EPFL

Some of Europe's Activities on photo-electrochemical devices and systems

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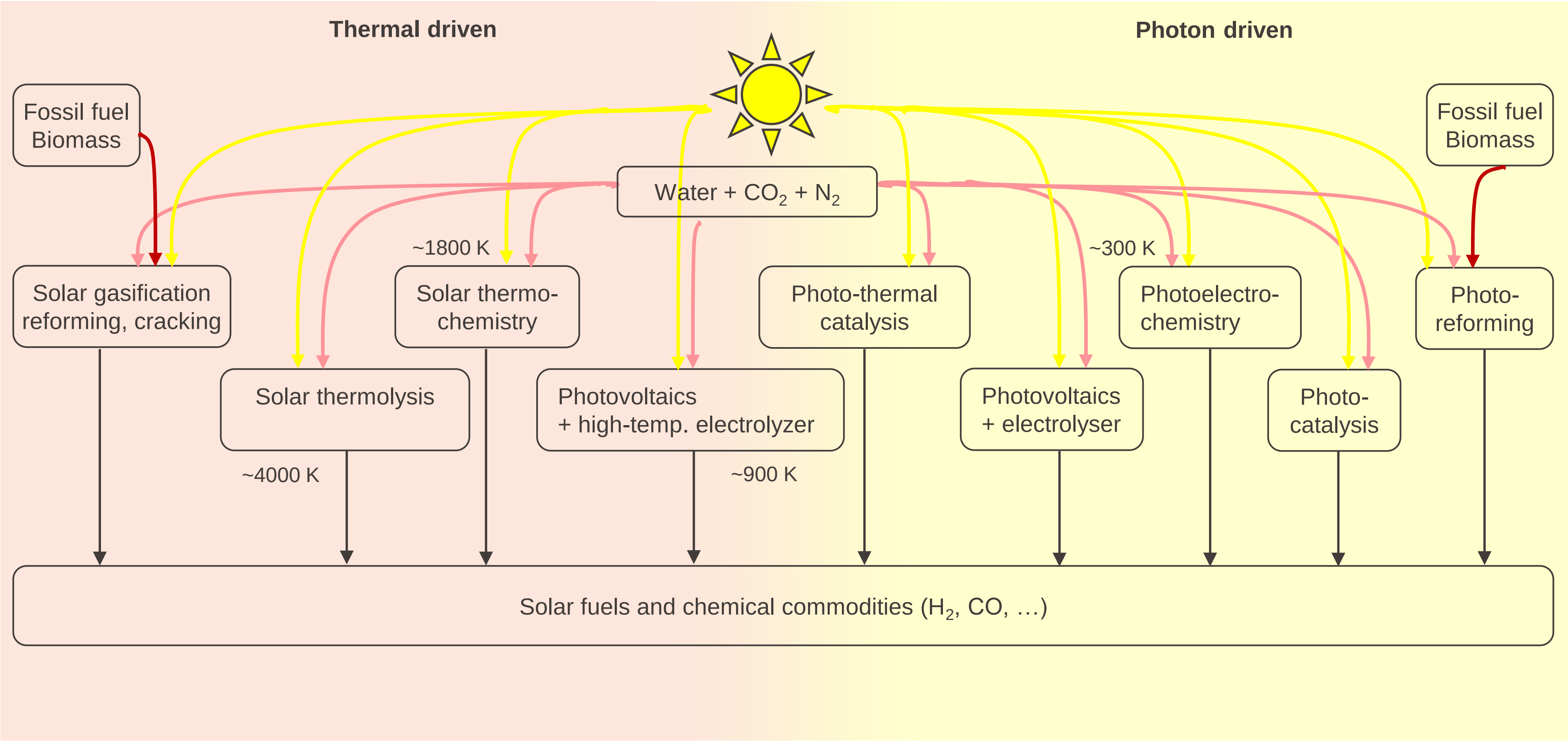
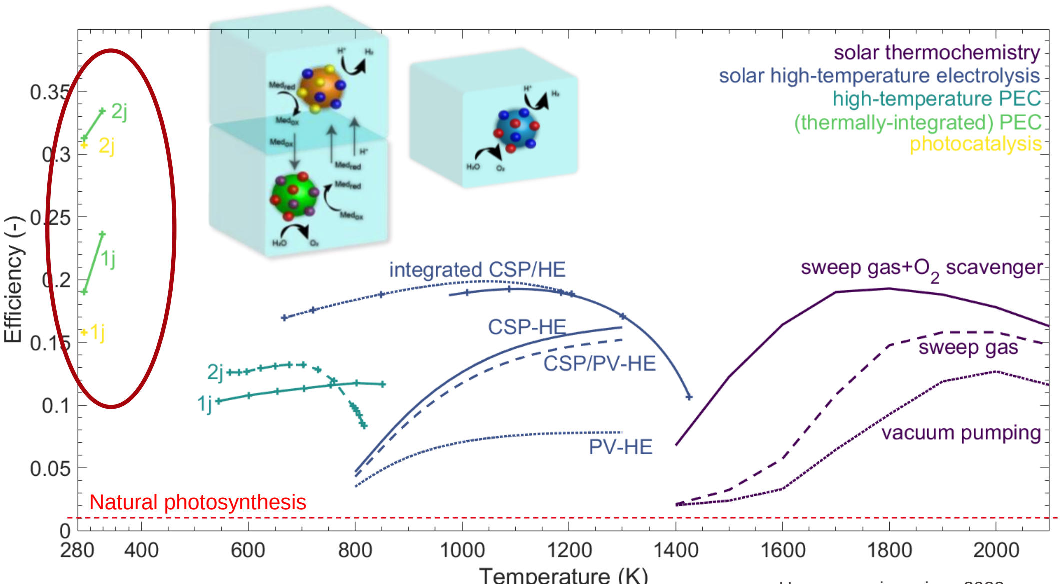
Ecole Polytechnique Fédérale de Lausanne

Technical Solar Fuel Approaches (Non-Biological)

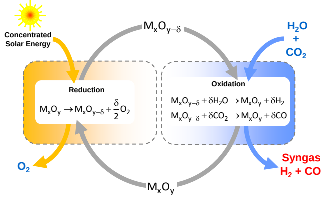
- Thermal and photon-driven, and combinations thereof

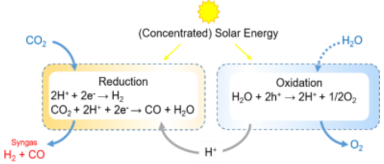


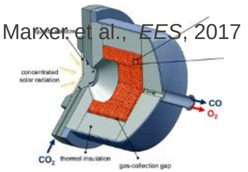
Theoretical Efficiency Limits



Haussener, in review, 2022

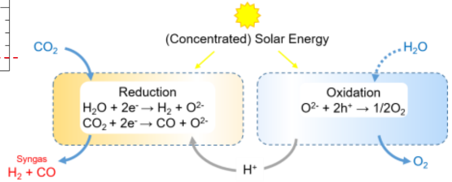


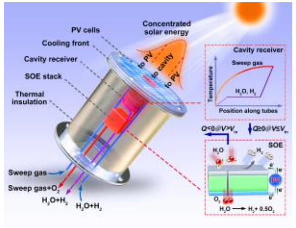




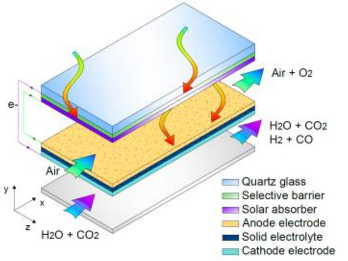
Marxer et al., *EES*, 2017

Tembhurne et al., *Nature Energy*, 4, 2019





Lin et al., *in review*;



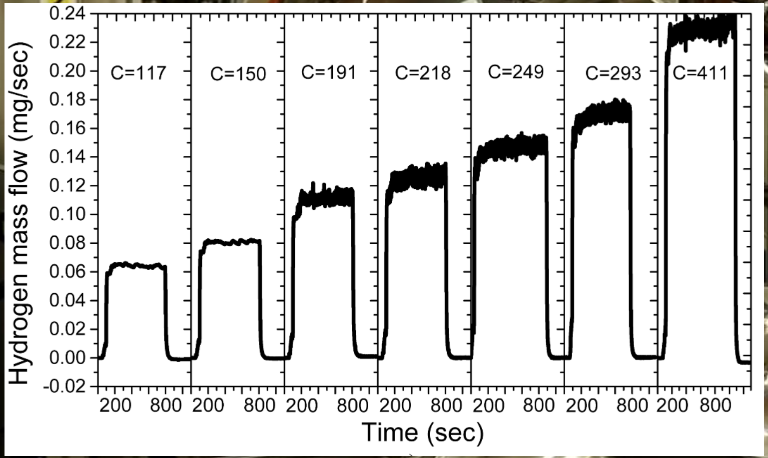
Gutierrez et al., *Sust Energy & Fuels*, 7, 2021;

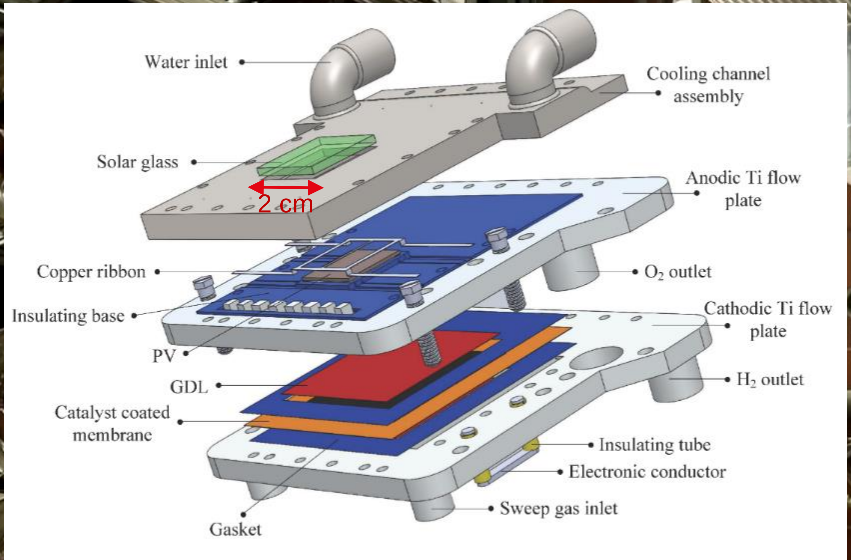
Lin et al, *J Power Sources*, 400, 2018

Lin et al., *Sol. Energy*, 155, 2017; Lin et al., *Energy*, 88, 2015

Nandy et al., *Chem Sci*, 29, 2021

Dumortier et al., *Energy Environ Sci*, 8, 2015; http://specdo.epfl.ch





Output power of PEC at 474 kW/m^2: 27 W

Current density in electrolyzer component: 0.88 A/cm^2

Current density in photoabsorber component: 6.04 A/cm^2

Efficiency: 17.1% solar-to-fuel

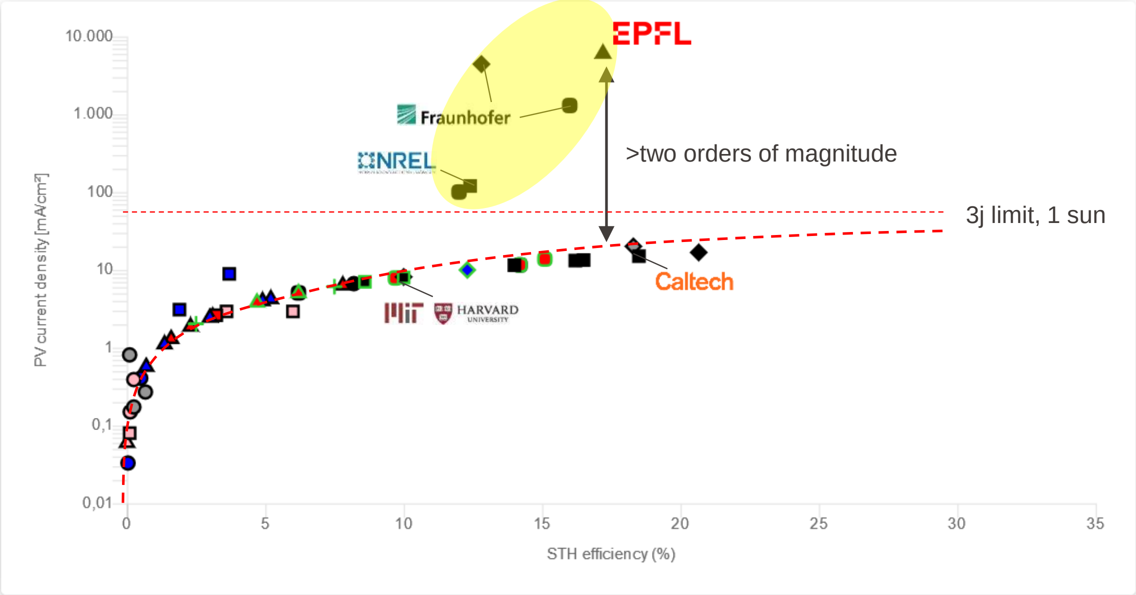
Tembhurne, Nandjou, Haussener, *Nature Energy*, doi: 10.1038/s41560-019-0373-7, 2019

Leveque, Bader, Lipinski, Haussener, *Optics Express*, 24, 2016

Comparison

SolarFuelsDB

- Dynamic and online tool: – http://specdc.epfl.ch/ and http://solarfuelsdb.epfl.ch



Concentrated irradiation
AND
Thermal management

w/o multi-module demonstrations
w/o multiple electrolyzer demonstrations

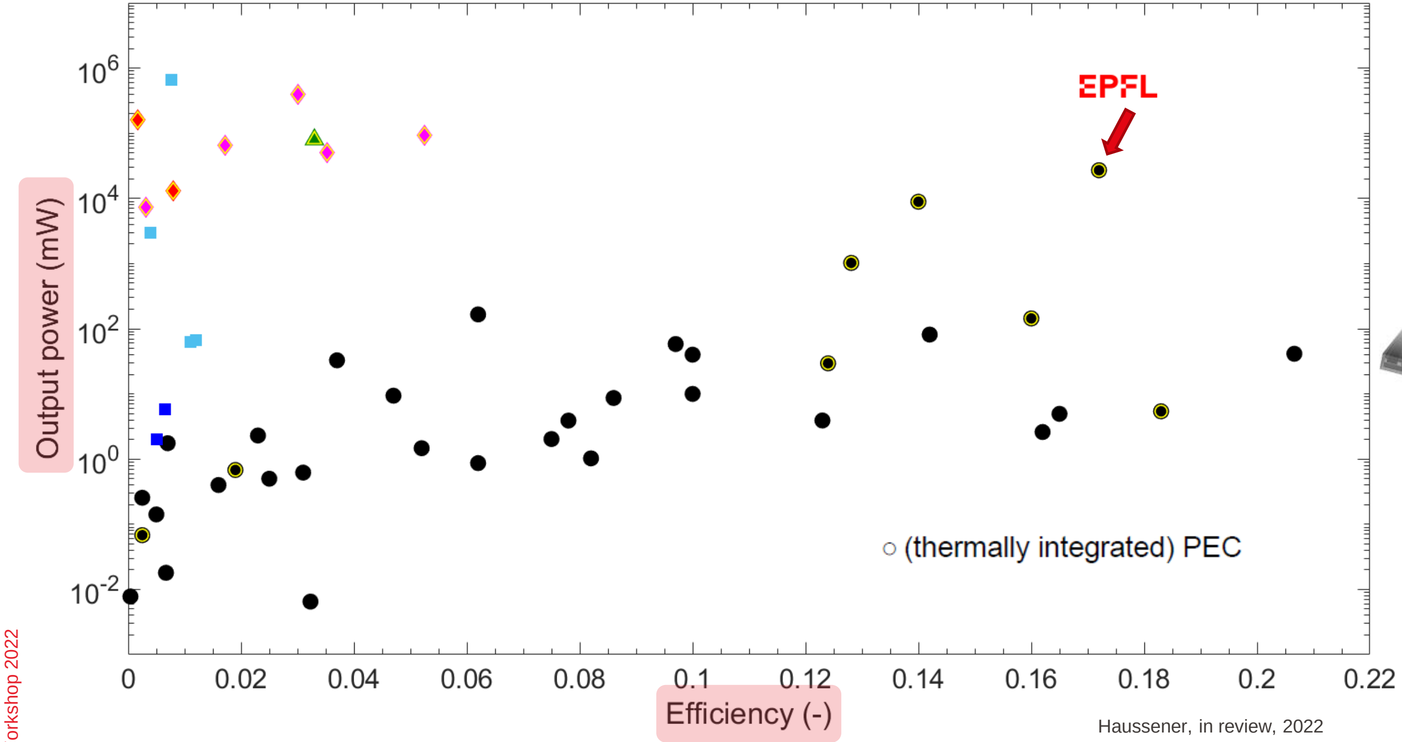
LEGEND

Fill color - PV / photoabsorber material	Boundary color - EC material	Symbol shape - PV / photoabsorber and EC configuration
All III-V	Rare metal-based (expensive)	○ 2J, integrated PVs and catalyst; + 3J, integrated PVs and catalyst
Partial III-V	Abundant (cheap)	□ 2J, integrated PVs, wired catalyst; Δ 3J, integrated PVs, wired catalyst
All Si		◇ 2J, non-integrated PVs or catalyst; O 3J, non-integrated PVs or catalyst
Partial Si		
Oxides and others		

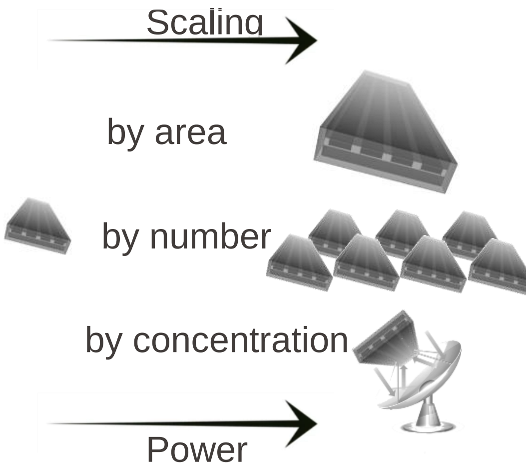
Tembhurne, Nandjou, Haussener, *Nature Energy*, doi: 10.1038/s41560-019-0373-7, 2019

Scaling?

SolarFuelsDB



Haussener, in review, 2022



Tembhurne, Nandjou, Haussener, *Nature Energy*, doi: 10.1038/s41560-019-0373-7, 2019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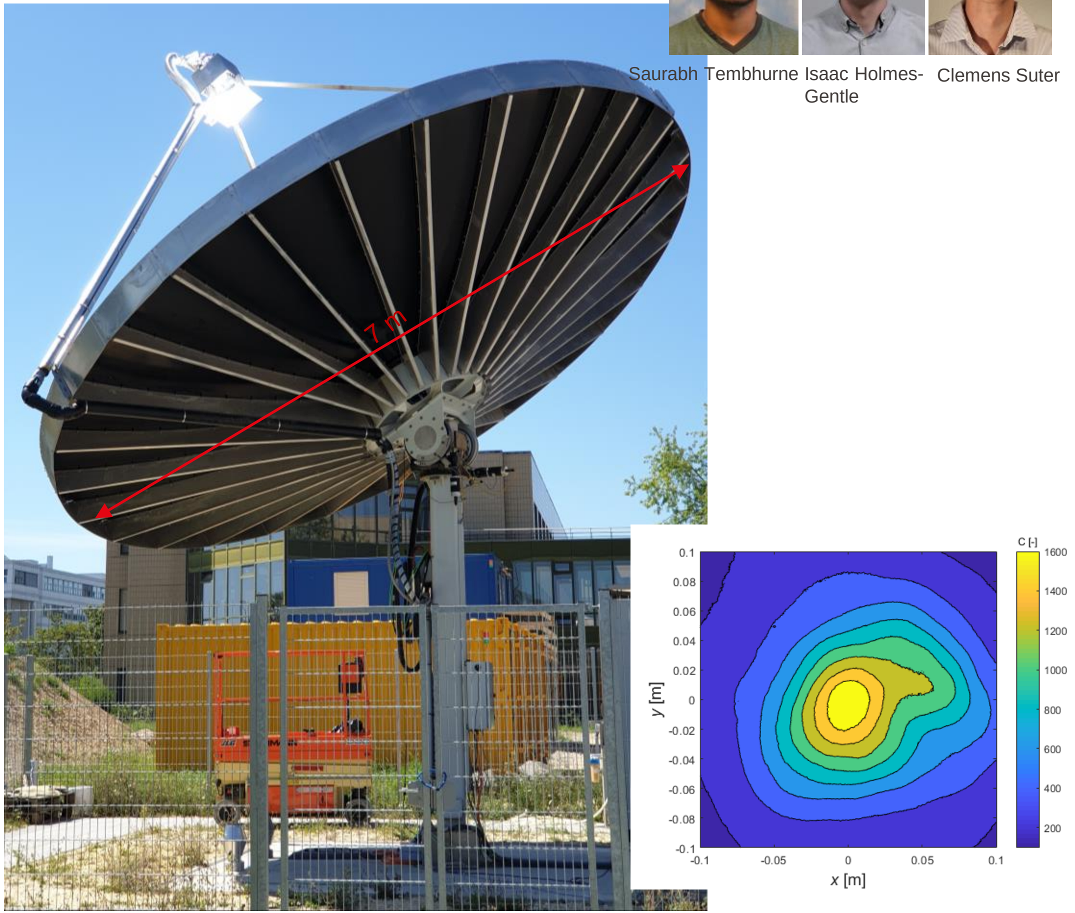
Scaling: From W to kW Power



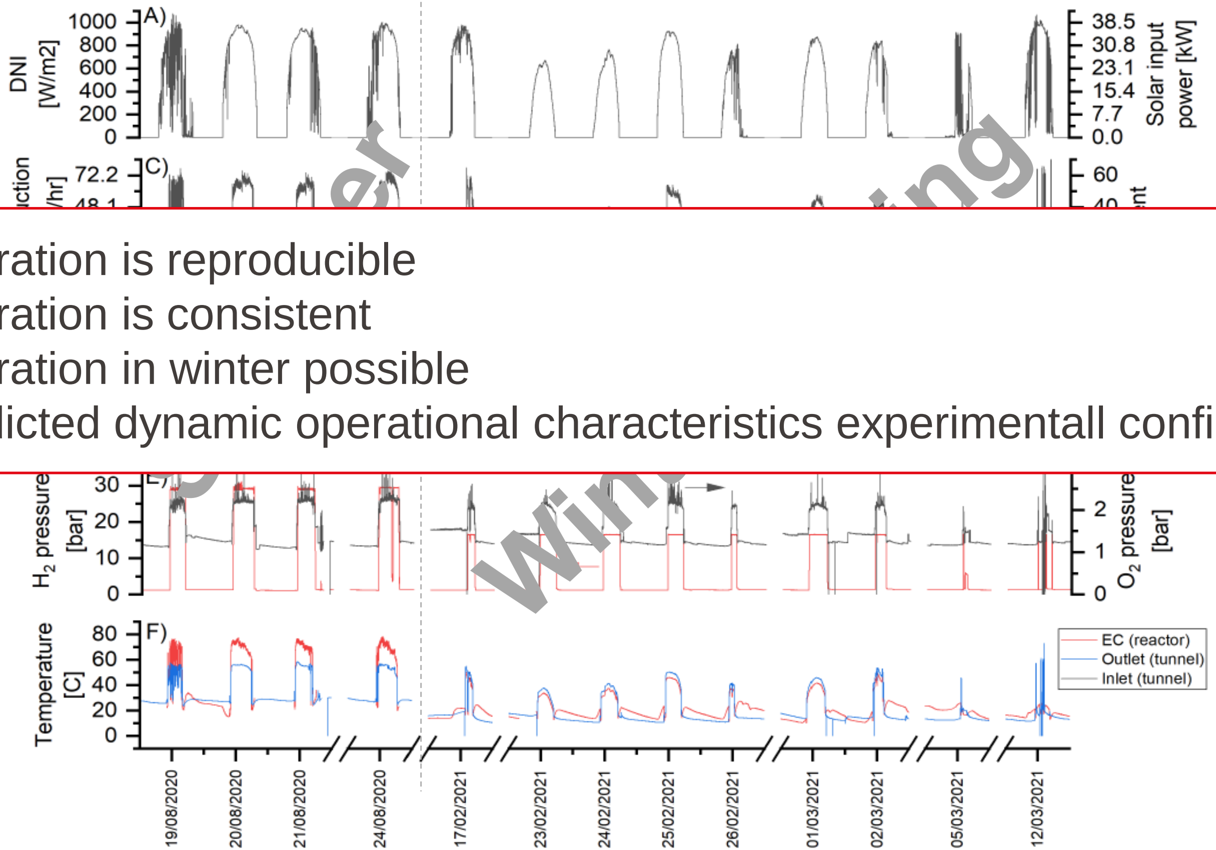
Saurabh Tembhurne Isaac Holmes-Gentle Clemens Suter

Haussener, LRESE

Tembhurne, Holmes-Gentle, Suter, Haussener, in preparation, 2022

Operational Versatility

- Operation for multiple seasons:



Operation is reproducible
Operation is consistent
Operation in winter possible
Predicted dynamic operational characteristics experimentall confirmed

Operational Performance

Date	Average DNI [W/m^2]	Oper. time [h]	η_{fuel} [%]	$\eta_{thermal}$ [%]	η_{IPEC} [%]	m_{H_2} [kg]	Power [kW]	Peak power [kW]	Peak H2 prod. rate [NL/min]	Mean DNI (at peak) [W/m^2]

This is a heat-fuel-oxygen co-generation system

Potential for:

- Co-generation of heat/electricity/fuel/oxygen
- Potential for grid-supported operation during night
- Potential for grid-supported operation for low irradiation intensity

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SoHHytec
Solar Fuel, the smarter way.

http:\\www.sohhytec.com

Industry
Steel production
Fertilizer production …

At least 2 other startups in Europe working on solar hydrogen via PEC

Fuel/Mobility

Haussener, in review, 2022

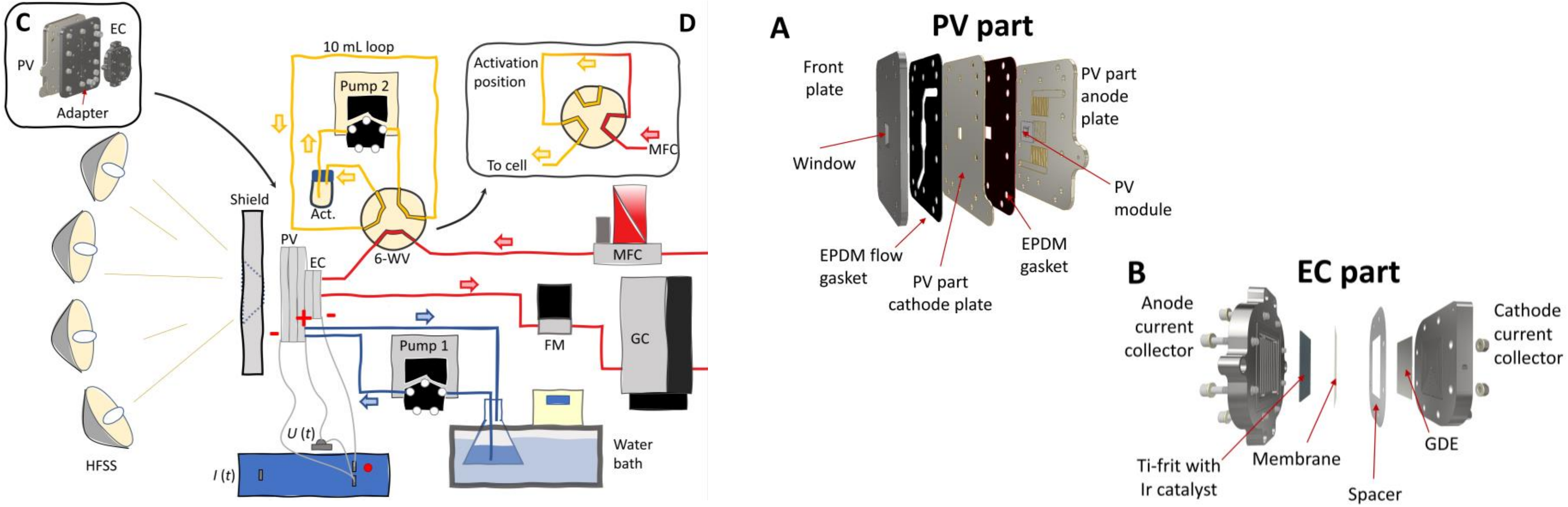
Electricity/(Seasonal) storage

Alternative Chemistry


Etienne Boutin Mahendra Patel

- Do design guidelines (thermal integration, concentrated radiation) also apply to CO_2 reduction?

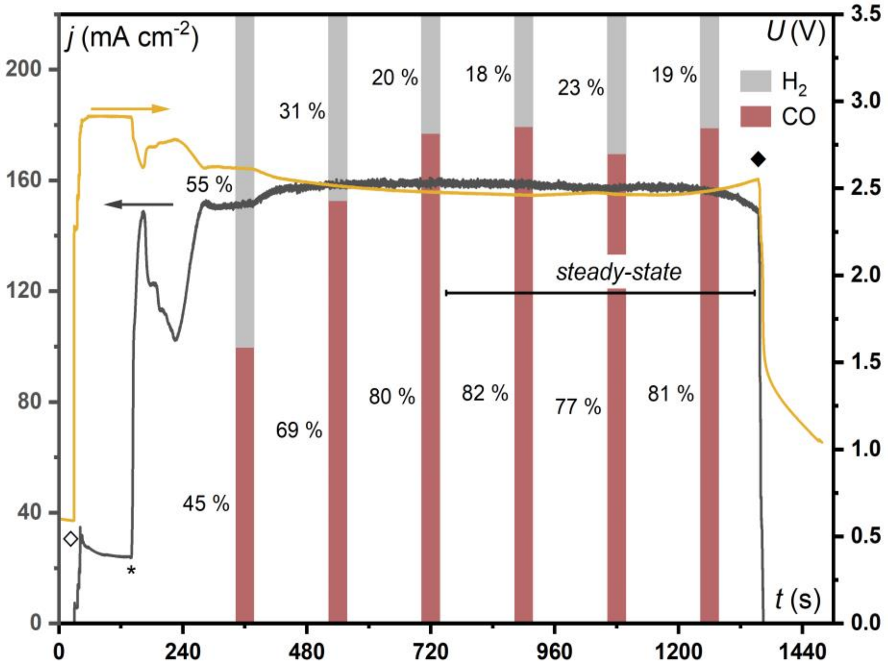
- Confirmation of design approach with silver catalyst in zero-gap gas diffusion electrode (GDE) configuration



Boutin, Patel, Kecsenovity, Suter, Janaky, Haussener, Adv. Energy Mat., 2022.

CO_2 Reduction with Concentrated Light

- Typical experimental run



*T*ypical 20 min experiment at 341 suns with the integrated PEC cell.

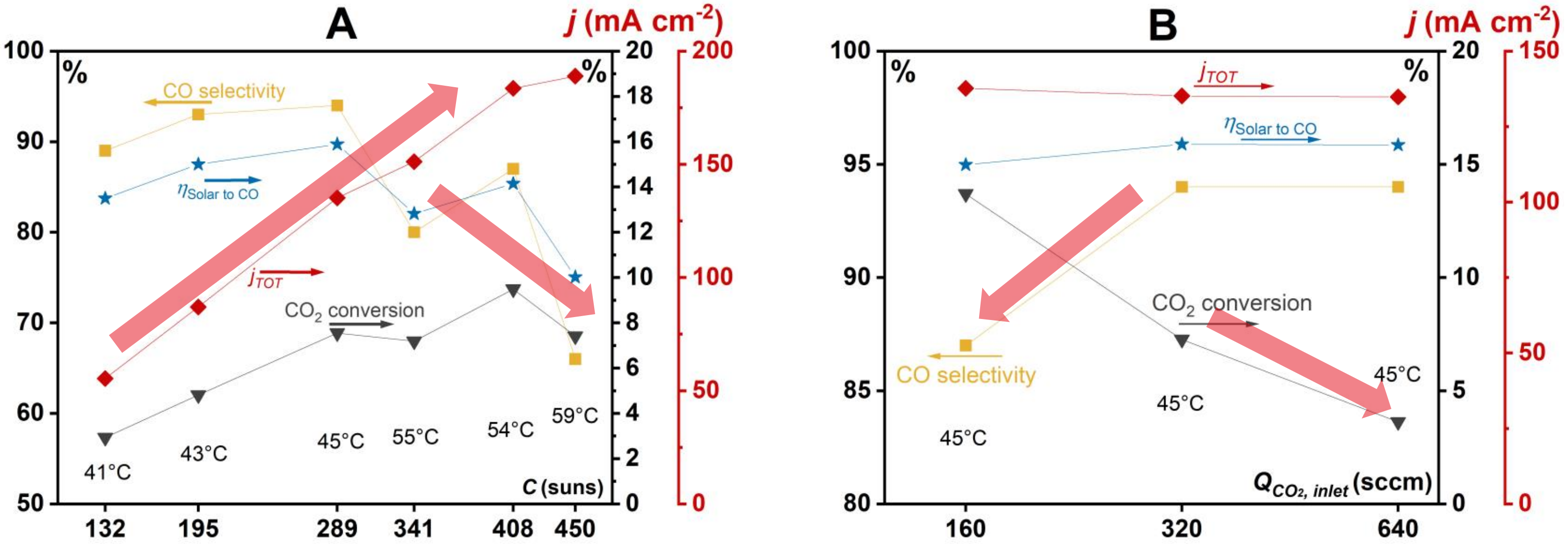
S_{CPV}: 0.92 cm^2.
Q_{CO2}: 312 sccm.
Averaged T_{water}: 55° C.

◇ : lamps switch on.
◆ : lamp switch off.
* : activation with 10 cm^3 of 1 M CsOH solution in 1:3 isopropanol/water mixture.

Boutin, Patel, Kecsenovity, Suter, Janaky, Haussener, Adv. Energy Mat., 2022.

CO_2 Reduction with Concentrated Light

- Playing with irradiation concentration

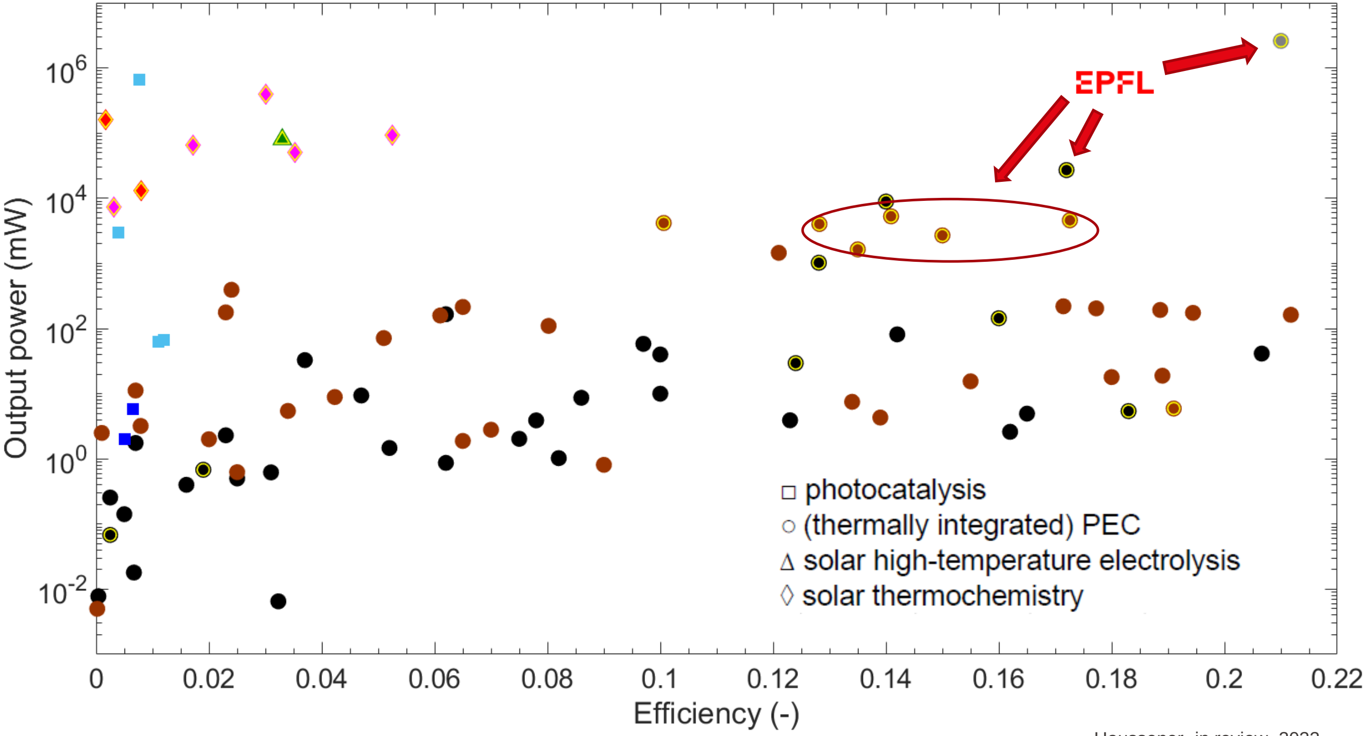


Boutin, Patel, Kecsenovity, Suter, Janaky, Haussener, Adv. Energy Mat., 2022.

Haussener, LRESE

Scaling?

SolarFuelsDB

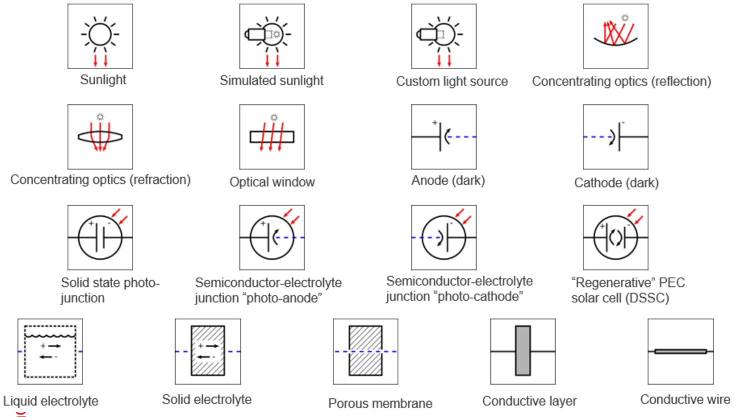


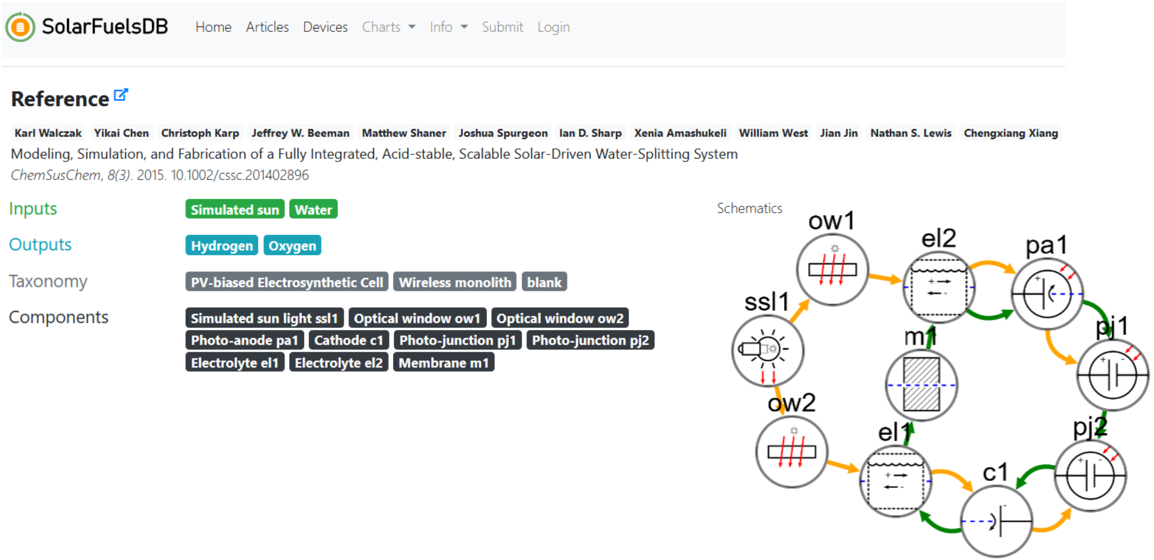
Haussener, in review, 2022

SolarFuelsDB

- Open, machine-readable database on solar fuel device demos
- Was launched at our workshop in December 2021
- Currently includes PEC for hydrogen
- Required the development of classification system

Isaac Holmes-Gentle

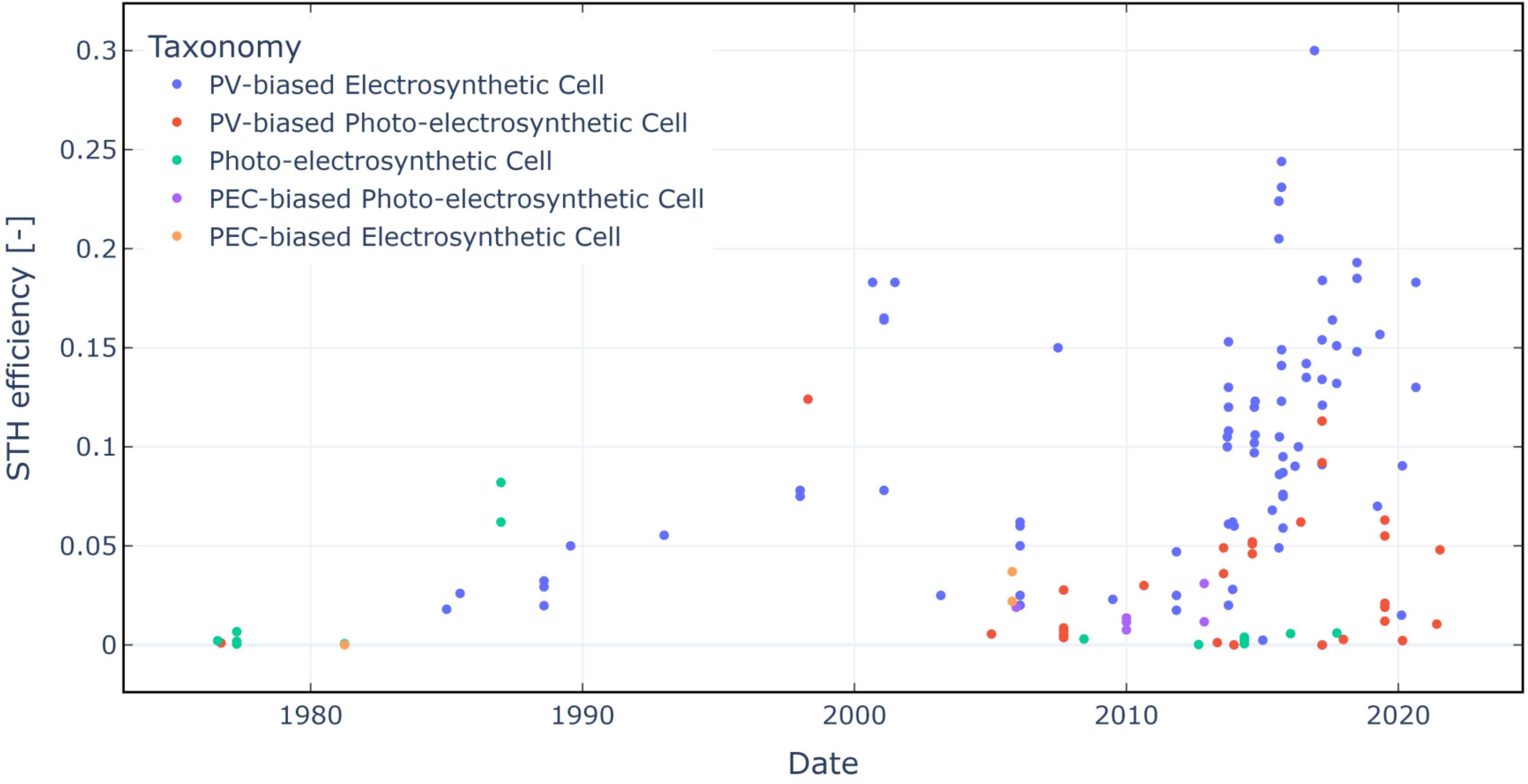




Haussener, LRESE

Solar-to-hydrogen vs. date published

SolarFuelsDB

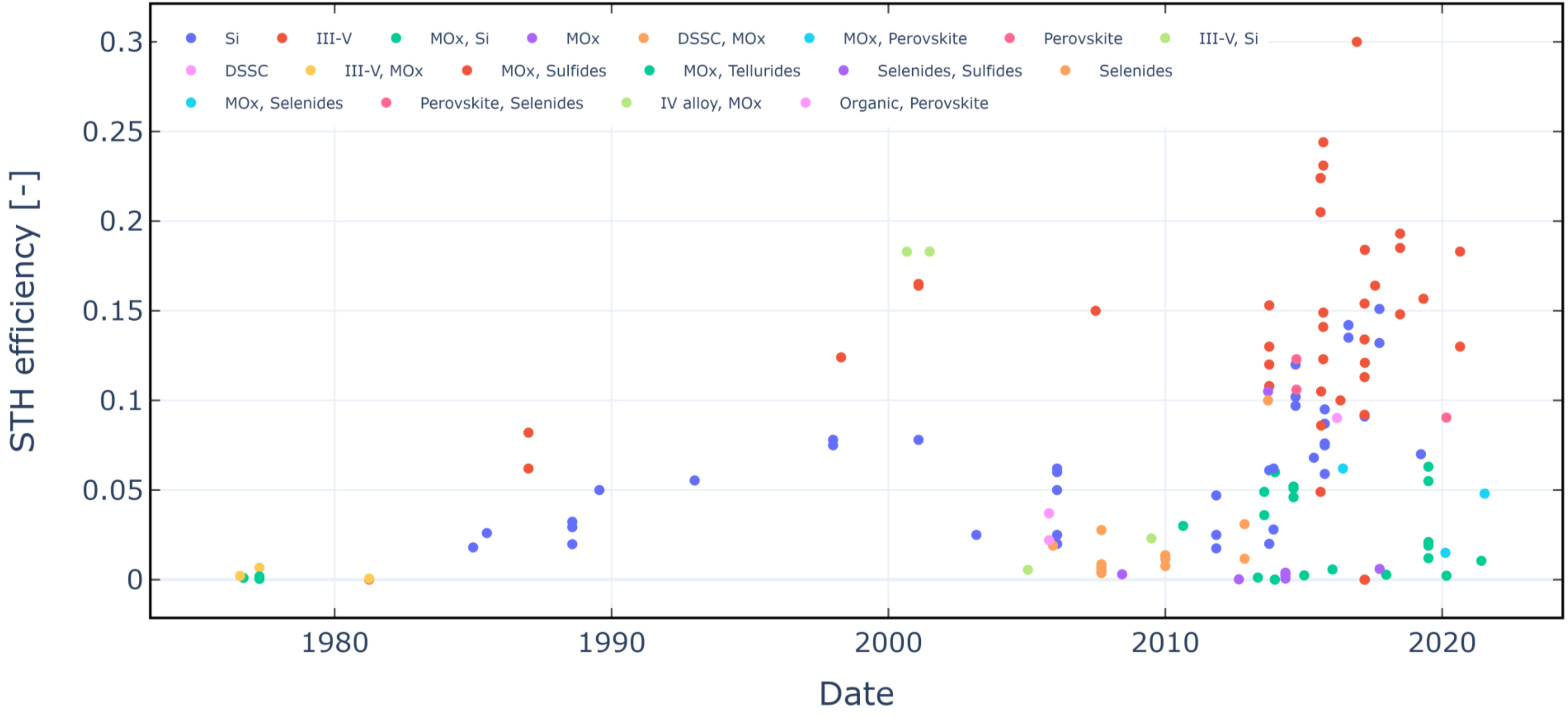


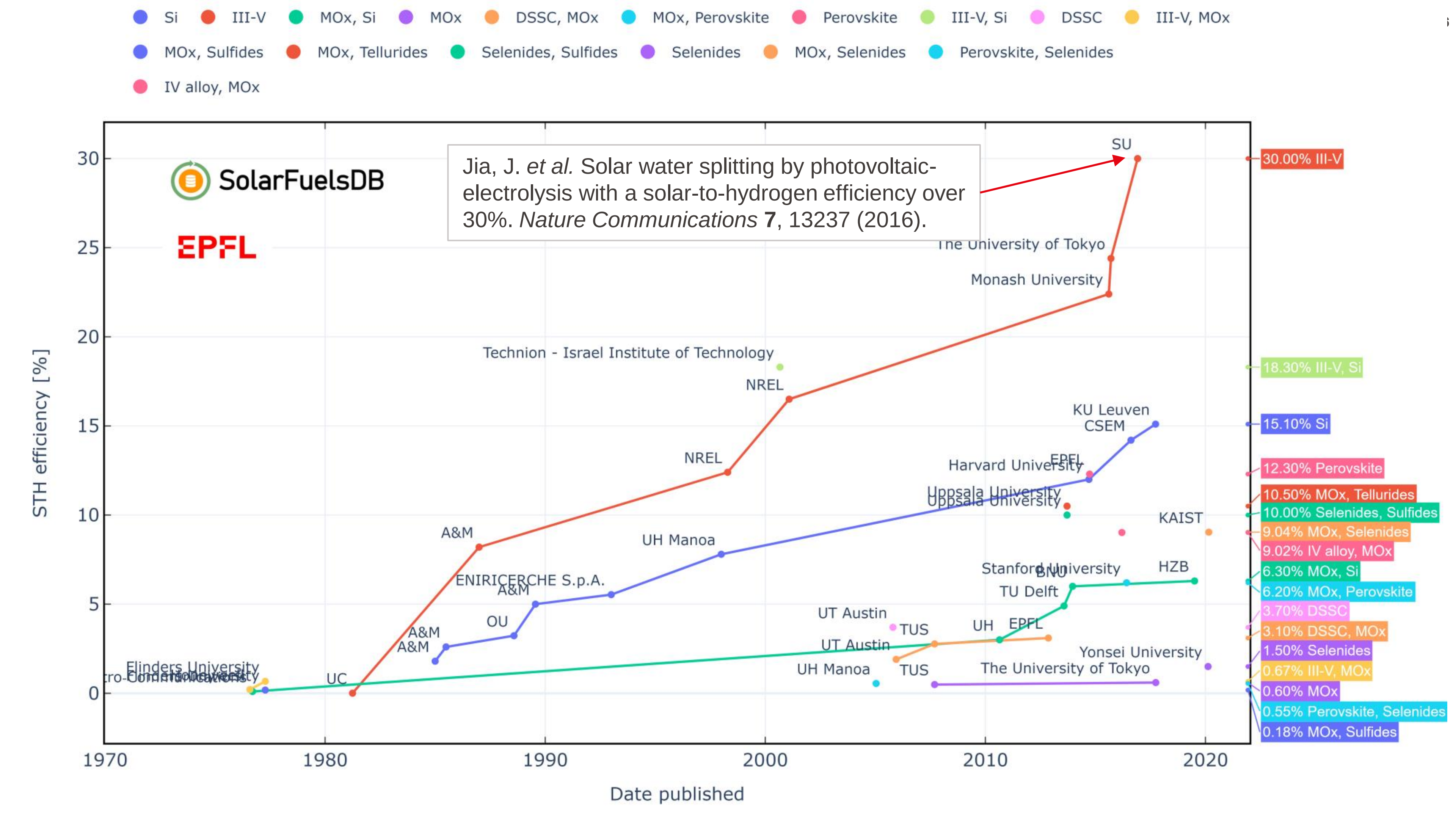
Taxonomy terms: Nielander, A. *et al.* A taxonomy for solar fuels generators. *Energy & Environmental Science* **8**, 16–25 (2015).

Solar-to-hydrogen vs. date published

SolarFuelsDB

Haussener, LRESE

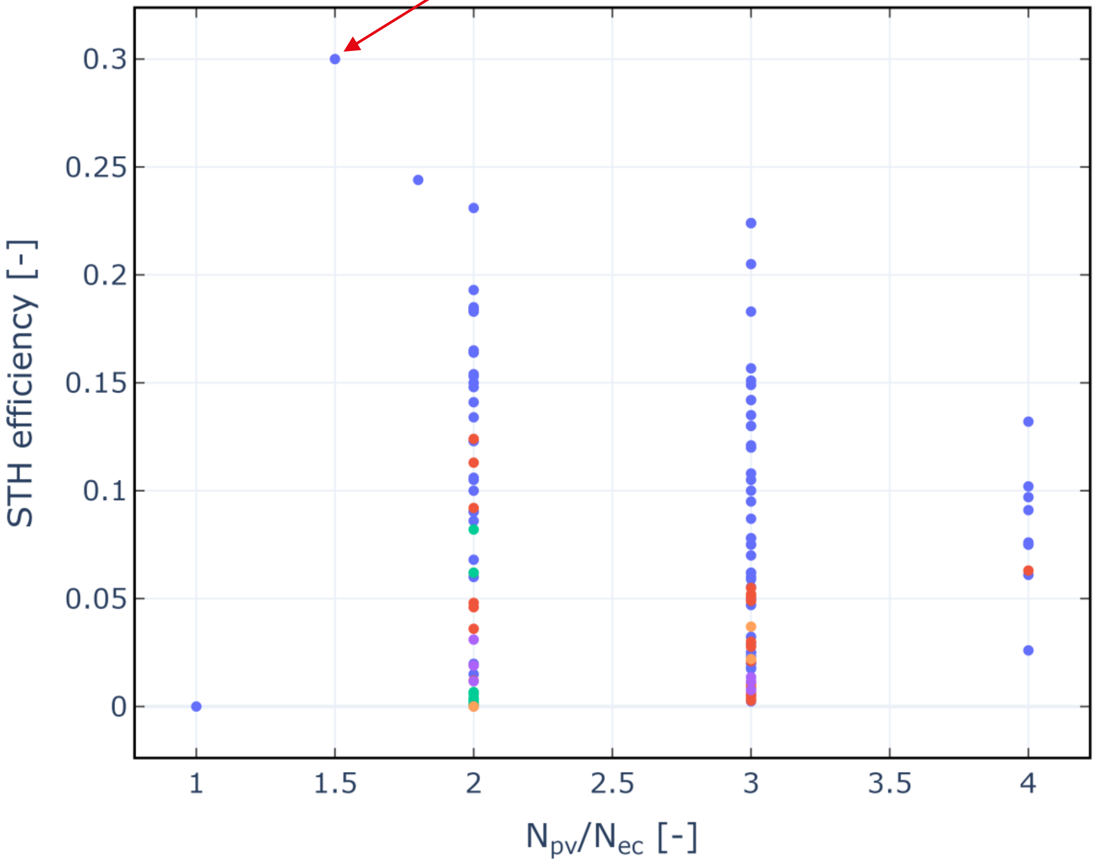


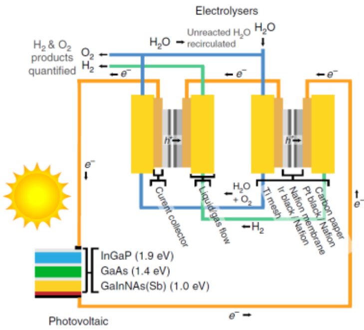


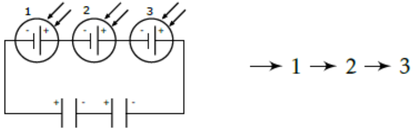
Si
III-V
MOx, Si
MOx
DSSC, MOx
MOx, Perovskite
Perovskite
III-V, Si
DSSC
III-V, MOx
MOx, Sulfides
MOx, Tellurides
Selenides, Sulfides
Selenides
MOx, Selenides
Perovskite, Selenides
IV alloy, MOx
SolarFuelsDB
EPFL
Jia, J. *et al.* Solar water splitting by photovoltaic-electrolysis with a solar-to-hydrogen efficiency over 30%. *Nature Communications* **7**, 13237 (2016).
SU
The University of Tokyo
Monash University
Technion - Israel Institute of Technology
NREL
NREL
KU Leuven
CSEM
Harvard University
EPFL
Uppsala University
Uppsala University
KAIST
UH Manoa
A&M
ENIRICERCHE S.p.A.
A&M
Stanford University
BNU
HZB
TU Delft
OU
UT Austin
TUS
UH
EPFL
A&M
A&M
UT Austin
Yonsei University
UH Manoa
TUS
The University of Tokyo
Flinders University
UC
30.00% III-V
18.30% III-V, Si
15.10% Si
12.30% Perovskite
10.50% MOx, Tellurides
10.00% Selenides, Sulfides
9.04% MOx, Selenides
9.02% IV alloy, MOx
6.30% MOx, Si
6.20% MOx, Perovskite
3.70% DSSC
3.10% DSSC, MOx
1.50% Selenides
0.67% III-V, MOx
0.60% MOx
0.55% Perovskite, Selenides
0.18% MOx, Sulfides
STH efficiency [%]
30
25
20
15
10
5
0
1970
1980
1990
2000
2010
2020
Date published

Matching Voltages

Jia, J. *et al.* Solar water splitting by photovoltaic-electrolysis with a solar-to-hydrogen efficiency over 30%. *Nature Communications* **7**, 13237 (2016).

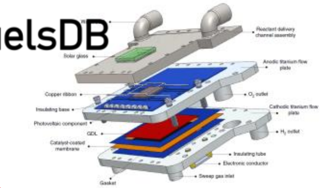




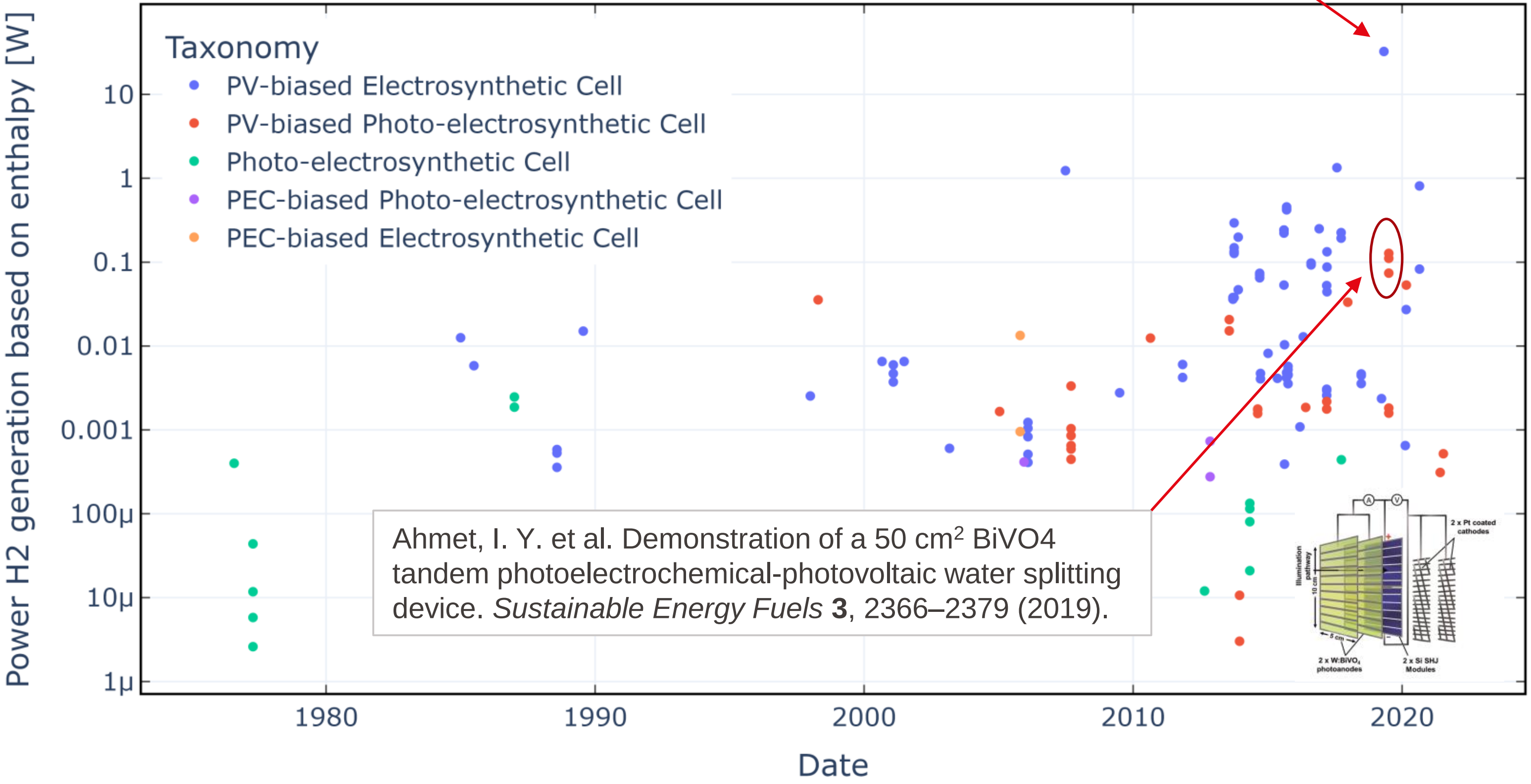


Preliminary trends – Size of devices

SolarFuelsDB

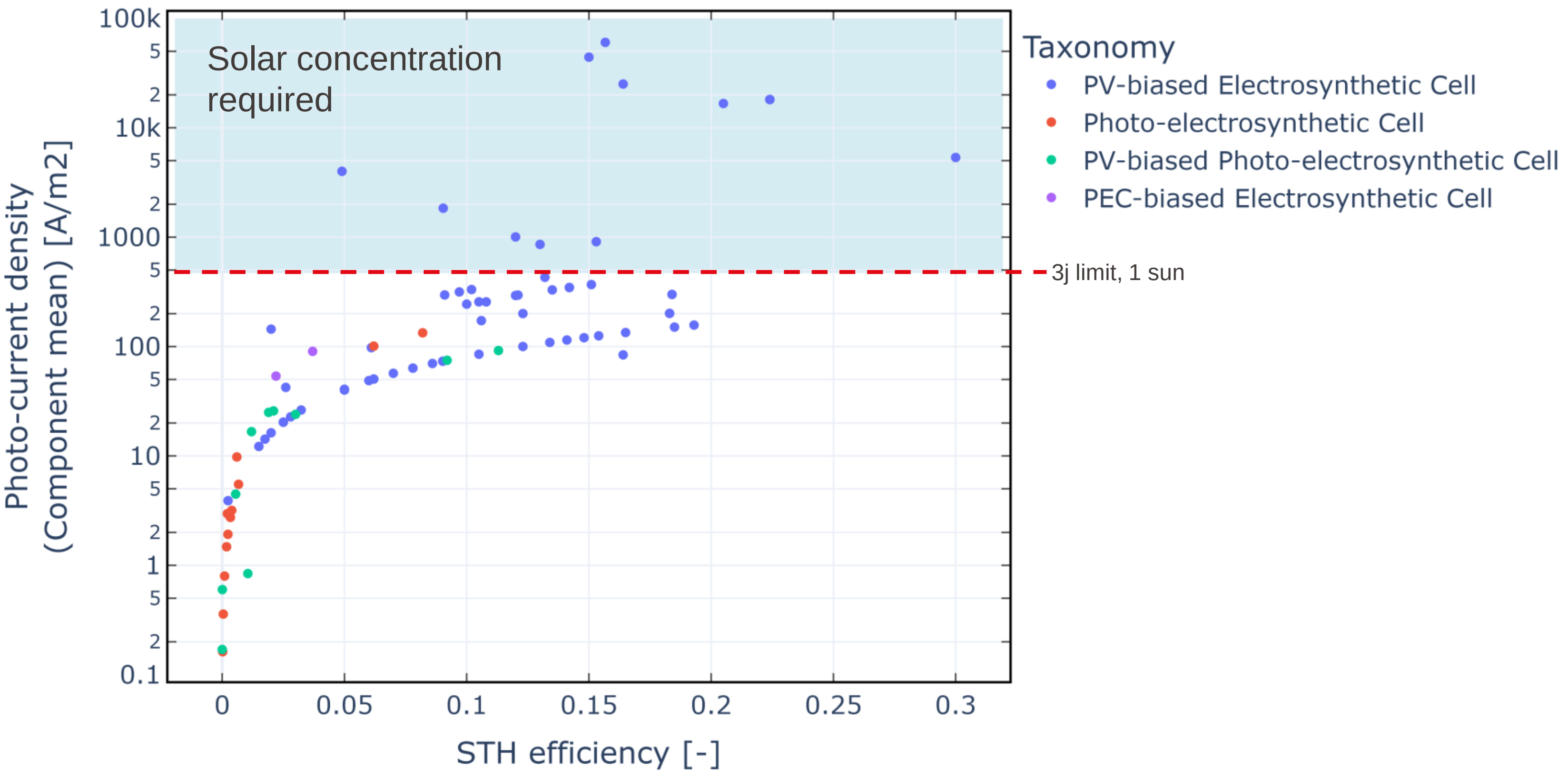


Tembhurne, S., et al. A thermally synergistic photo-electrochemical hydrogen generator operating under concentrated solar irradiation. *Nature Energy* **4**, 399–407 (2019).



Ahmet, I. Y. et al. Demonstration of a 50 cm^2 $BiVO_4$ tandem photoelectrochemical-photovoltaic water splitting device. *Sustainable Energy Fuels* **3**, 2366–2379 (2019).

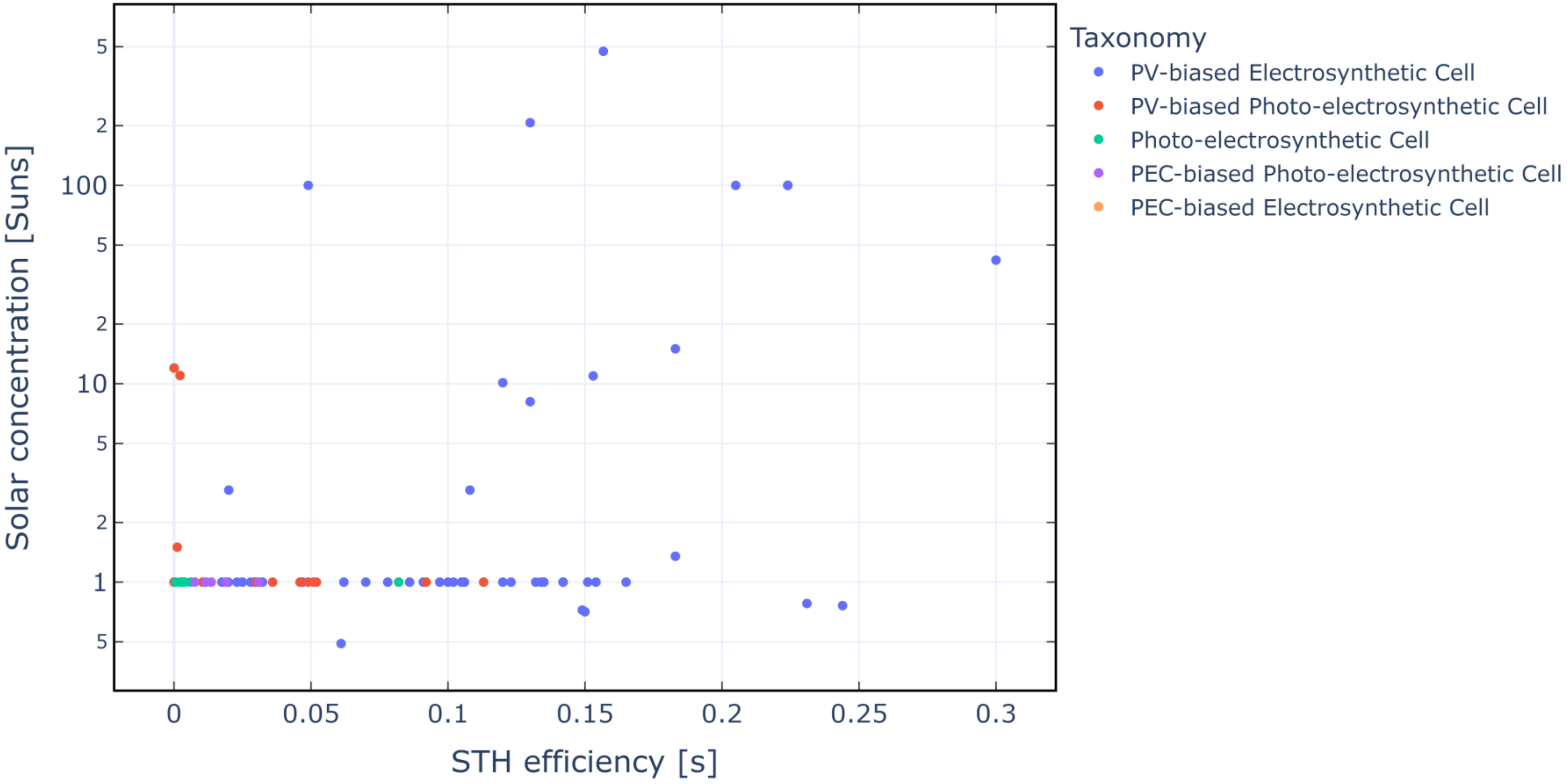
Photo-current density



SolarFuelsDB

Haussener, LRESE

Solar concentration



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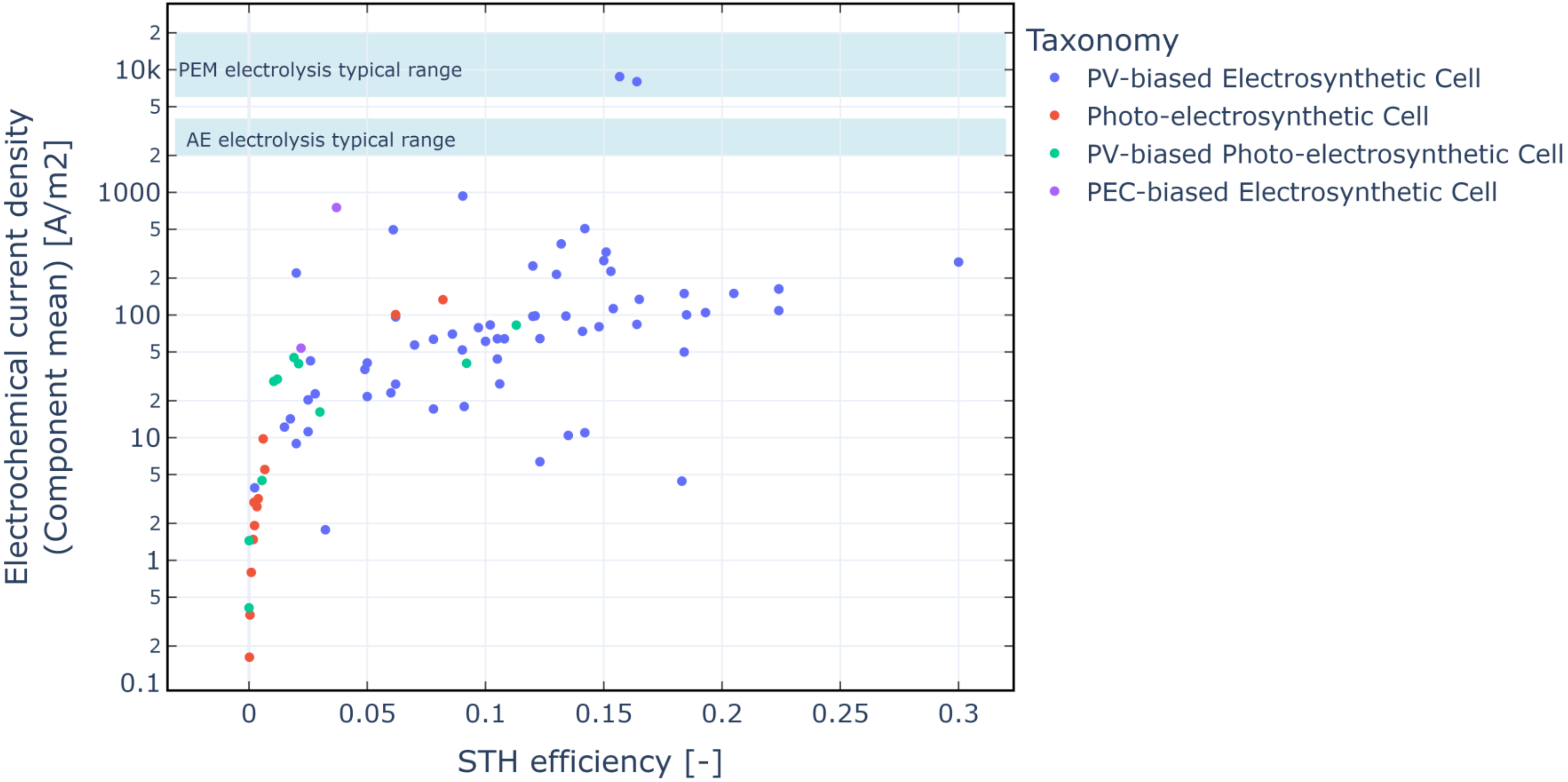
Electrochemical current density

SolarFuelsDB



Haussener, LRESE

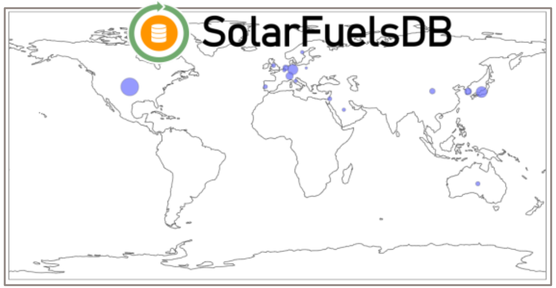
Total experiment time vs. date published

SolarFuelsDB

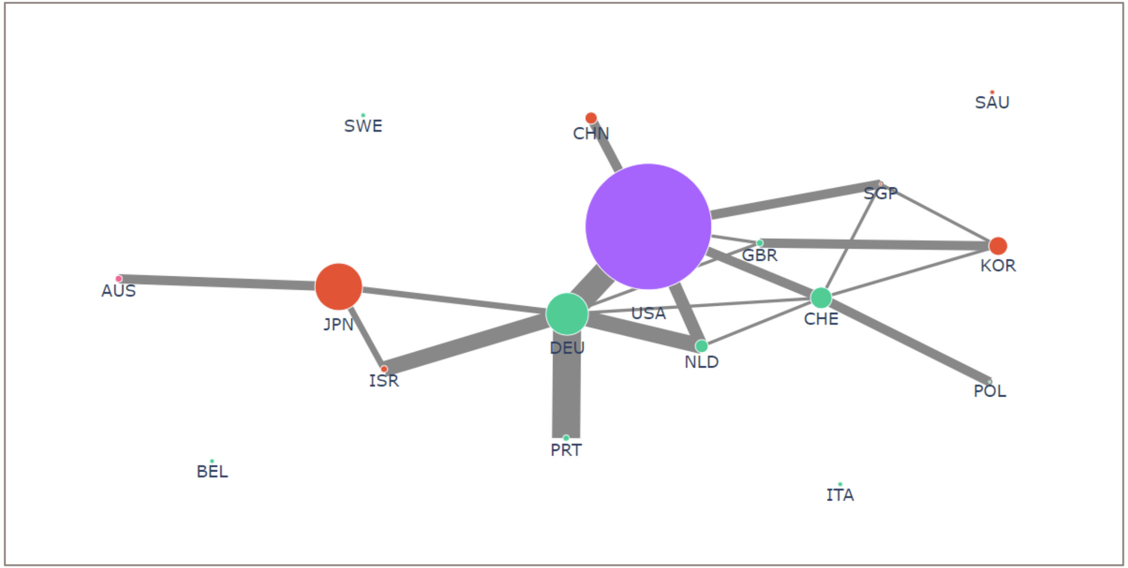
Bibliographic analysis

USA - United States of America
ISR - Israel
DEU - Germany
ITA - Italy
NLD - Netherlands
CHE - Switzerland
GBR – UK of Great Britain
JPN - Japan
KOR - Korea
PRT - Portugal
SWE - Sweden
CHN - China
POL - Poland
SAU - Saudi Arabia
AUS - Australia
BEL - Belgium
SGP - Singapore

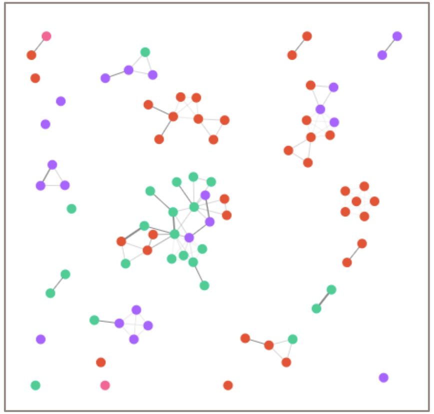
Africa
Asia
Europe
North America
South America
Australia



Bubble charts on map – number of articles



Country-based “social network”



Institution-based “social network”

Activities in Europe - Consortia

- Canary Islands: PV/wind/ocean-EC, water desalination for hydrogen in transportation, MW-scale, 9 partner — SEAFUEL
- PEC for water and CO_2 splitting, 13 partner — a-leaf
- PEC for oxo-chemical production, 14 partner — SunCO2Chem
- PEC for hydrogen, 1m^2 scaled version, 5 partner — FOTO H2
- PEC for CO_2 reduction without OER, 14 partner — DECADE
- PEC+PC+EC for water and CO_2 splitting, 14 partners — FLOW PHOTO CHEM
- Solar-driven chemistry, 1 billion flagship in preparation — SUN ERGY
- PEC and PC for water splitting and beyond, 14 partners — SOLAR 2 CHEM
- PEC and thermochemistry for storable fuels, 9 partner — SUN to X: Solar Energy for Carbon-Free Liquid Fuel

Activities in Europe – Three Selected Activities

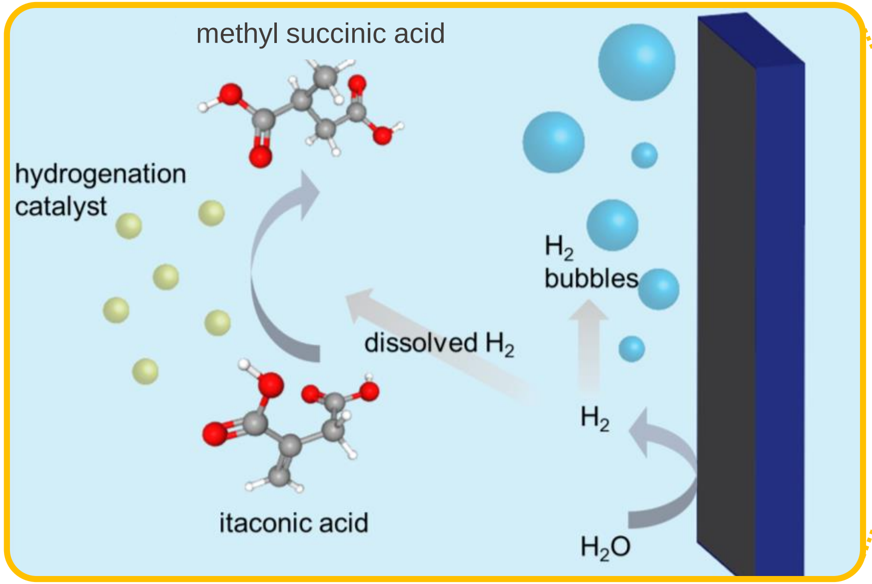
HZB: Keisuke Obata, Xinyi Zhang, Babu Radhakrishnan, Ibbi Y. Ahmet, Roel van de Krol, Fatwa Abdi

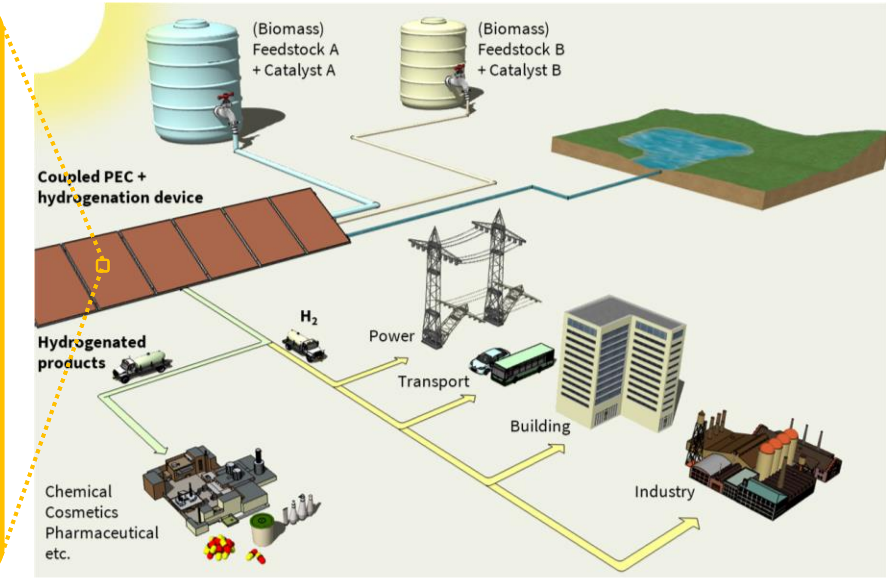
TU Berlin: Michael Schwarze, Tabea A. Thiel, Reinhard Schomäcker

Funding:

- Deutsche Forschungsgemeinschaft (DFG), Excellence Cluster "UniSysCat"
- Helmholtz Association, Excellence Network "ExNet-0024"
- Helmholtz Energy Materials Foundry (HEMF)

Coupled hydrogen production and hydrogenation

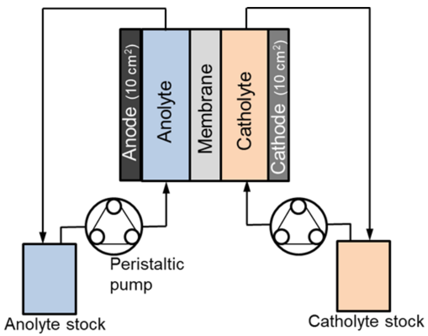




- Hydrogen produced by PEC is used *in situ* to hydrogenate feedstock to valuable chemicals and decrease LCOH
- Case study: hydrogenation of itaconic acid (IA) to methyl succinic acid (MSA) with homogeneous Rh-based catalyst
- Rate of H_2 production by PEC matches well with hydrogenation rate ⟶ ideal for coupling these processes
- Heat integration enhances the hydrogenation kinetics
- Flexible to switch to other hydrogenation reactions by simply exchanging catholyte (contains catalyst + feedstock)

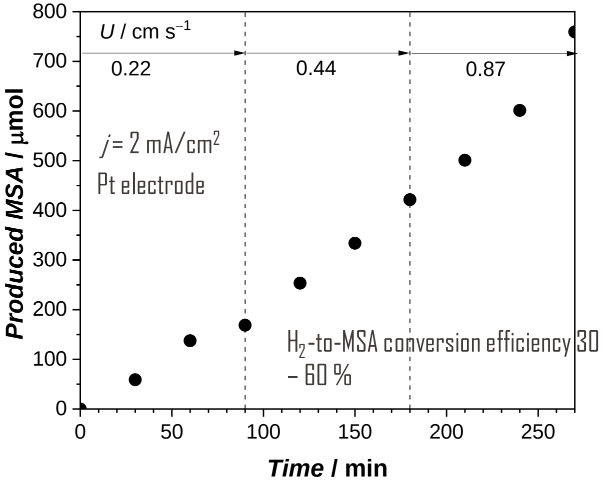
K. Obata et al. ***submitted***

Demonstration of coupled reactions



phosphate buffer (KP_i)

phosphate buffer
+ itaconic acid
+ Rh catalyst



	Lifetime / years	H_2-to-MSA conversion / %	Annual net energy balance / MJ m^{-2} $year^{-1}$
Solar water splitting	5	-	−631
	10	-	−248
	28	**-**	**0**
Solar coupled hydrogen-ation	**5**	**12**	**0**
	5	60	2,633
	5	100	4,809

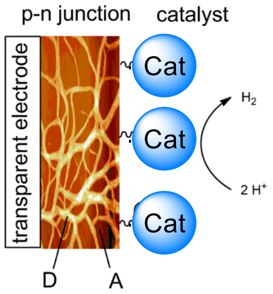
Assumptions: STH = 3%, 3.4 kWh/day/m²

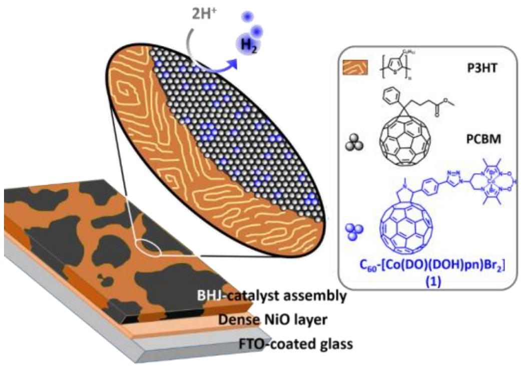
- H_2-to-MSA conversion efficiency as high as 60% demonstrated using photo-electrochemically produced H_2
- Coupled approach does not show any deactivation of MSA production, whereas direct electrochemical hydrogenation terminates after ~120 min.
- Net energy analysis shows the benefit of coupling hydrogenation process to PEC: energy payback time decreases from 28 to 5 years (assuming STH = 3% and modest H_2-to-MSA conversion efficiency of 12%)

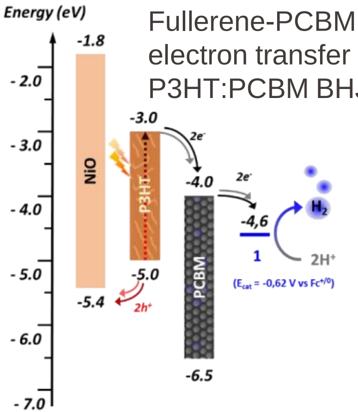
K. Obata et al. ***submitted***

Hybrid photocathodes for H_2 evolution: Optimizing the interfaces

Haussener, LRESE

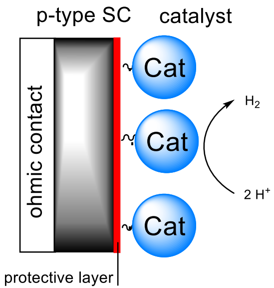


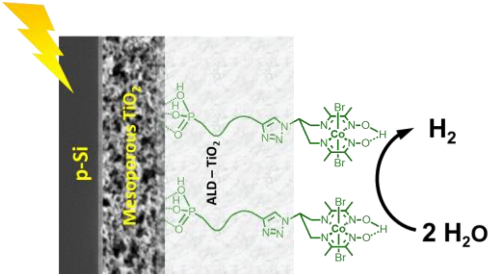


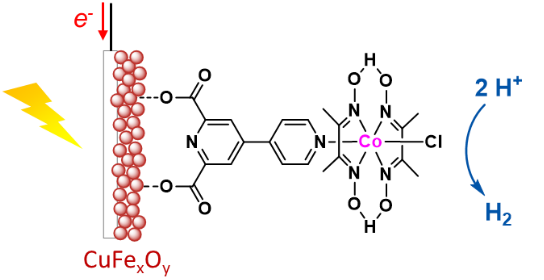


Fullerene-PCBM interaction favors electron transfer from the P3HT:PCBM BHJ and the catalyst

Artero et al. *Chem Sci.* ***2022***







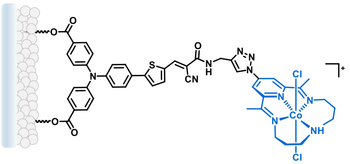
Artero et al. Chem. Sci. **2019**

Artero et al. Green Chem. **2020**

TiO_2 ALD coating passivates the inorganic semiconductor support and stabilizes the grafting of the catalyst onto its surface

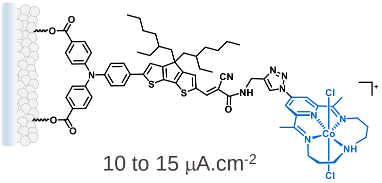
Dye-sensitized photocathodes for H_2 evolution and CO_2 valorization

Catalyst engineering



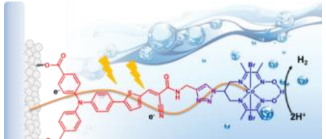
10 to 15 µA.cm^{-2}
96 ± 14 nmol$_{H2}$.cm^{-2}
65 ± 17 % F.E.
13 ± 1 TONs

Dye engineering



10 to 15 µA.cm^{-2}
187 ± 25 nmol$_{H2}$.cm^{-2}
66 ± 7 % F.E.
21 ± 6 TONs

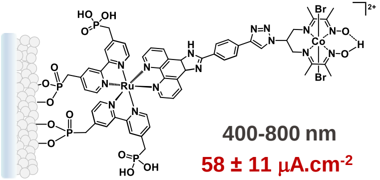
Chavarot-Kerlidou, Artero et al., ACS Catal. **2021**



Kaeffer, JACS **2016**

10 to 15 µA.cm^{-2}
10 to 30 nmol$_{H2}$.cm^{-2}
10 % F.E.
< 3 TONs

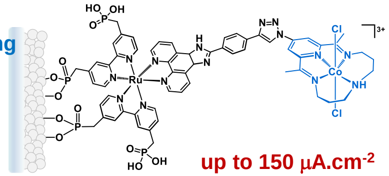
Dye engineering



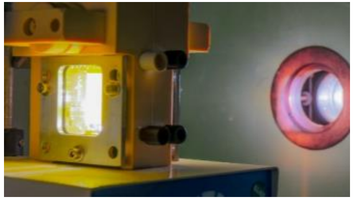
400-800 nm	Sim. AM1.5G
58 ± 11 µA.cm^{-2}	**84 ± 7 µA.cm^{-2}**
28 ± 2 nmol$_{H2}$.cm^{-2}	60 ± 9 nmol$_{H2}$.cm^{-2}
24 ± 5 % F.E.	26 ± 7 % F.E.
5 ± 1 TONs	13 ± 2 TONs

Chavarot-Kerlidou, Artero et al., ACS Appl. Mater. Interfaces **2021**

Catalyst engineering



up to 150 µA.cm^{-2}
200 to 300 nmol$_{H2}$.cm^{-2}
50 % F.E.
100 to 150 TONs



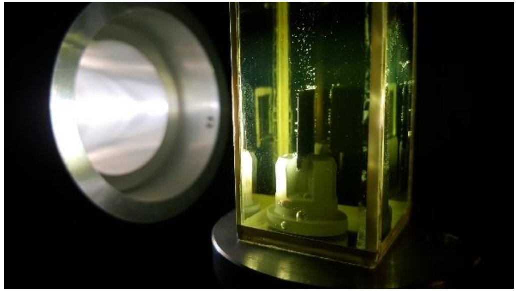
Chavarot-Kerlidou, Artero et al., unpublished

Integrated with $BiVO_4$ photoanode in a unassisted PEC device for water splitting (STH = 4.6 x 10^{-3}%) and CO_2-to-CO conversion (STF = 1.3 x 10^{-2}%)

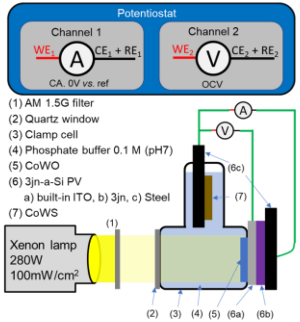
Self assembly and mononotoring of an artificial leaf

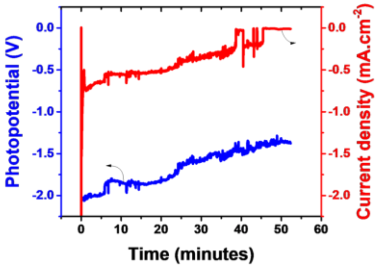
Nocera and coll, *Science* **2011**

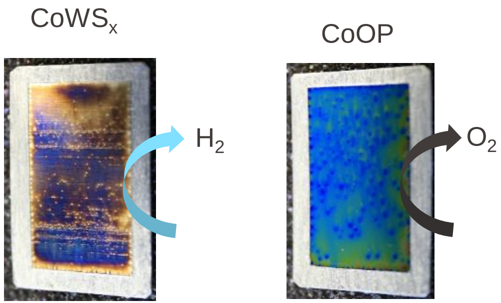
Elaboration of a single $[Co\{WS_4\}_2]^{2-}$ precursor for simultaneaous photodeposition of both catalysts



Tran, Artero et al., unpublished

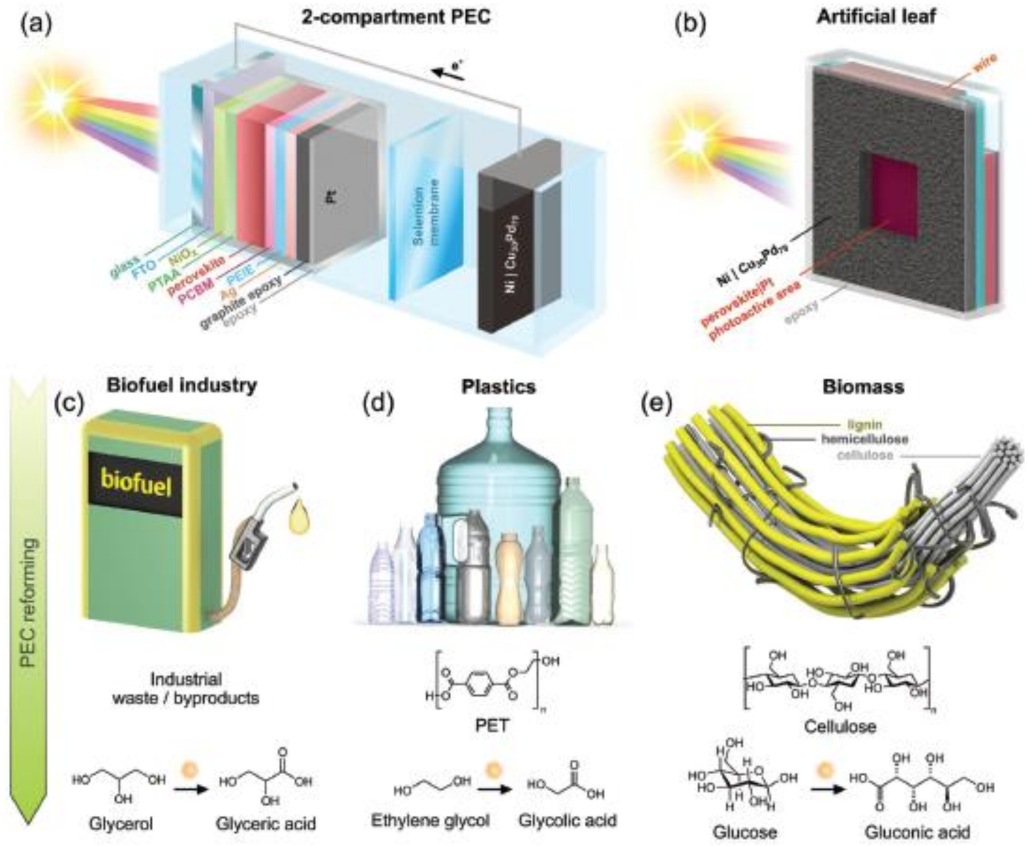


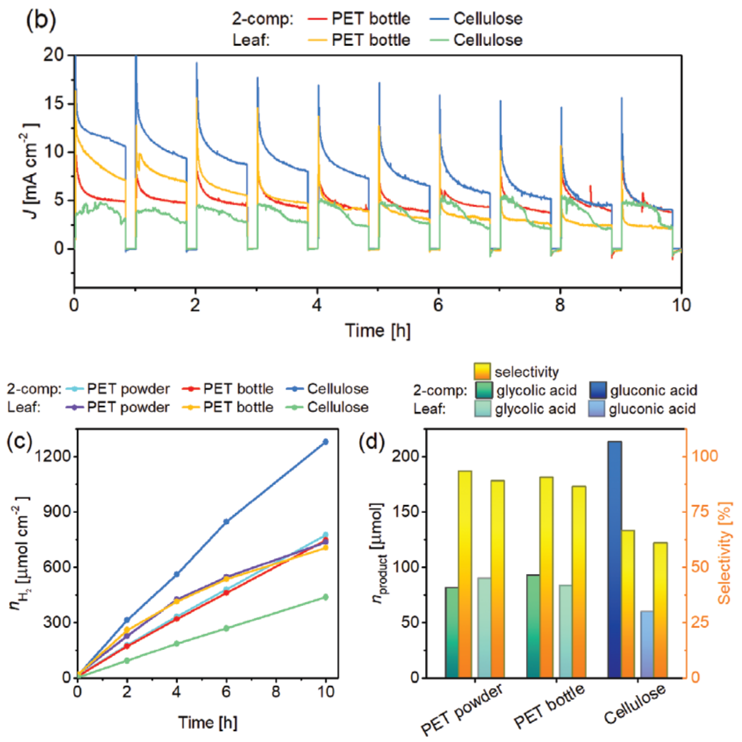




Performances : 2-3% STH
Simplified fabrication with deposition of 2 distinct catalysts from the same solution
Monitoring with bipotentiostat allowed to gain insights into the operational conditions

PEC H2 production coupled to oxidation of solid waste streams





Bhattacharjee et al., Adv. Functional Materials, 2021

Acknowledgements

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