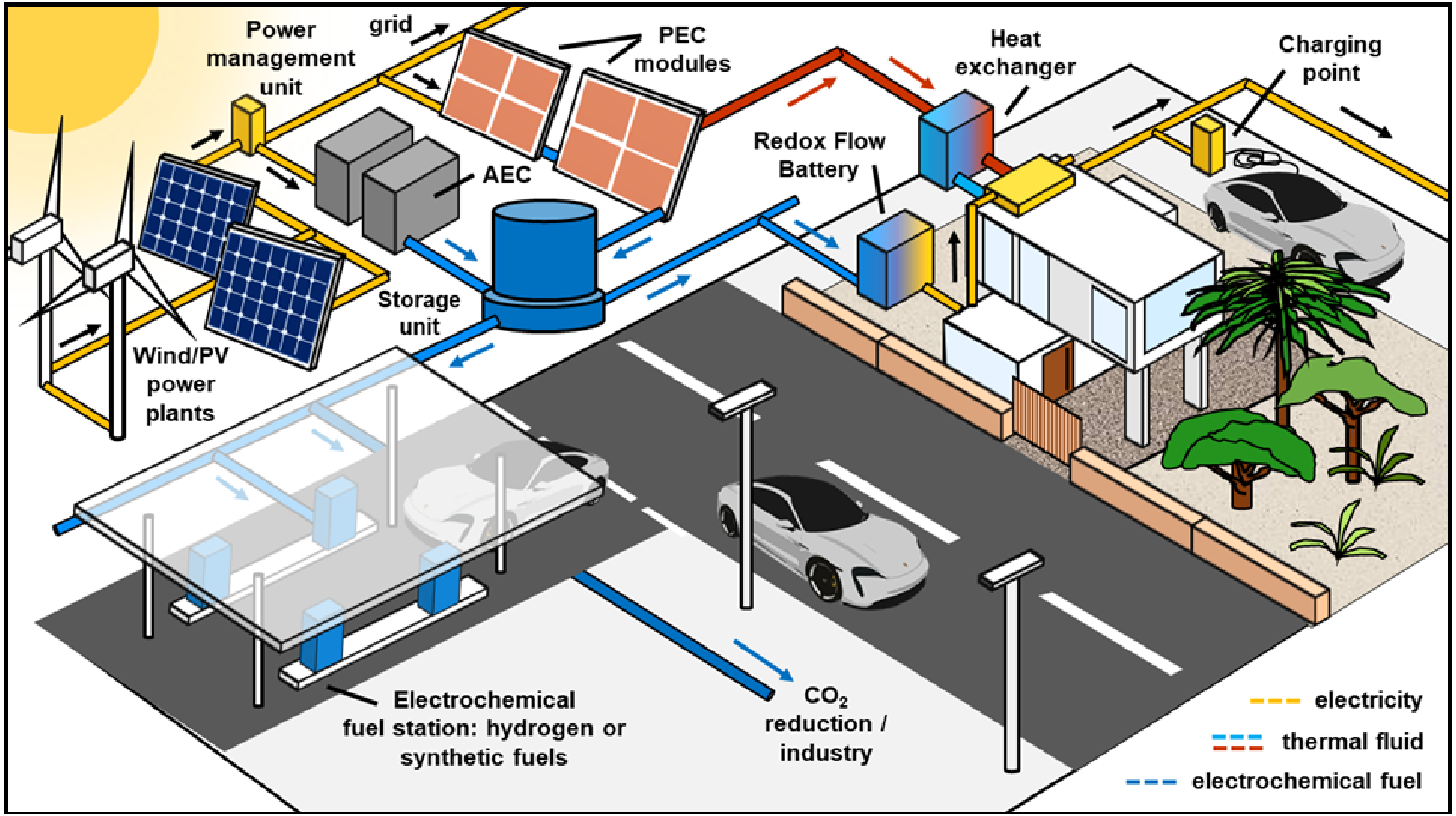
If these targets are not met, PEC-H_2 production will tend to become **another research topic without any practical application in society**.

Renewable-H_2 production is experiencing an **unparalleled economic stimulus**, ideal for bridging **lab research** with **commercial interests**.

The European Commission proposed a **1.8×10^{12} € package** to make the energy transition, **stating that green-H_2 is a key priority**.

With the feet on the ground: the best way to move forward is to recognize that PEC devices will operate very close to their fundamental thermodynamic limits, at large-scale.

This implies a **solid convergence between academics and the industry**; self-centered ambitions involving the use of scarce and expensive materials or very complex techniques must be left aside.



Power management unit
grid
PEC modules
Heat exchanger
Charging point
Redox Flow Battery
AEC
Storage unit
Wind/PV power plants
Electrochemical fuel station: hydrogen or synthetic fuels
CO_2 reduction / industry
electricity
thermal fluid
electrochemical fuel

And how can Physics play a significant role in this topic?

Interface engineering

Physical deposition methods

Selective contacts

Advanced characterization

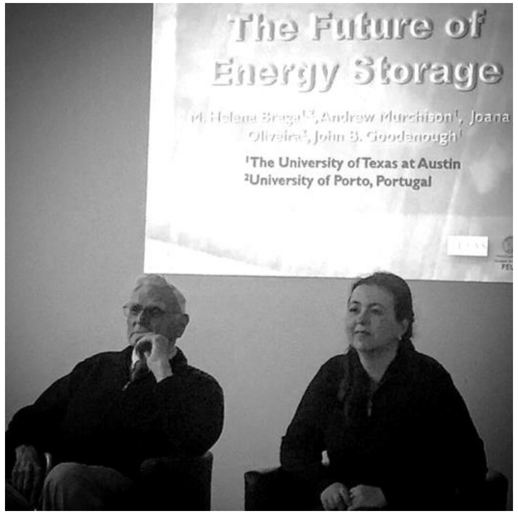
Optimization of current collection

Phenomenological modelling

Deep understanding of recombination phenomena

(...)

"Lithium-ion batteries are not the solution, they are just one little help that gives you, young engineers, some time to find a proper solution for energy storage at an industrial scale."



Professor John Bannister Goodenough

one of the inventors of lithium-ion batteries, Nobel Prize in Chemistry

The Voice of Industry, FEUP, Porto, Portugal, 2018

THANK YOU FOR YOUR ATTENTION