Green valorization of biomass residues by solar-driven photoelectrochemical processes

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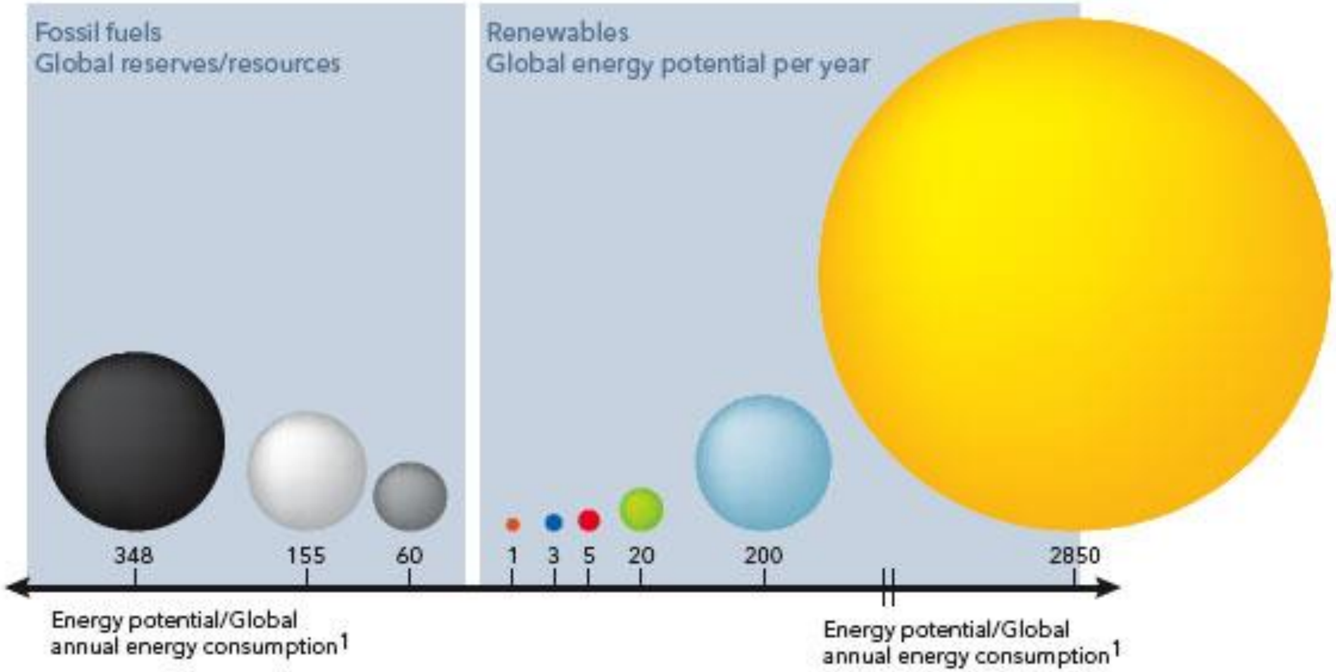
Solar Energy



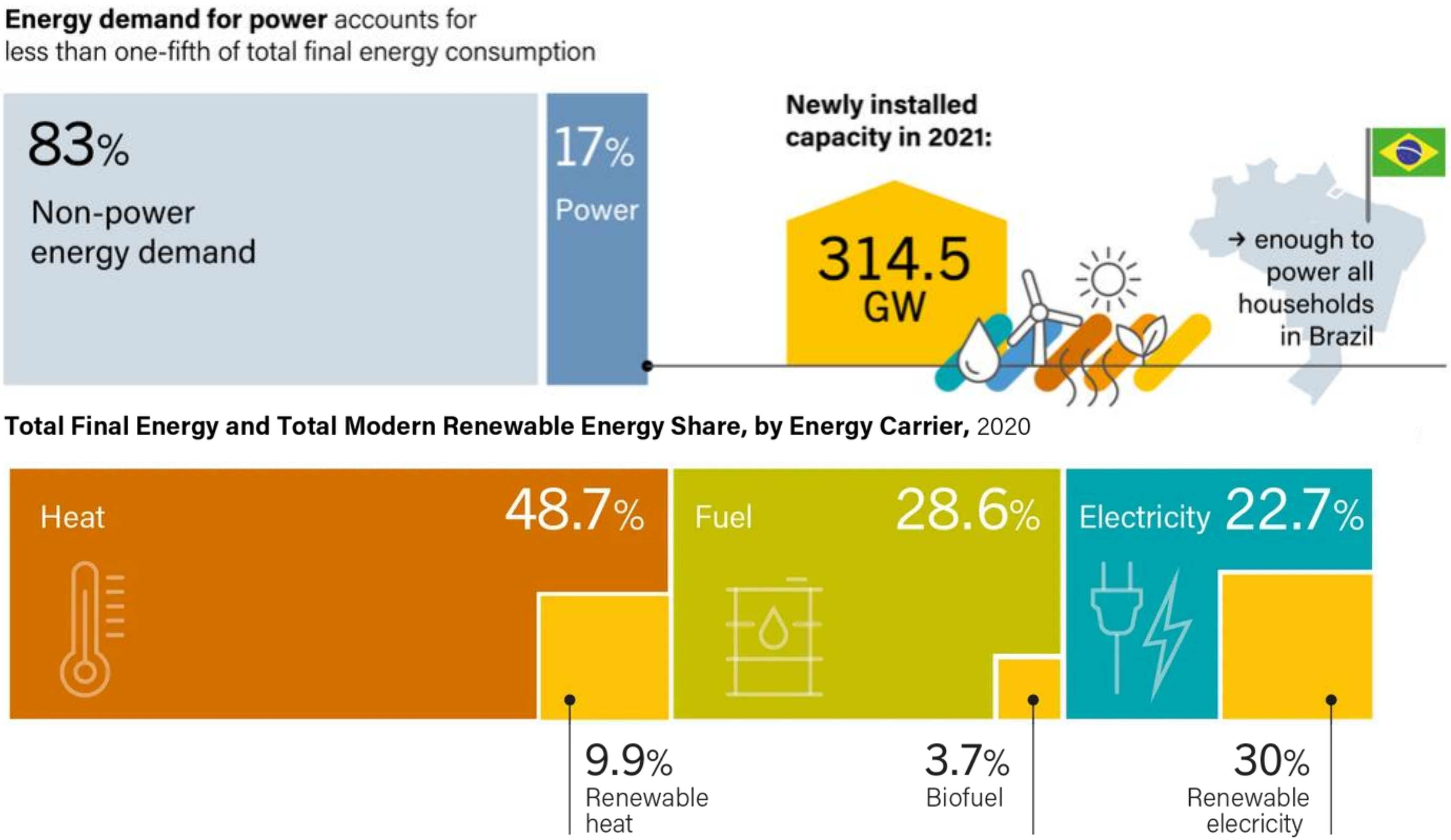
	Energy potential Reserves/Resources[2]	Thereof conventionally utilizable[2]
Coal	~ 135.000 EJ	
Natural gas	~ 60.400 EJ	~ 12.000 EJ
Crude oil	~ 23.000 EJ	~ 9.800 EJ

Global energy demand 2006: ~ 470 EJ

	Energy potential (amount of energy p. a.)[2]	technologically utilizable (state of the art)[2]
Solar radiation	~ 1.111.500 EJ	~ 1.482 EJ
Wind energy	~ 78.000 EJ	~ 195 EJ
Biomass	~ 7.800 EJ	~ 156 EJ
Geothermal	~ 1.950 EJ	~ 390 EJ
Hydro/tide power	~ 1.170 EJ	~ 78 EJ

Data source: German Federal Institute for Geosciences and Natural Resources.

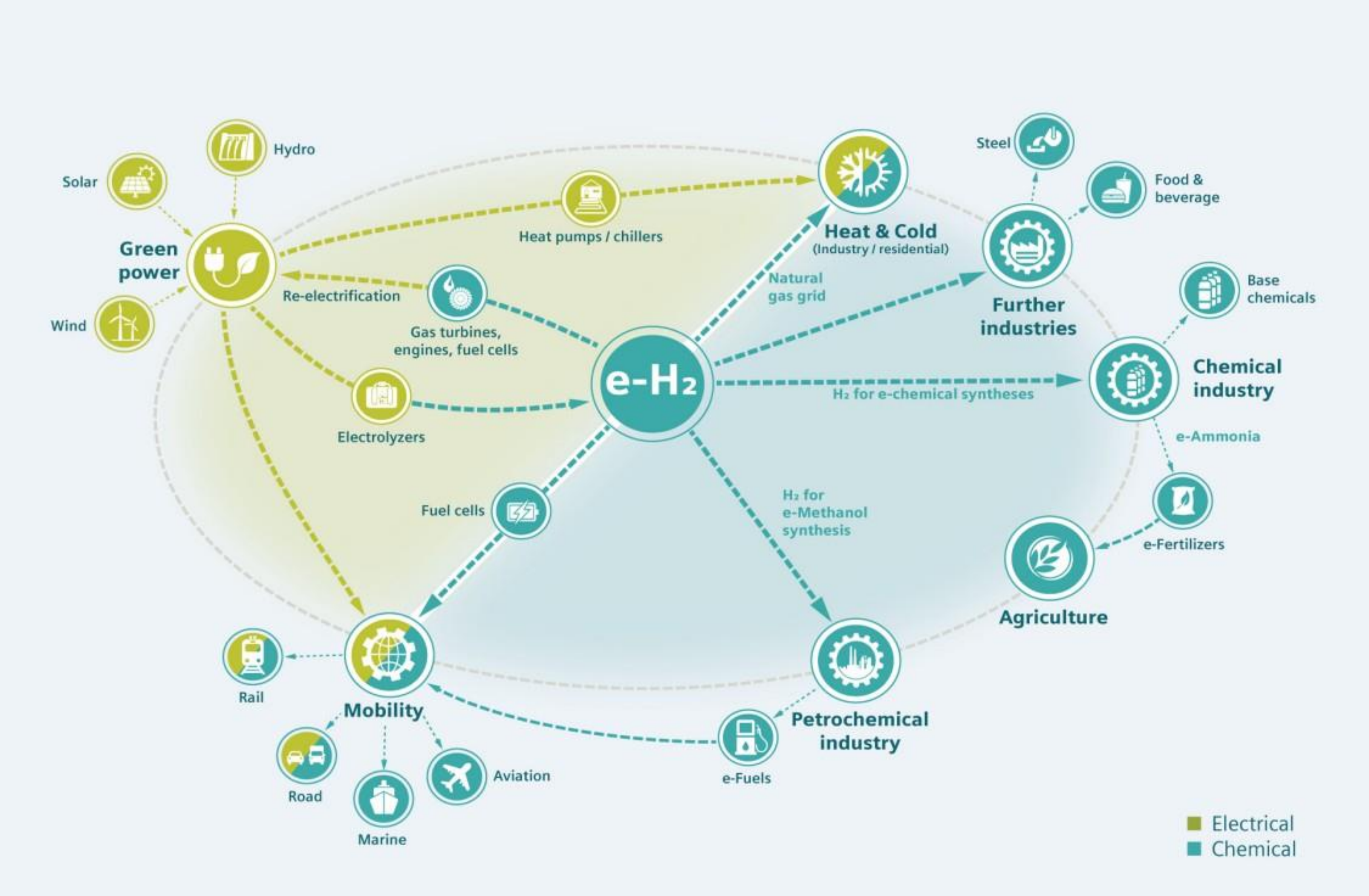
Energy transition and solar fuels



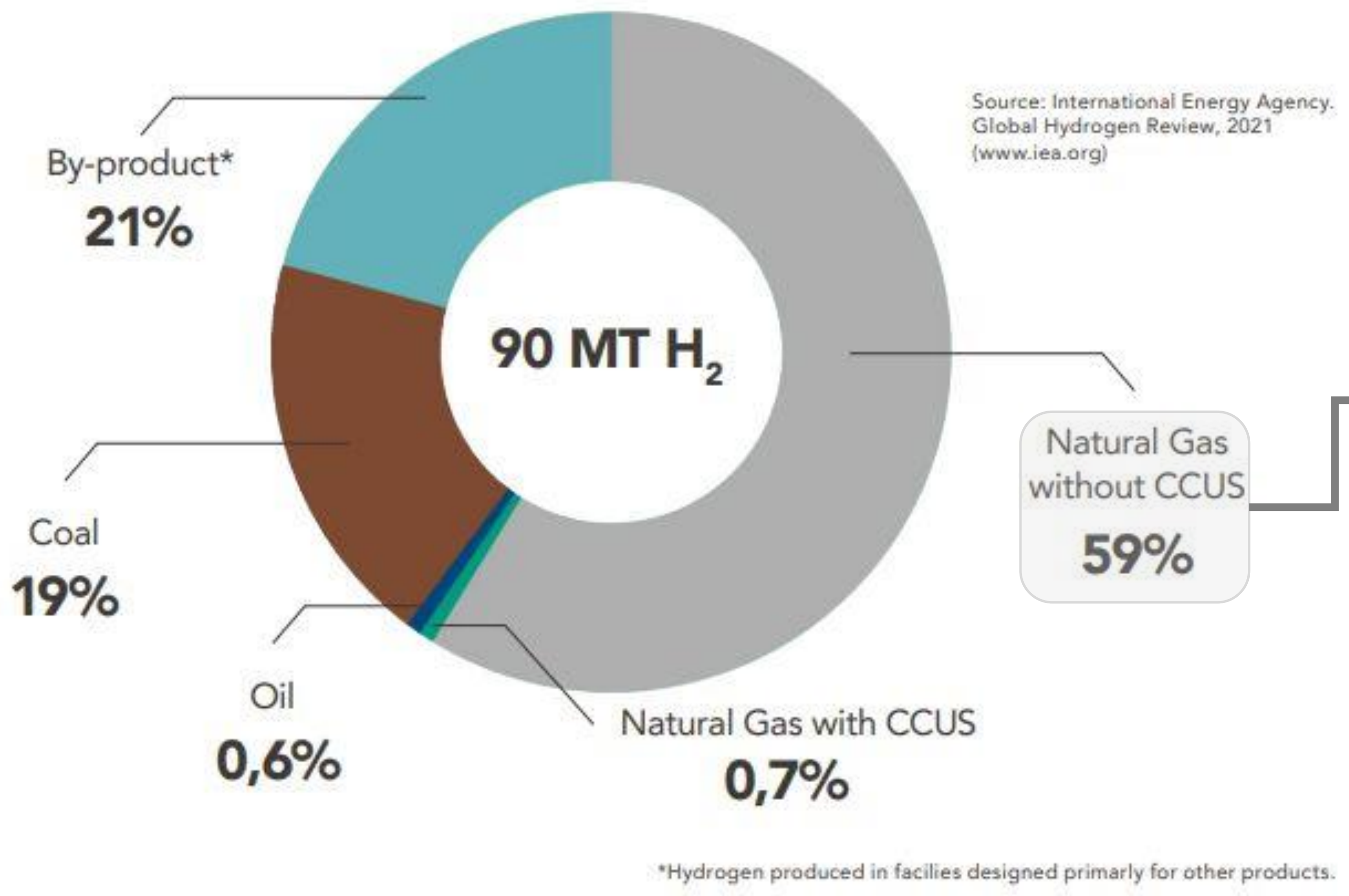
Our main energy carriers are liquid or gaseous fuels
We also need renewable feedstocks for the industries

https://www.ren21.net/gsr-2023/modules/energy_demand

H_2 as key energy vector



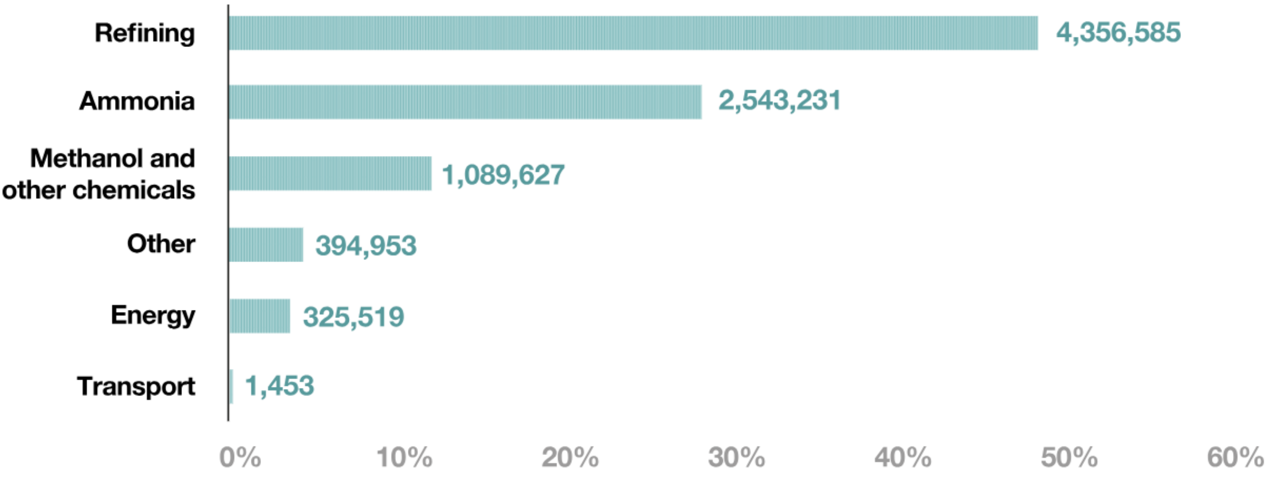
Current H_2 industrial production methods



10-12 kg CO_2-eq/kg H_2

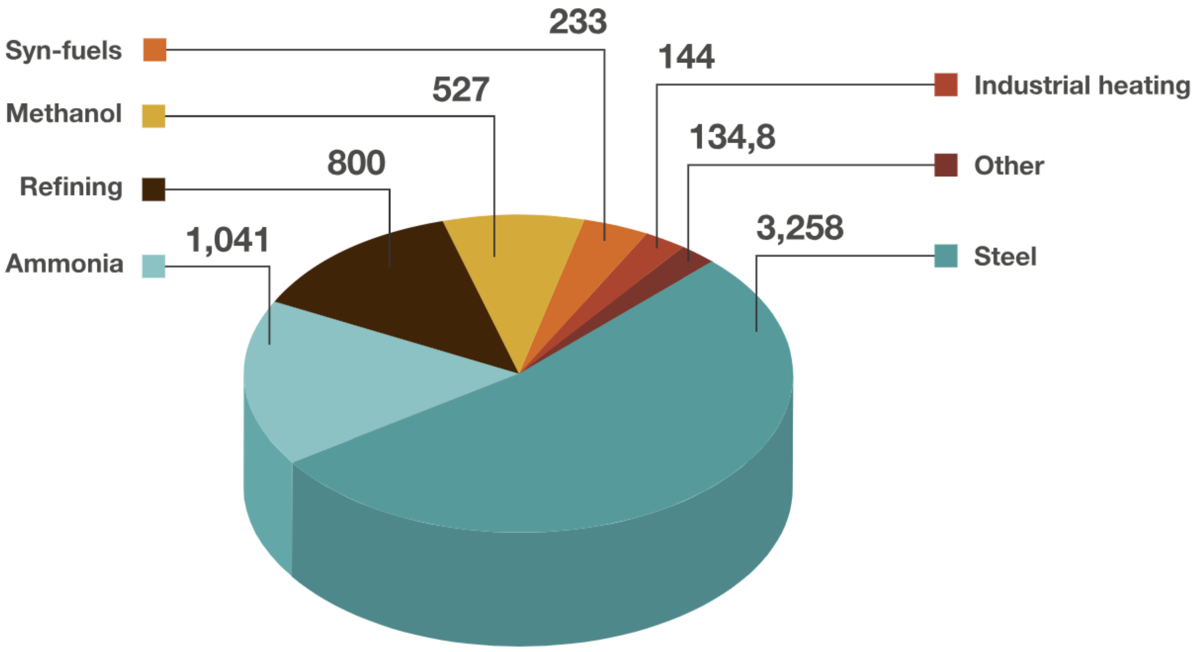
Potential uses for low carbon hydrogen

Total demand for hydrogen in 2020 by application



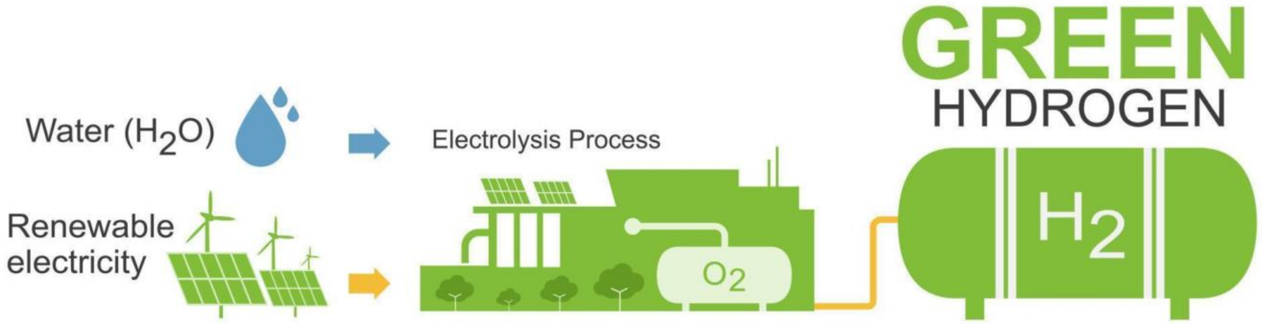
Source: Fuel Cells and Hydrogen Observatory

Planned clean hydrogen annual consumption in announced projects by 2030 by the industrial sector

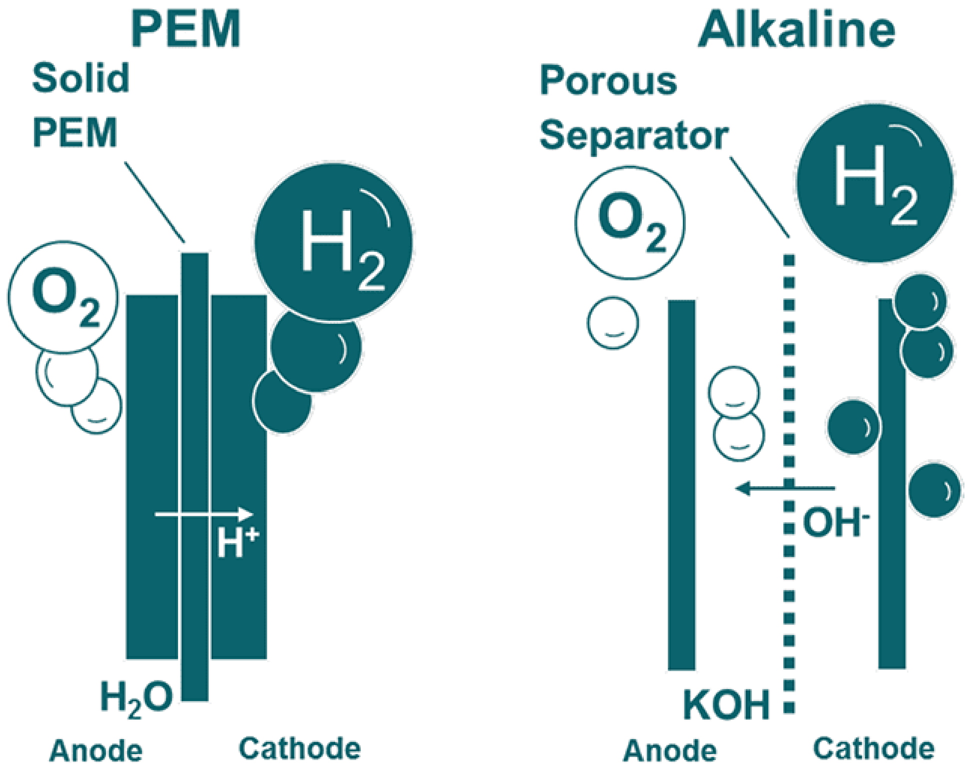


Source: Clean Hydrogen Monitor 2022, Hydrogen Europe

How to produce low carbon hydrogen?



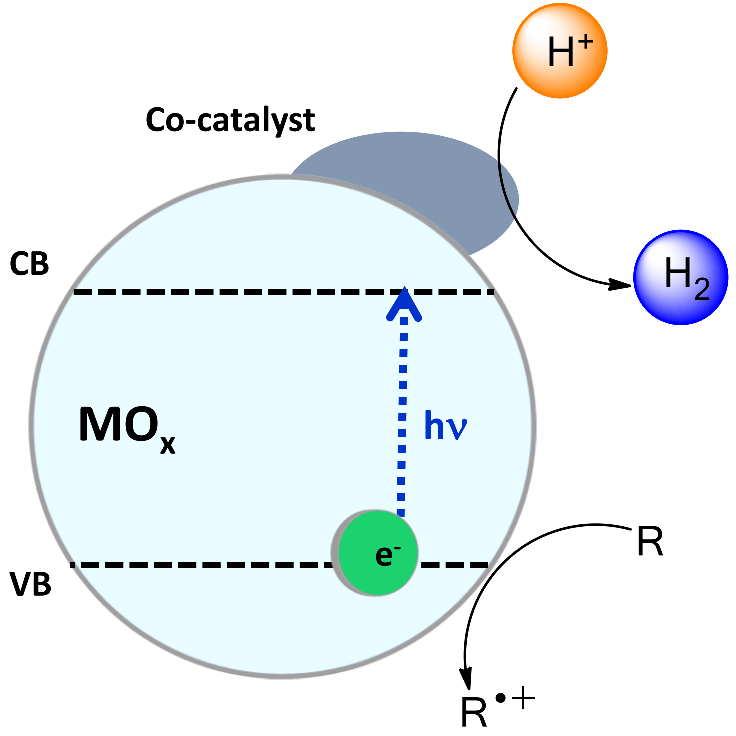
Main electrolyzer technologies

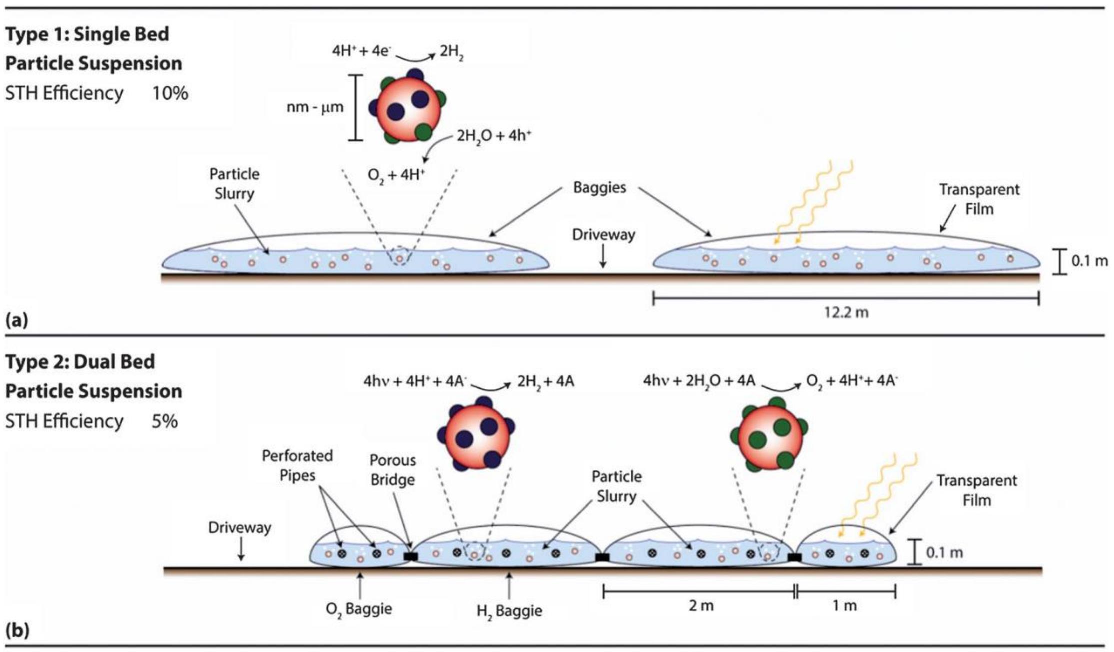


Mature technology but with higher production costs compared to natural gas reforming

Direct solar-to-hydrogen production

Photocatalysis (PC)

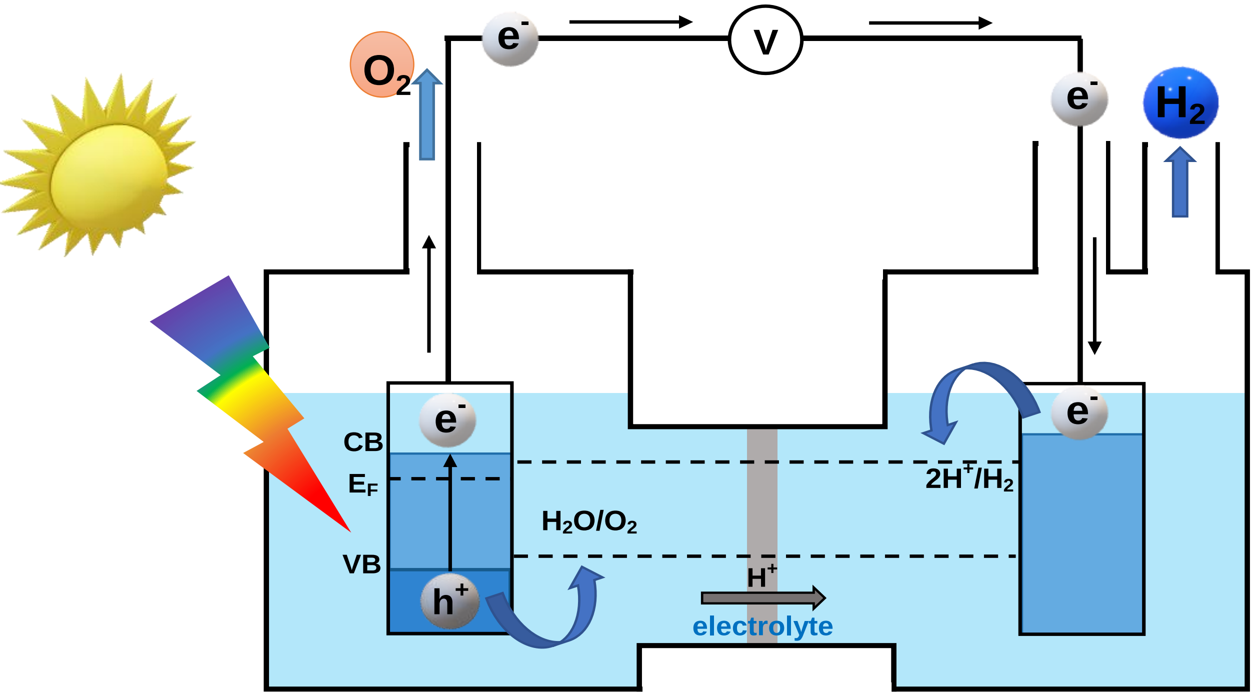


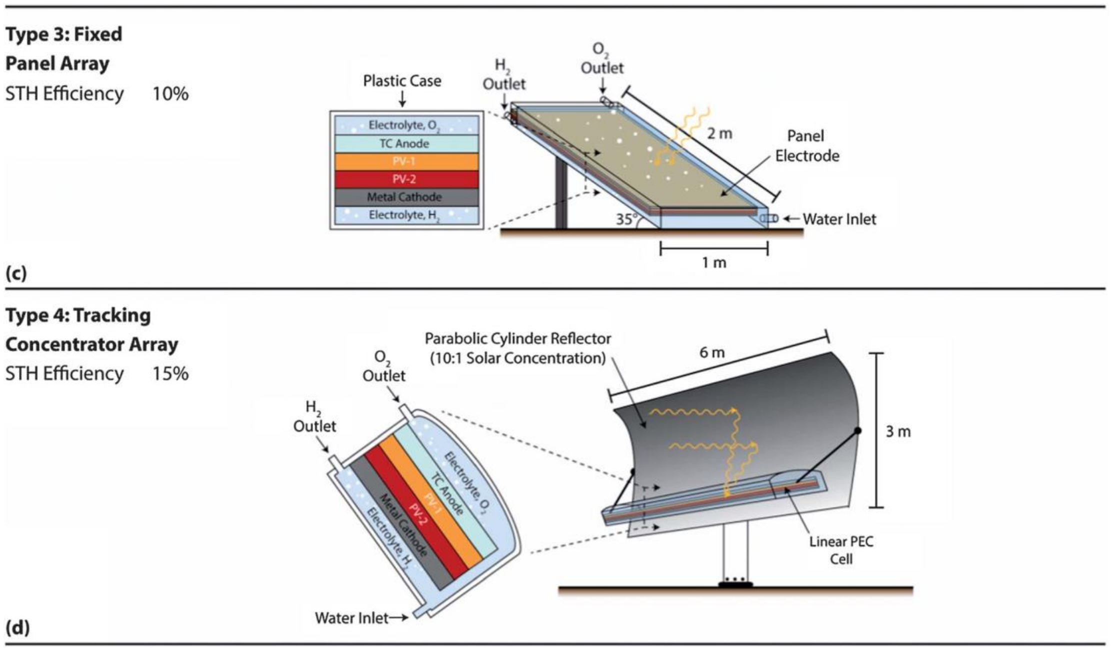


Energy Environ. Sci., 2013, 6, 1983–2002

Direct solar-to-hydrogen production

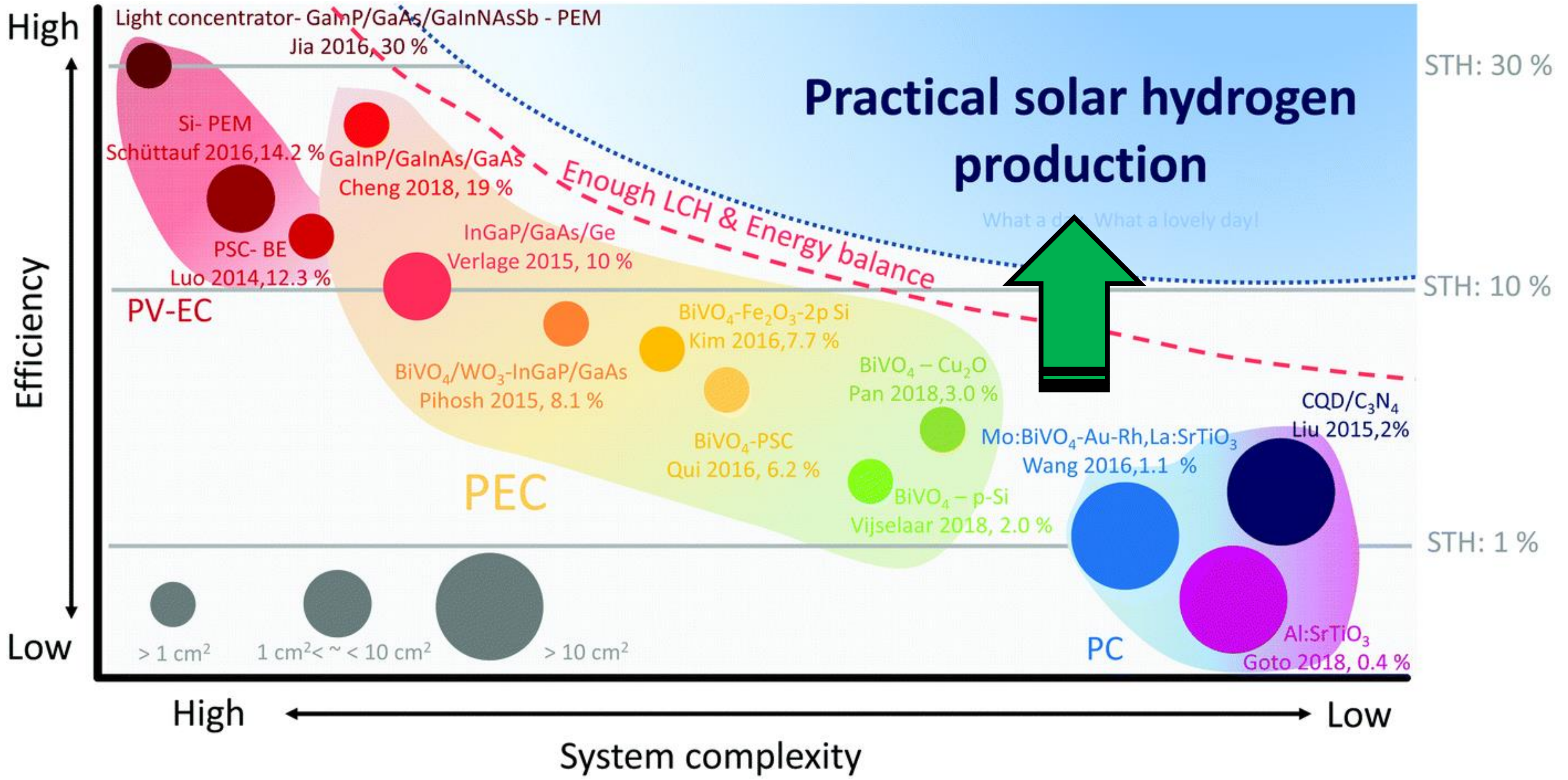
Photoelectrochemical cells (PECs)





Energy Environ. Sci., 2013, 6, 1983–2002

Challenges for upscalling

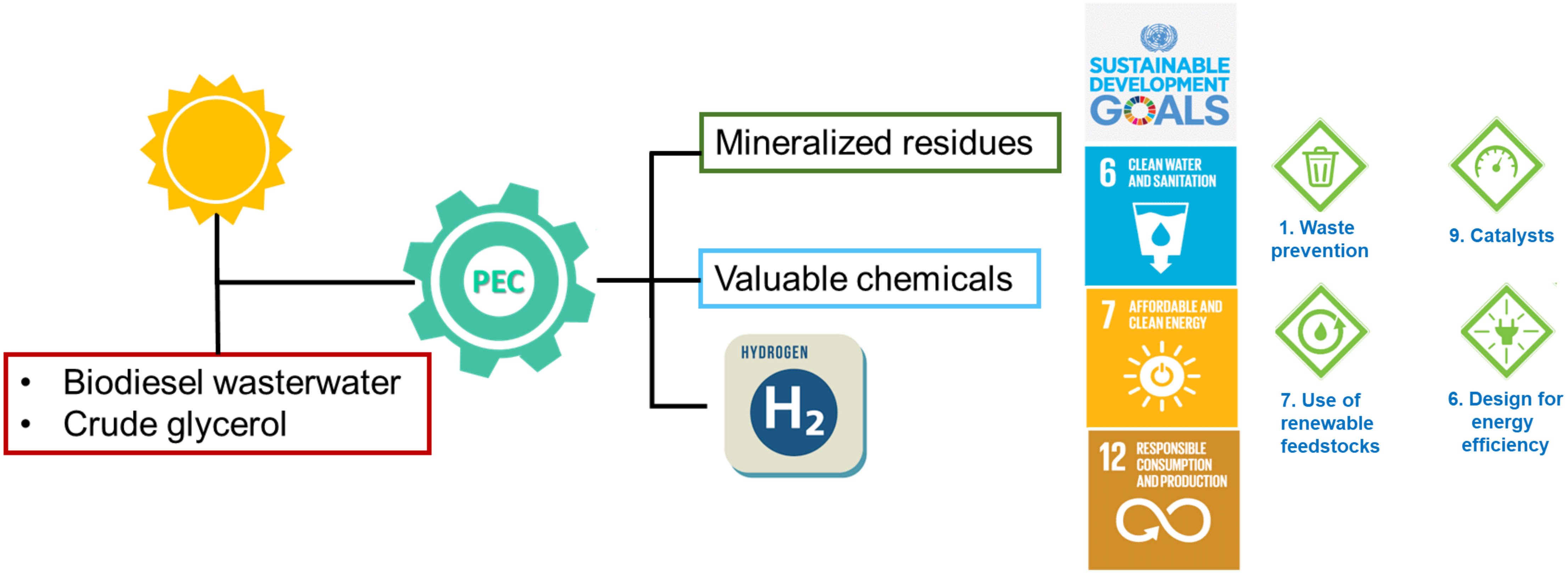


Water oxidation to molecular oxygen is the “bottleneck” for solar-to-hydrogen conversion

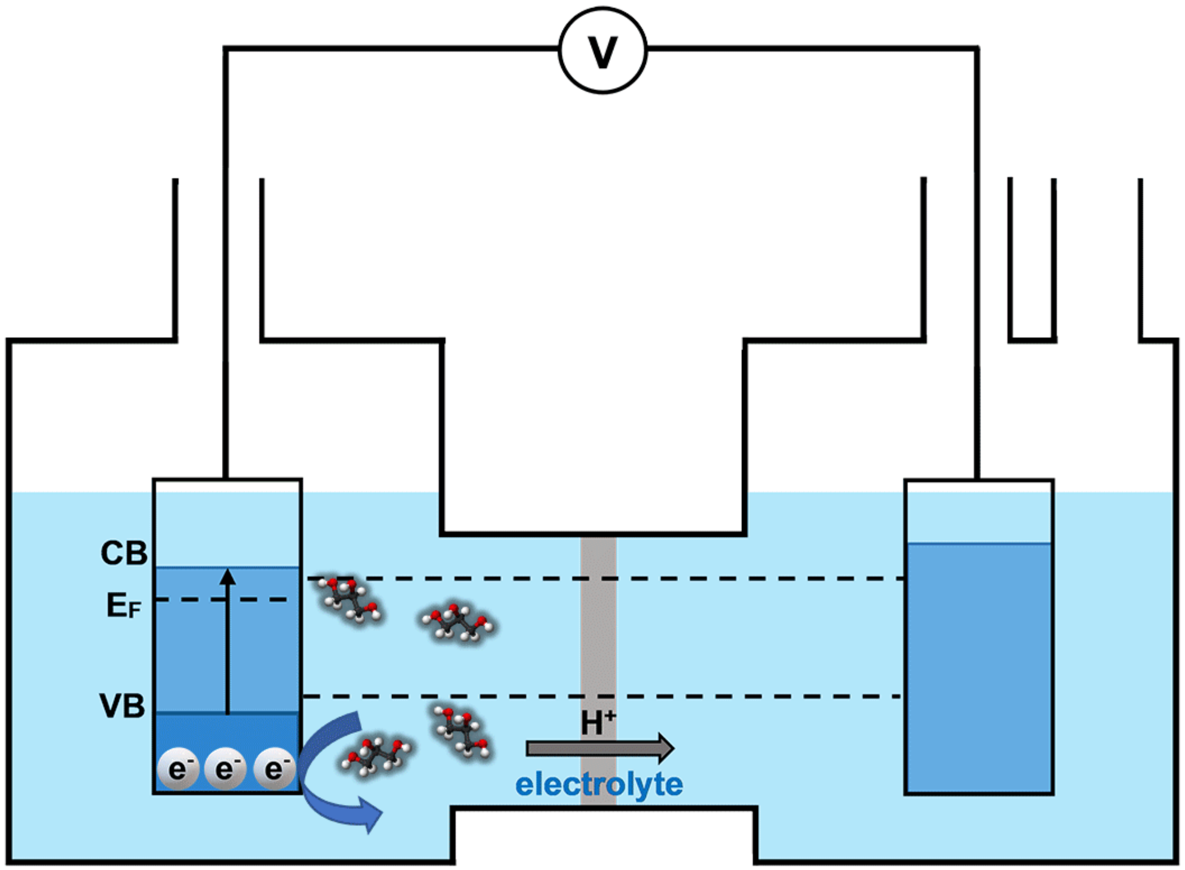
$$R\text{-}H + H_2O \rightarrow R\text{-}OH + H_2 \ (\Delta G^o < 0)$$

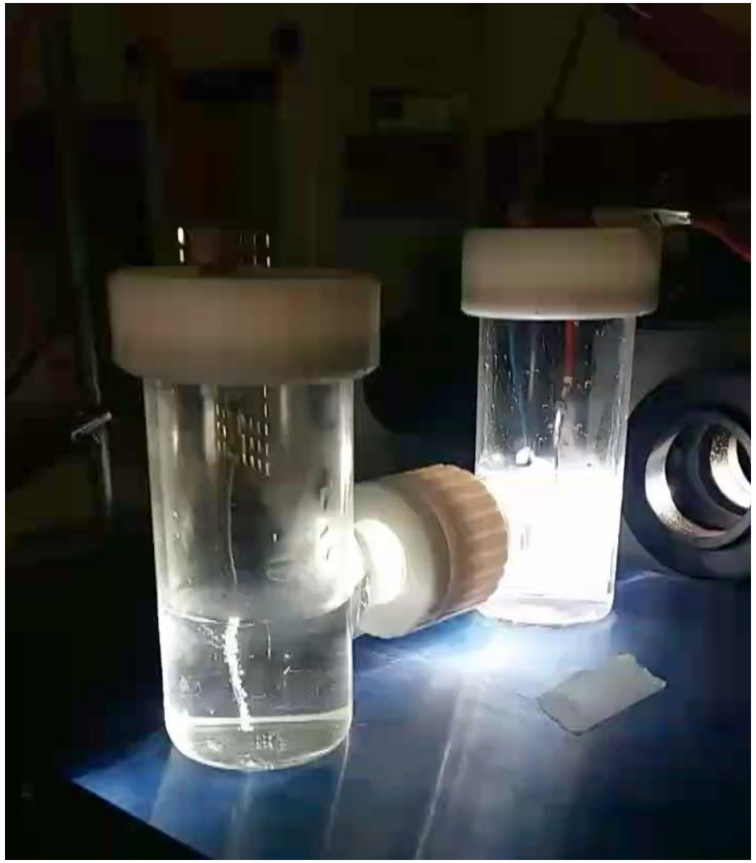
Photoelectroreforming as an alternative for the water splitting

Development of solar-driven photoelectrochemical cells for conversion of biomass residues into clean H_2 fuel and valuable chemicals



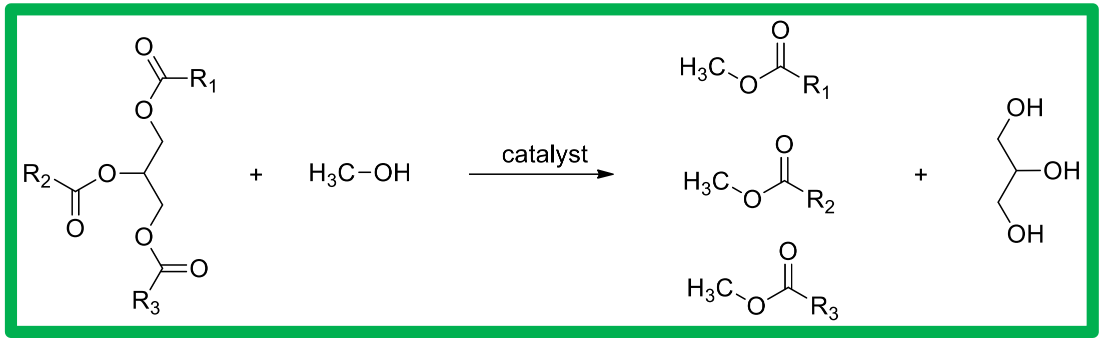
Biomass photoelectroreforming: how does it work?





Glycerol as substrate for photoelectroreforming?

It is a byproduct of the transesterification of natural oil to produce biodiesel

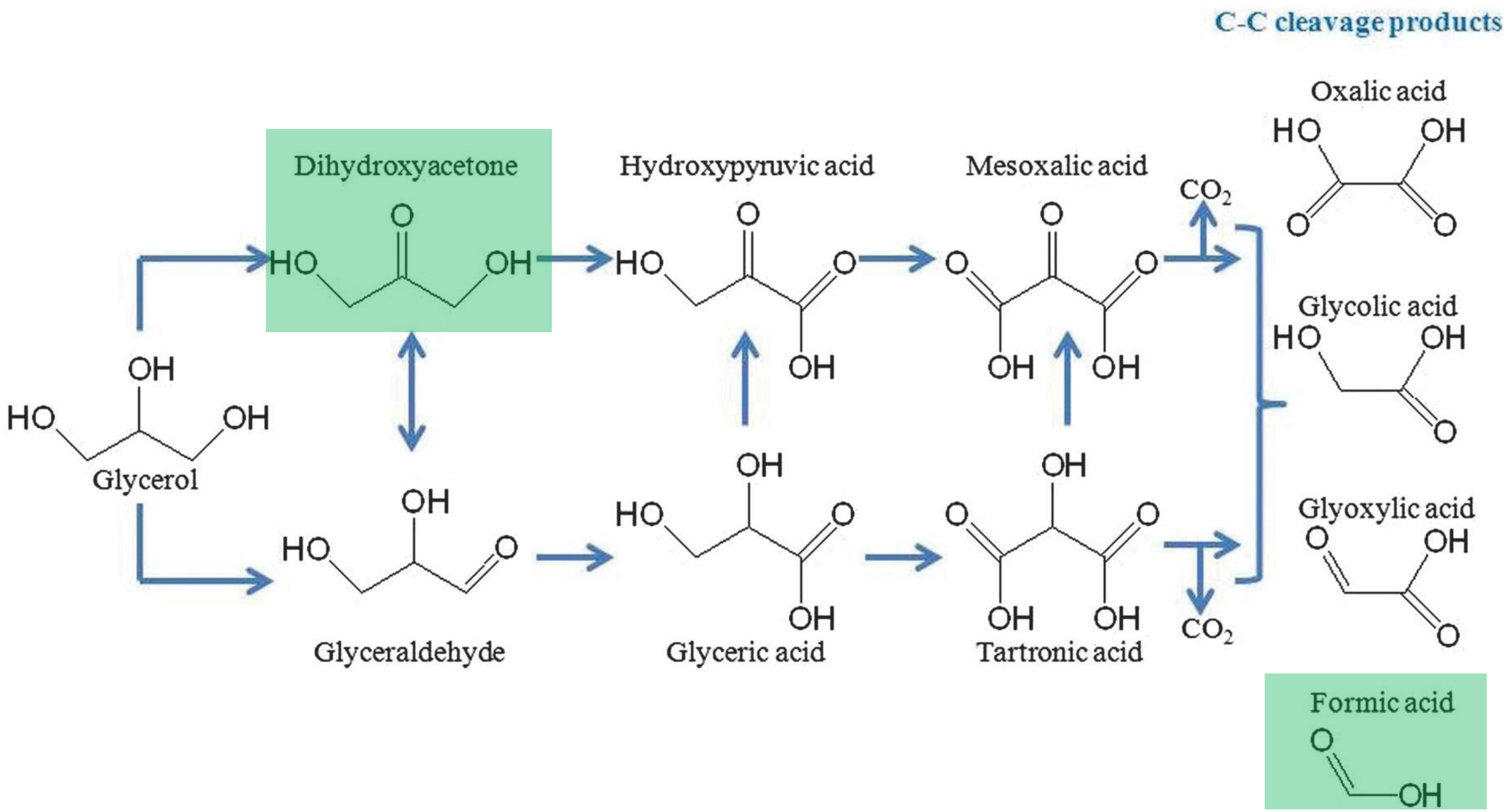


Crude glycerol

- ~10 m^3 of glycerol is produced for each 100 m^3 of biodiesel
- The production is 8 times higher than the current demand
- Purification is not attractive economically
- Storage, transportation and suitable destination is an economic and logistic issue

Long term storage or incorrect disposal can lead to soil and natural water contamination

Glycerol as substrate for photoelectroreforming?



Glycerol is a suitable Chemical platform to obtain valuable organic molecules of industrial interest

Chem. Soc. Rev. **2014**, *43*, 765

Glycerol photoelectroreforming – research strategy

Green Chemistry for Life

PHOSAGRO

2020 Green Chemistry for Life research grants

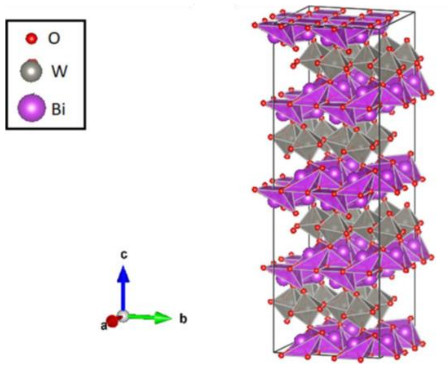
Dr Patrocinio Antonio Otavio de Toledo

Fundacao de Apoio Universitario, Uberlandia, Brazil

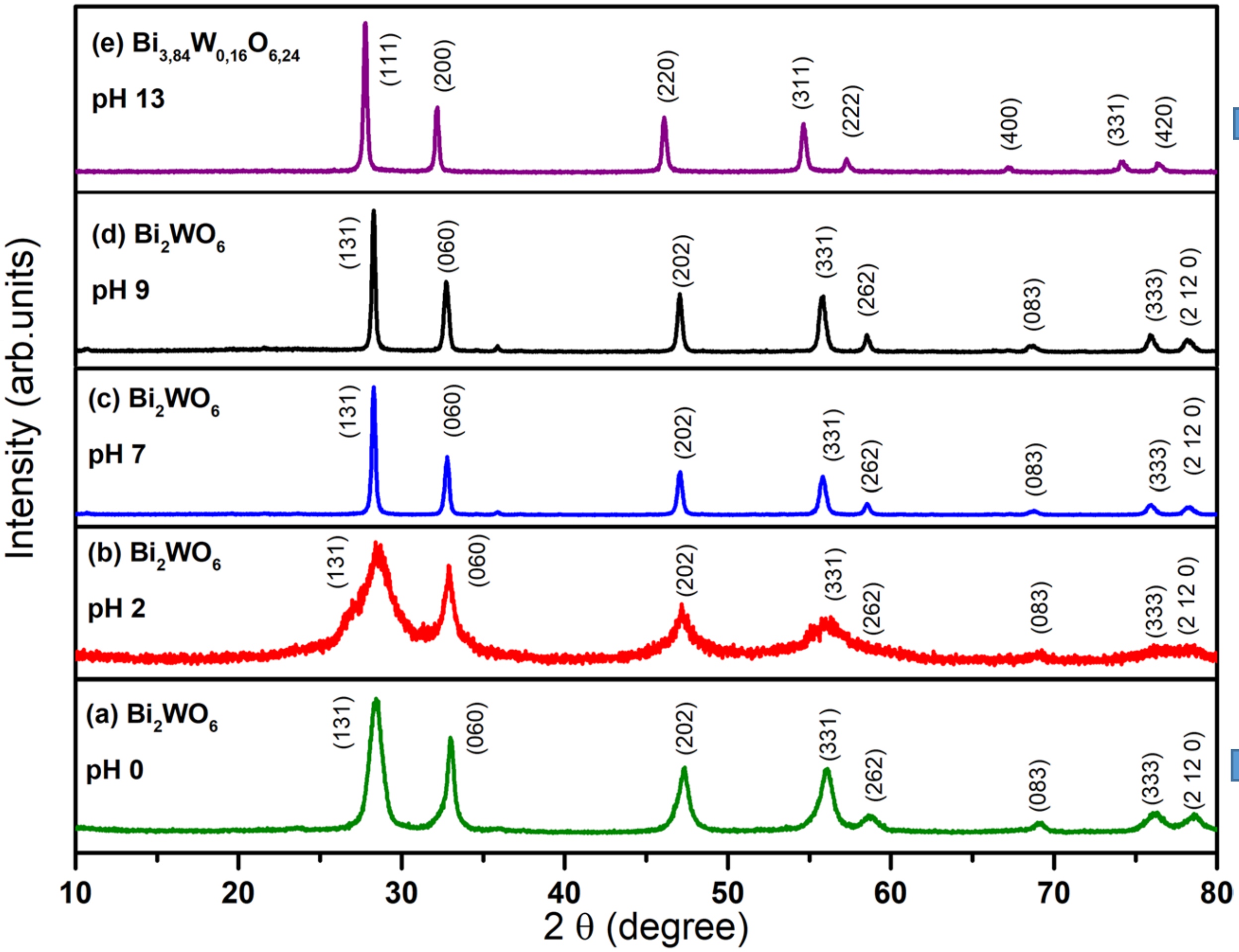
for Project: "Green valorisation of biomass residues by solar-driven photoelectrochemical processes

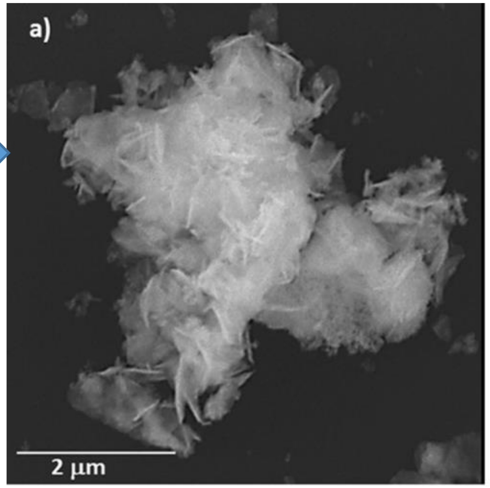
1. Synthesis and characterization of semiconducting nanomaterials based on Earth abundant elements
2. Development of cost-effective strategies for thin film deposition and device assembly
3. Optimization of the operation parameters aiming at high PEC efficiency and product selectivity
4. Long term stability tests and upscaling to pilot scale (TRL 7)

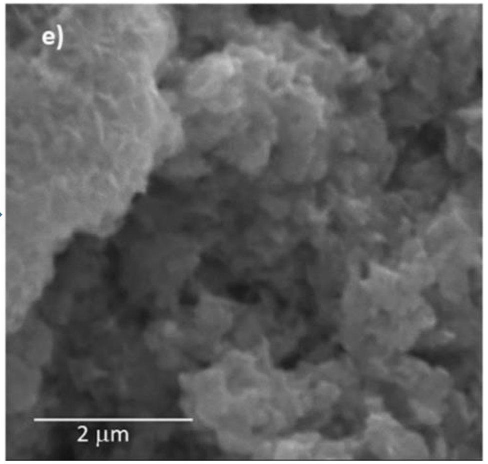
Glycerol photoelectroreforming – some key results



Bi_2WO_6 nanoparticles







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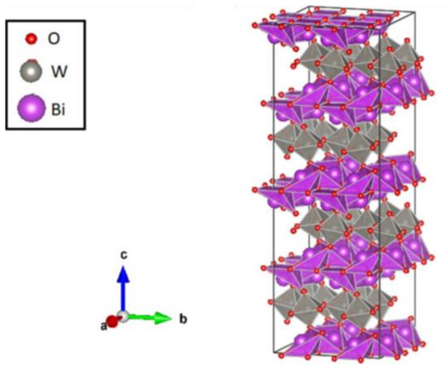
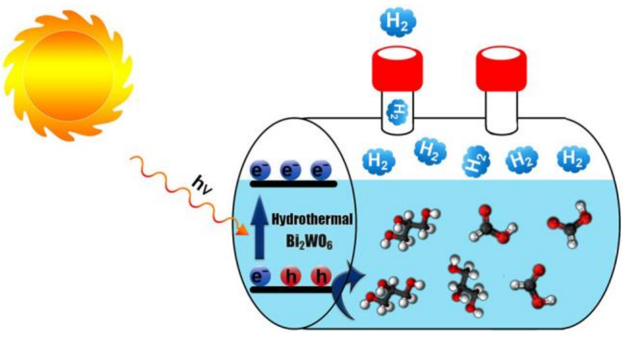
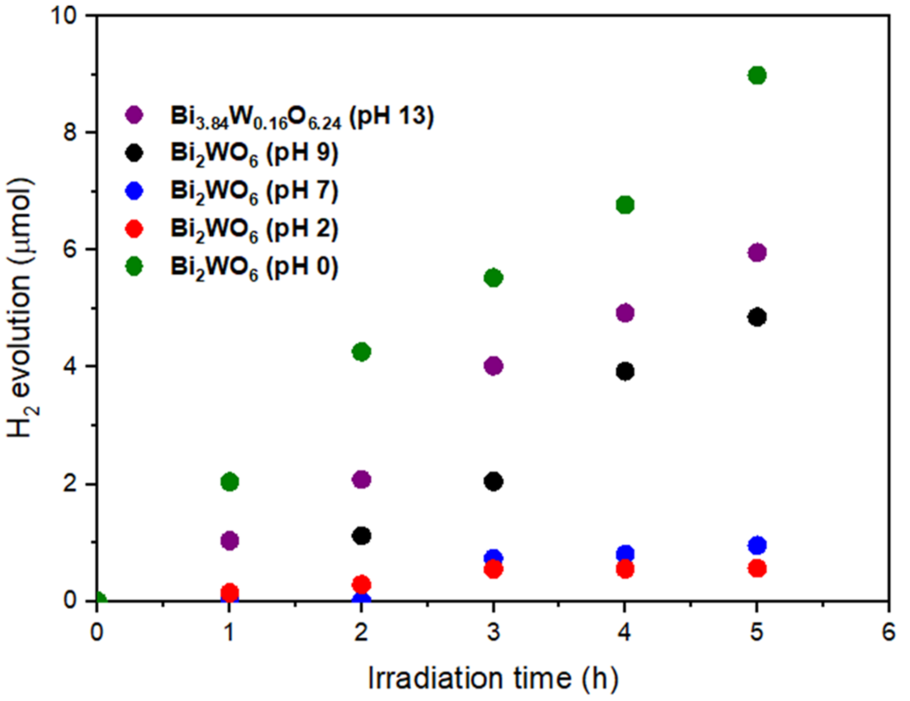
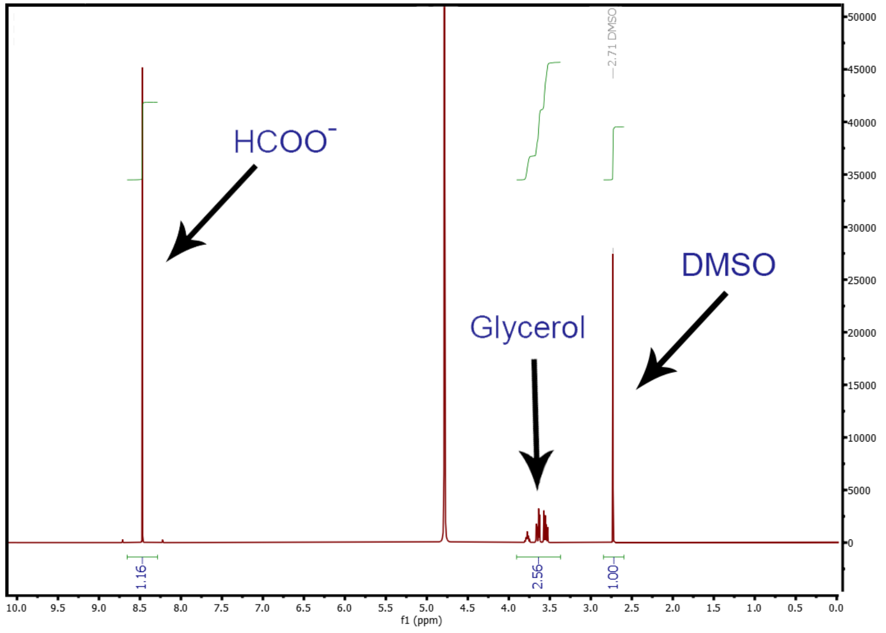


Bi_2WO_6 nanoparticles





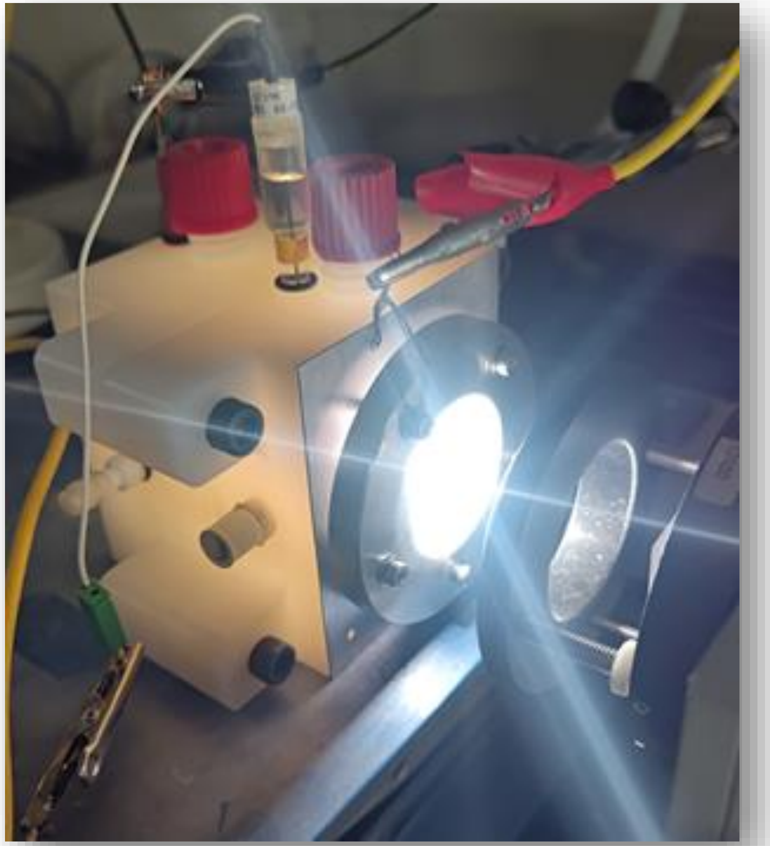
10 % Glycerol solution; λ> 350 nm (100 mW cm^{-2})

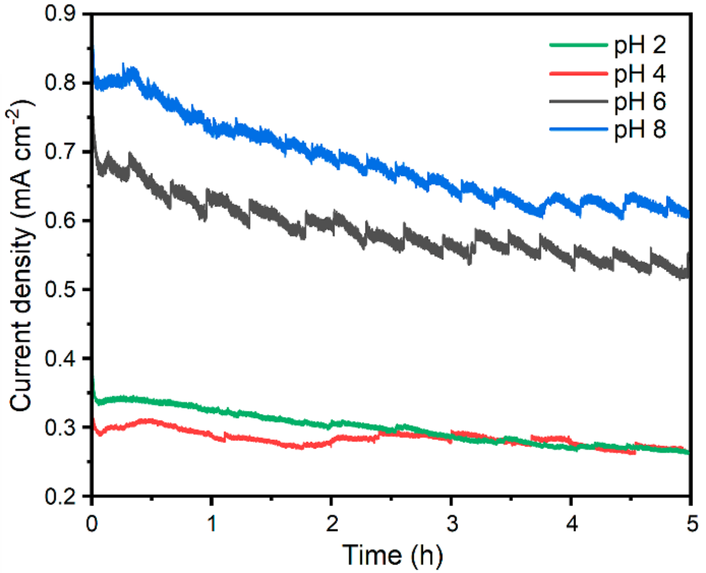


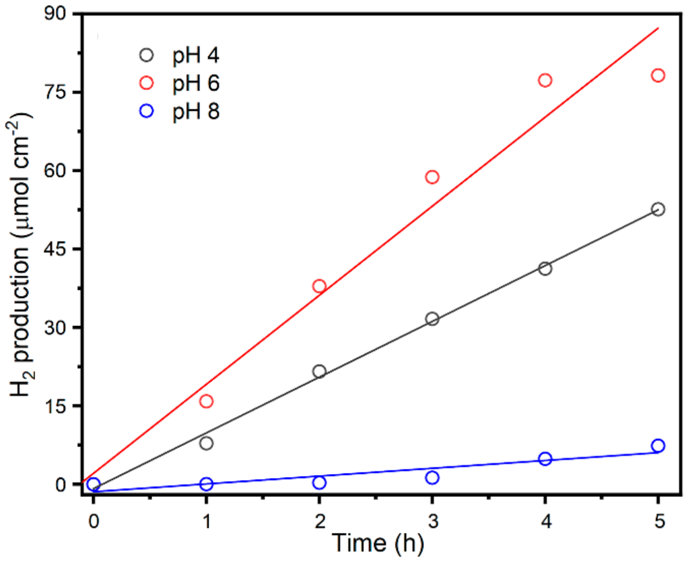
Samples	Conversion	Product selectivity		ξ H_2
		Formic acid	DHA	
$Bi_{3.84}W_{0.16}O_{6.24}$ (pH 13)	63±6%	87±2%	<0.1%	1.2±0.1%
Bi_2WO_6 (pH 9)	49±5%	41±2%	0.1%	1.0±0.1%
Bi_2WO_6 (pH 0)	80±6%	99±1%	<0.1%	1.4±0.1%

Photochemical & Photobiological Sciences 2022, 21, 1659

Glycerol photoelectroreforming – some key results



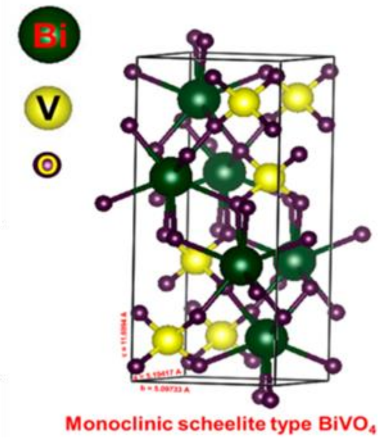




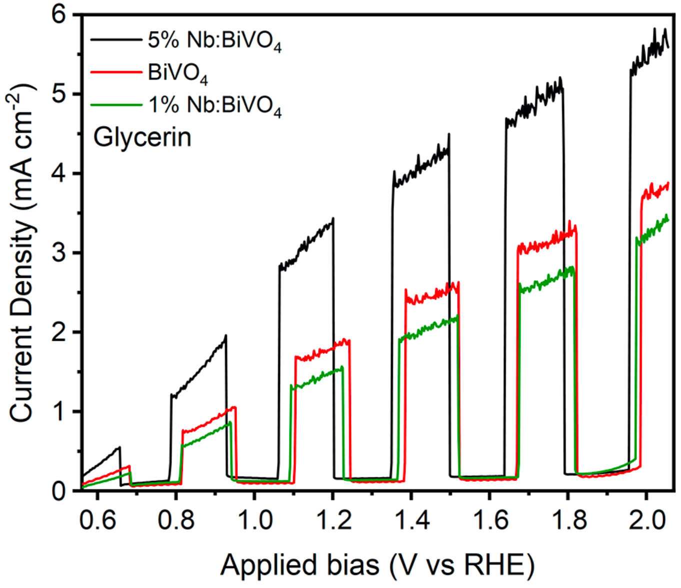
pH	Average current density (mA cm^{-2})	H_2 Production rate (μmol h^{-1} cm^{-2})	F. E. (H_2)	glycerol consumption	C-based selectivity (HCOOH)
4	0.29	10.7	95%	43%	88%
6	0.59	19.7	100%	65%	41%
8	0.70	2.0	17%	70%	13%

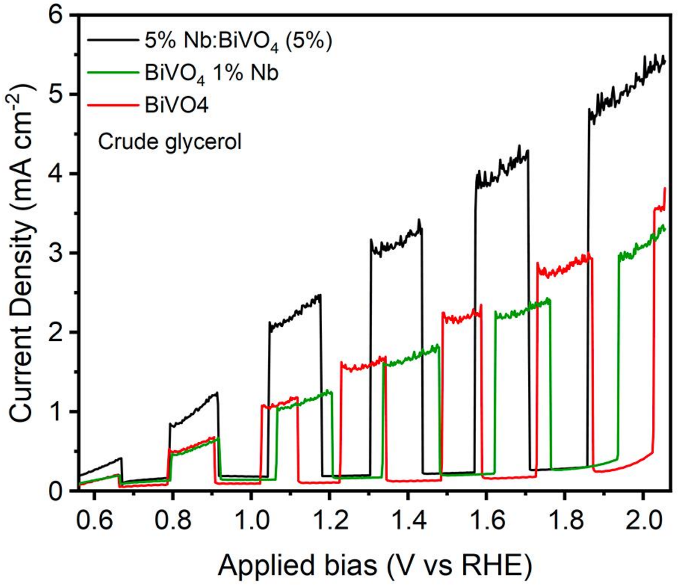
Applied Catalysis A **2022,** *646,*118867

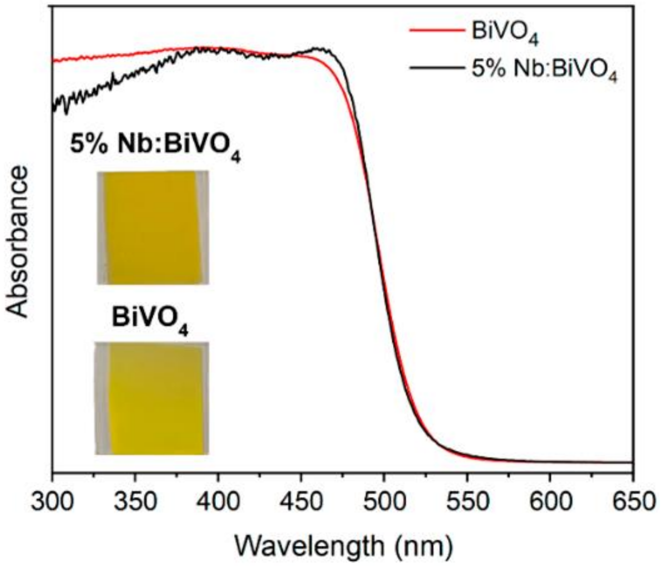
Glycerol photoelectroreforming – some key results



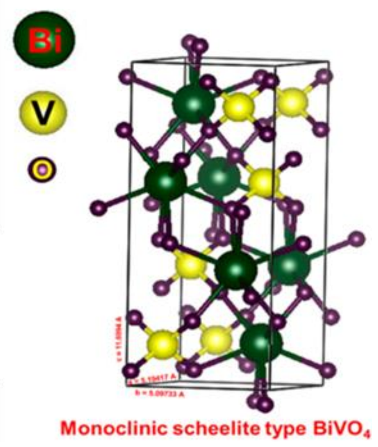
Nb-doped $BiVO_4$ photoanodes



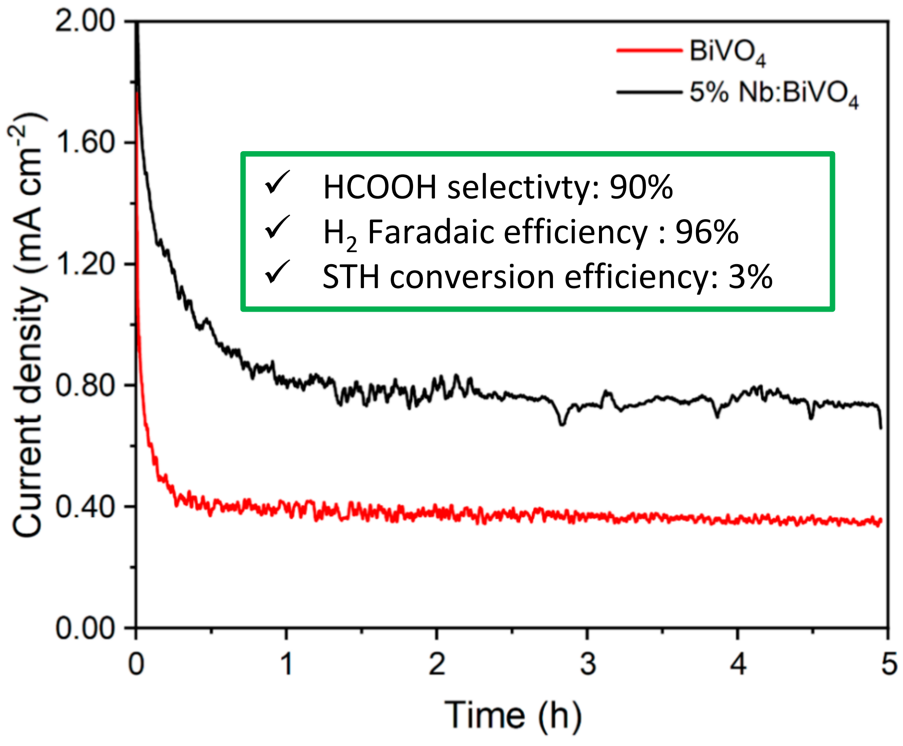


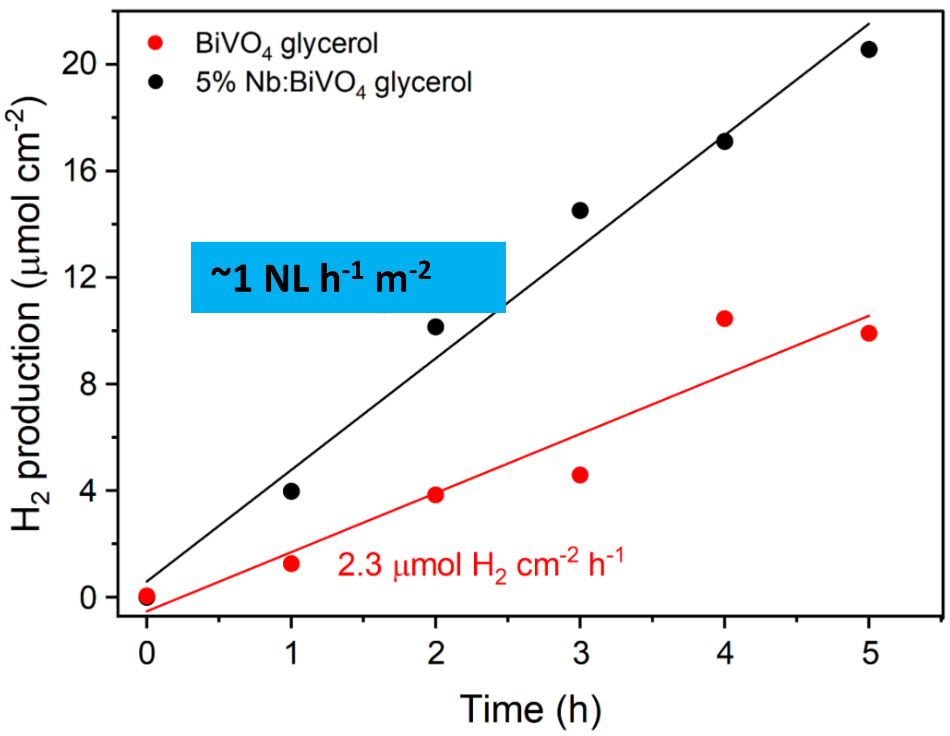


Glycerol photoelectroreforming – some key results



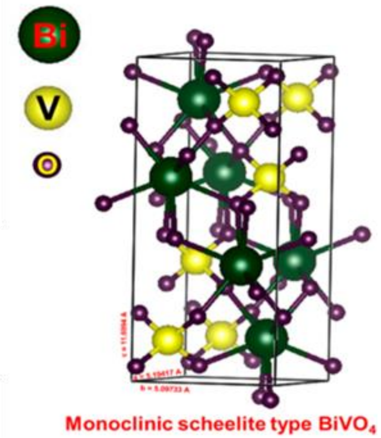
Nb-doped $BiVO_4$ photoanodes





Nascimento L.L. *submitted*

Glycerol photoelectroreforming – some key results



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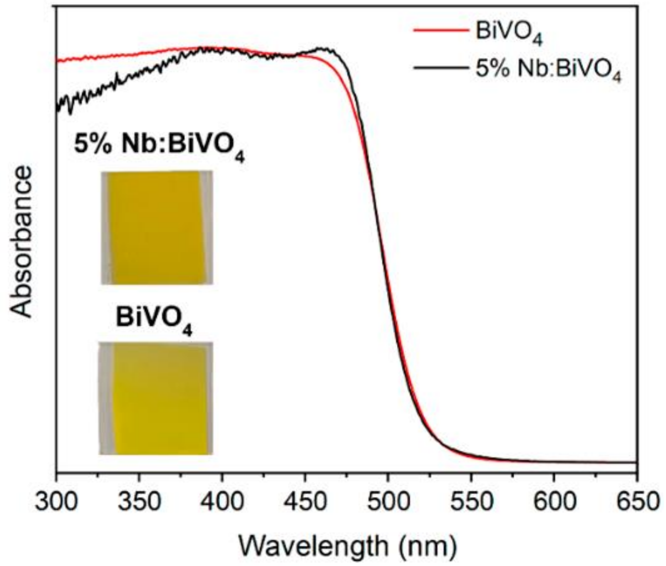
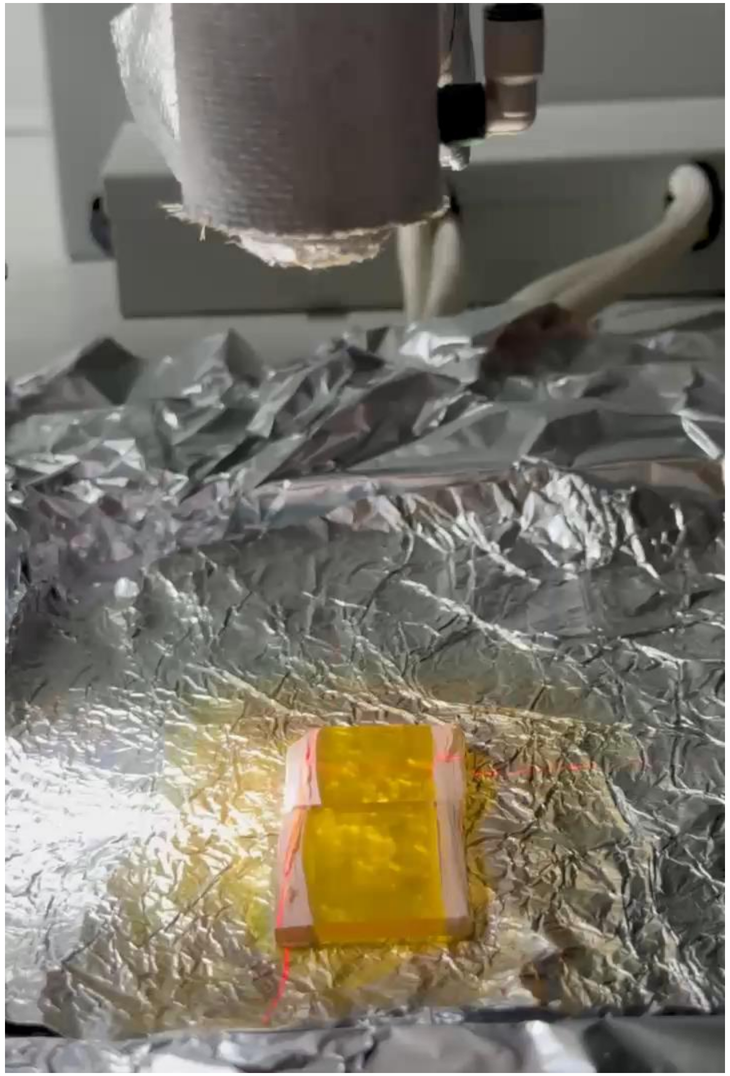
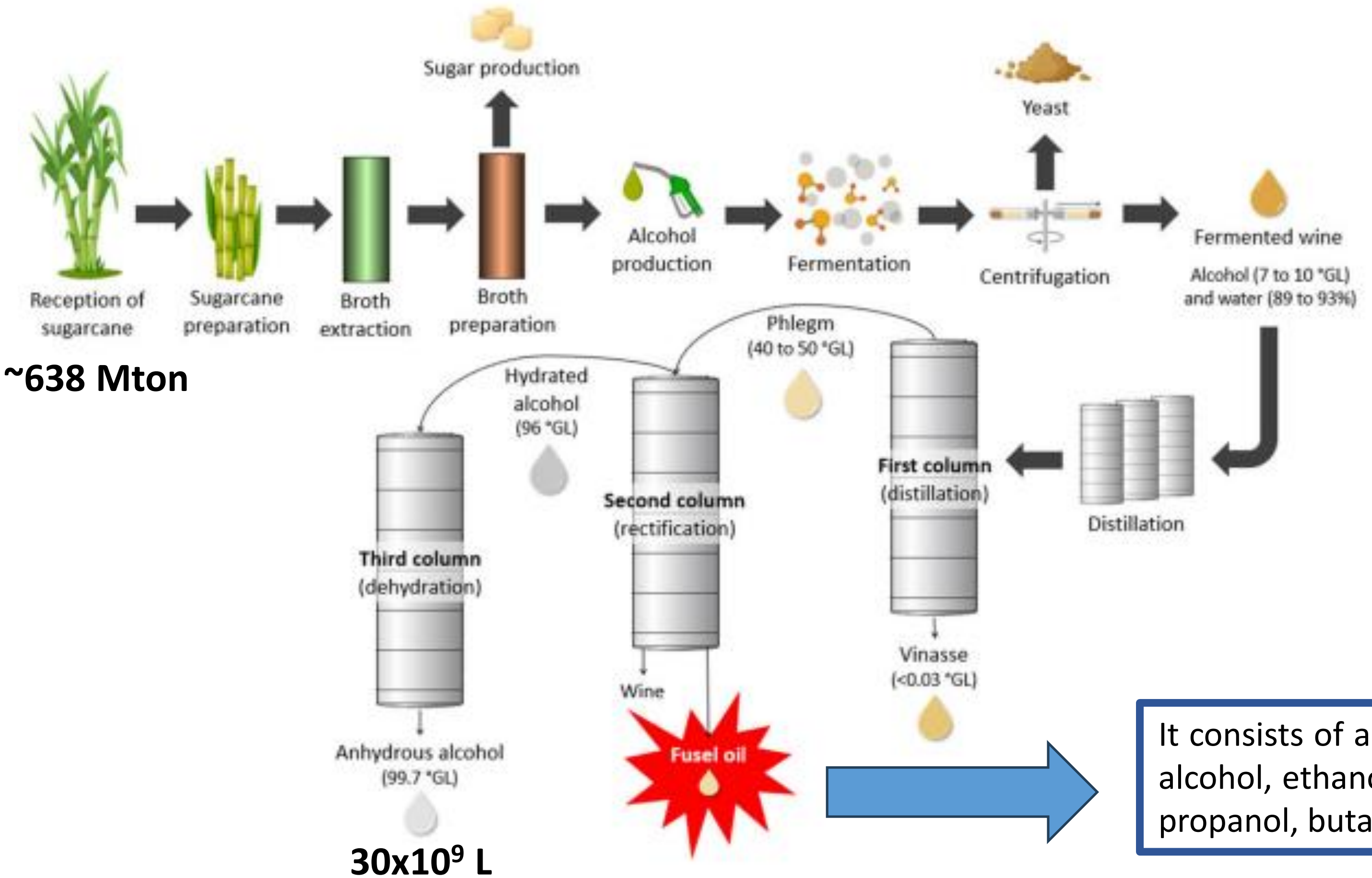




Homogeneous photoanodes through Computer-controlled deposition

Can other residues be used for photoelectroforming?

Bioethanol production in Brazil



~638 Mton

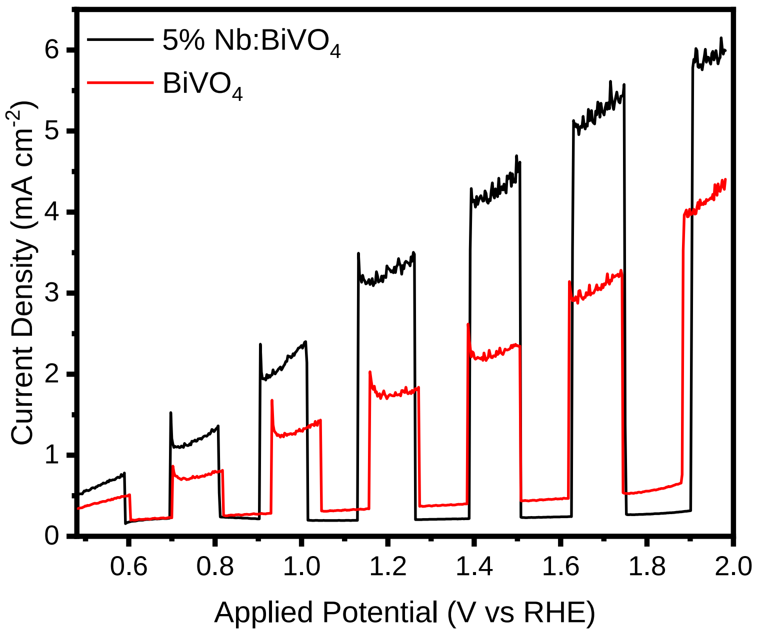
$30x10^9$ L

For 100 L of ethanol, it is also produced:

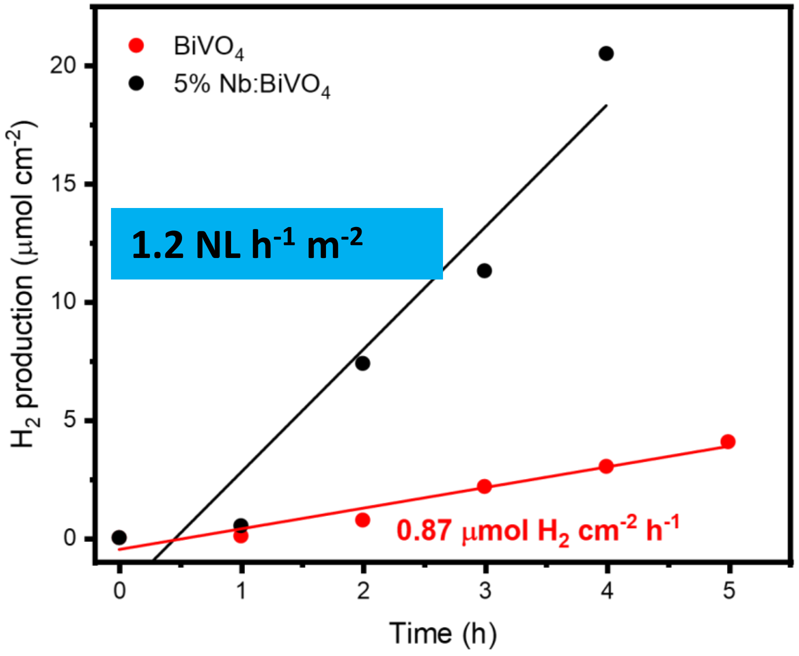
- 1000 L of vinasse
- **0,2 L of fuseloil**
- **3 L of flegmas (diluted fuseoil)**

It consists of an azeotropic mixture between C3-C5 alcohols, mainly isoamyl alcohol, ethanol and water and others trace compounds such as isobutanol, propanol, butanol, furfural.

Flegmass photoelectroreforming



Flegmass 100%, 0.1 mol/L K_2SO_4
1000 W m^{-2} A.M. 1.5G



- ✓ Optimal performance at neutral pH
- ✓ High selectivity to formic acid (90%)
- ✓ Performance 5 times better than TiO_2 (Standard system)
- ✓ Long term stability thanks to the Nb(V) doping
- ✓ Reduced water use

Conclusions and perspectives

- Low carbon H_2 production can play a key role on the descarbonization of industrial processes
- Its production costs need to be reduced to efficiently compete with the current production methods (natural gas reforming / coal gasification)
- Direct solar-to-hydrogen conversion can be a suitable method to reduce the costs of low carbon H_2
- The use of biomass residues as substrates for H_2 production is an energy efficient pathway that can also lead to the production of valuable organic substrates increasing the economic attractiveness of the process.
- Further R&D is needed to scale-up the photoelectrochemical cells

Acknowledgments

UFU

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Conselho Nacional de Desenvolvimento Científico e Tecnológico

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Thank you!