Solar Energy Conversion Devices and Plants

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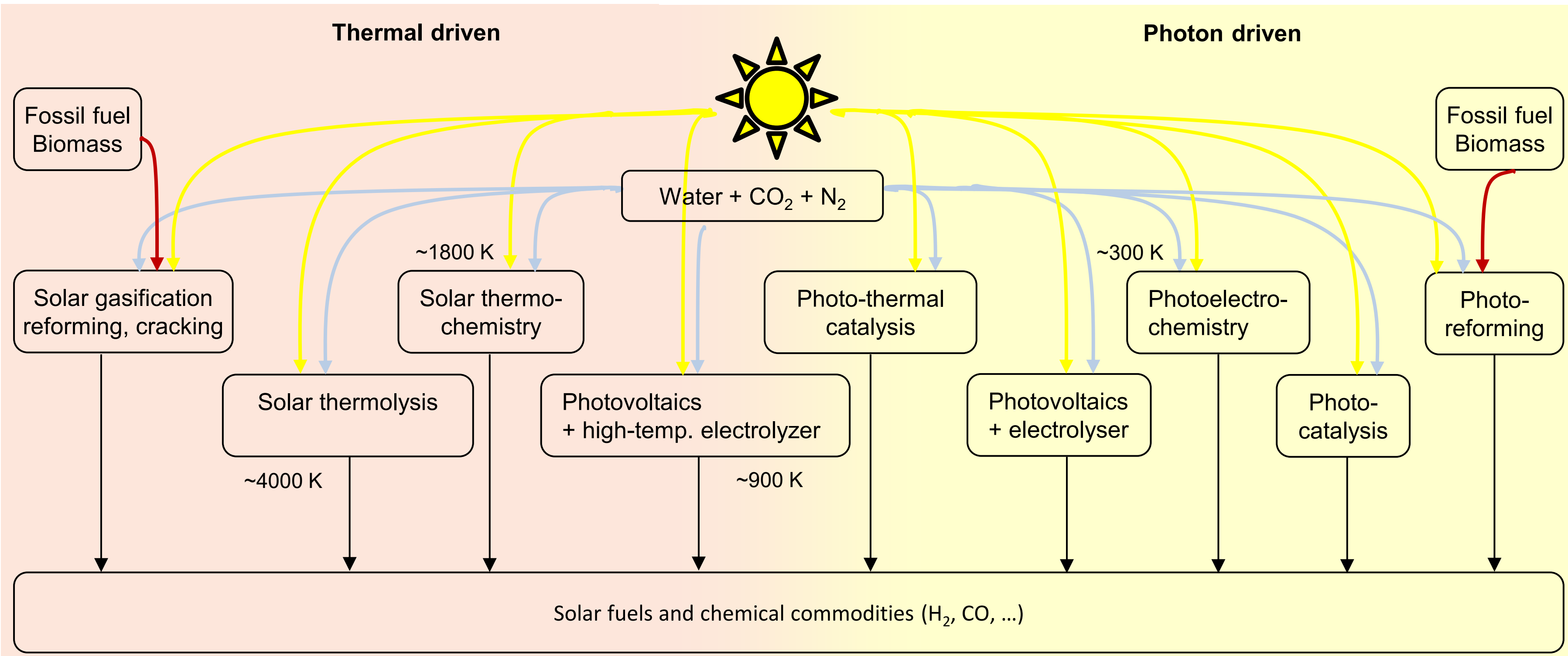
Outline

- Photo-driven electrochemistry
  - Working principle of photoelectrochemical device
  - High-temperature photoelectrochemistry
  - PEC demonstrations and scaling
  - Photocatalytic approaches
  - Beyond water splitting

Solar Fuels

- Pathways

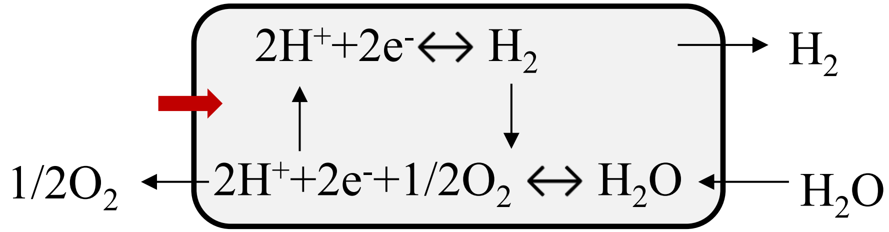


High-temperatures → Concentration (only direct sunlight)

Photon-energy → not full solar spectrum

Photoelectrochemistry

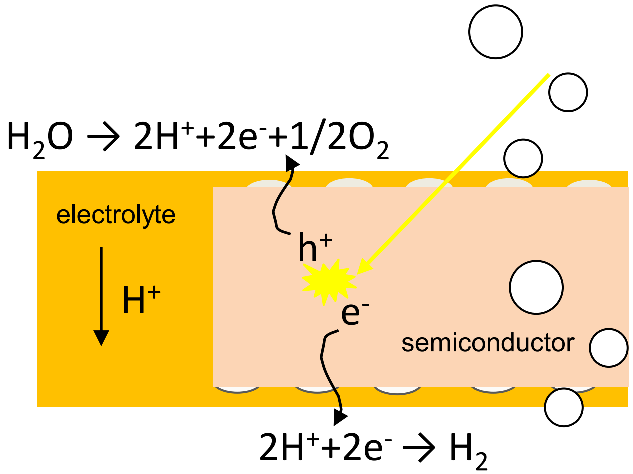
- Photoelectrochemical processes
  - Solar energy is used as photon energy for the internal production of charge, which is separated at the solid-liquid junction
  - Multi-step water-splitting reactions (E_0=1.23 V):



  - Works at room temperature
  - Spectral distribution of solar radiation important

Photoelectrochemistry

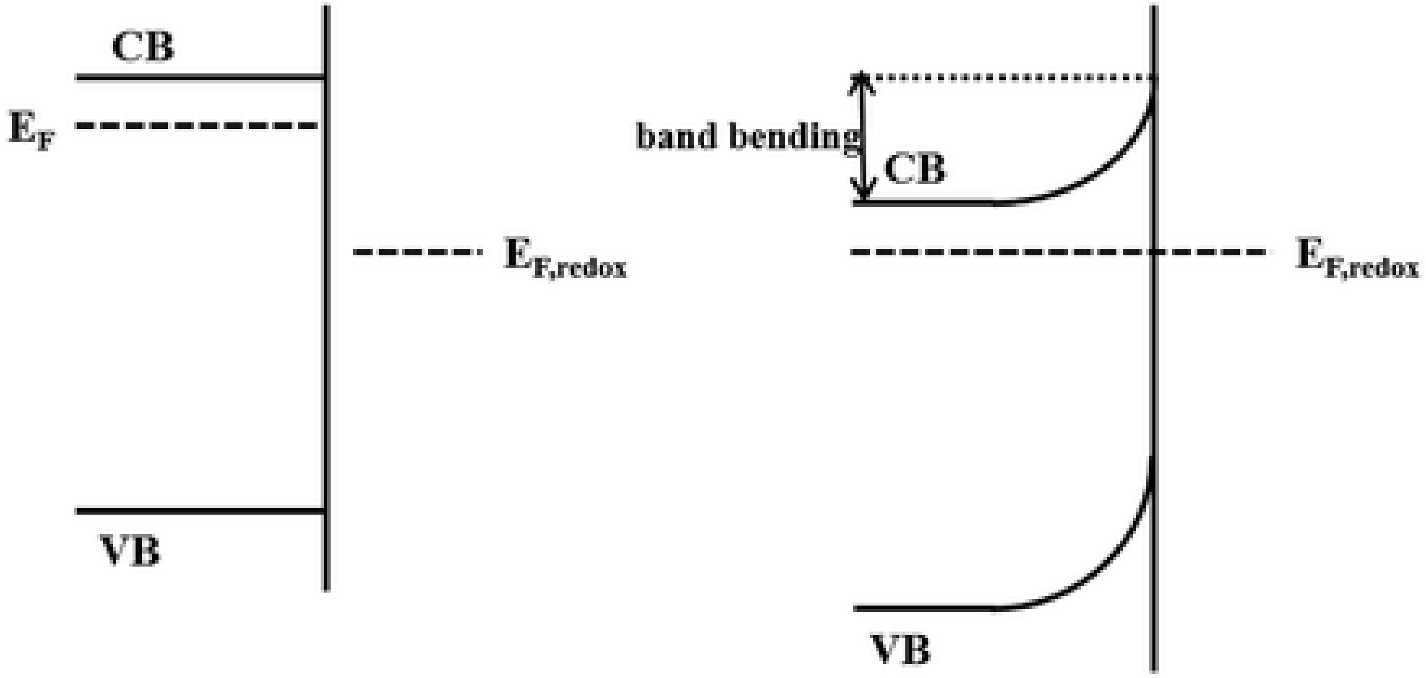
- Photoelectrochemical processes
  - Processes:
    - Solar absorption
    - Electron-hole generation
    - Use electron and holes at liquid-solid interface
    - Ionic transport



Photoelectrochemistry

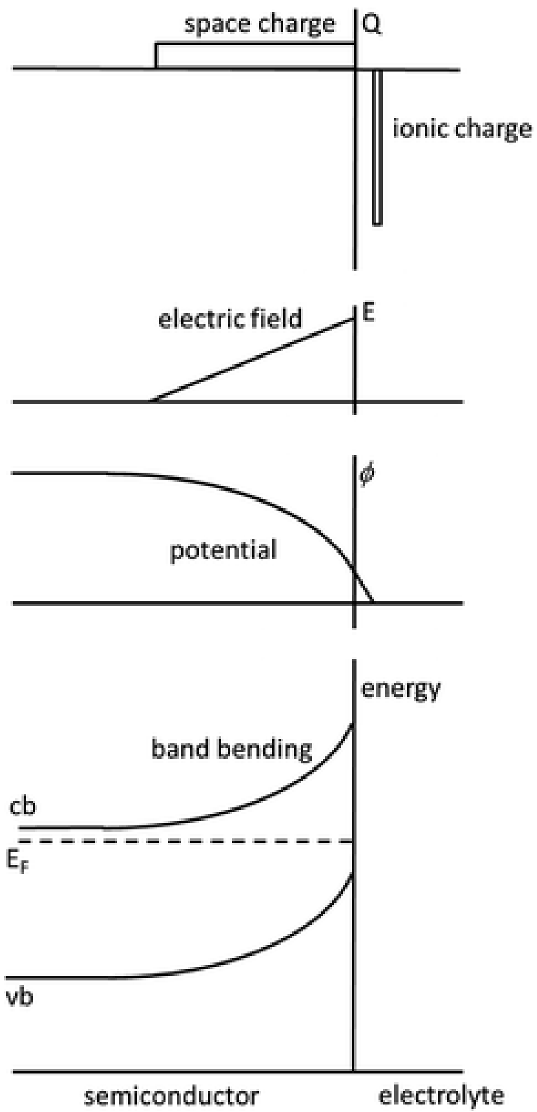
- Working principle (in dark):

  n-doped semiconductor



Photoelectrochemistry

- Working principle (in dark): n-doped semiconductor



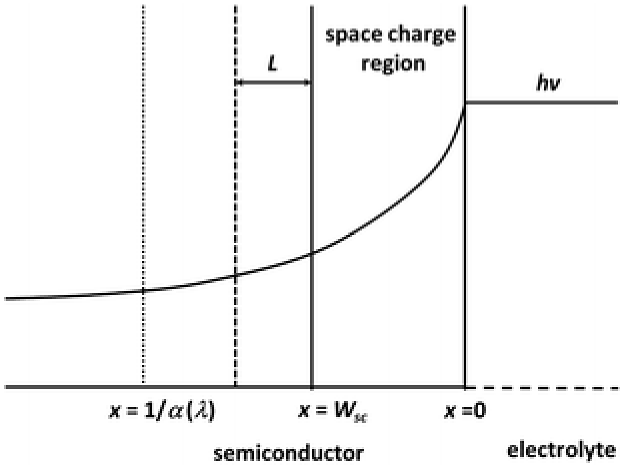
Space charge layer thickness:

$$W_{sc} = \sqrt{\frac{2\Delta\phi_{sc}\varepsilon\varepsilon_0}{qN_d}}$$

Photoelectrochemistry

- Working principle (under illumination):

  n-doped semiconductor

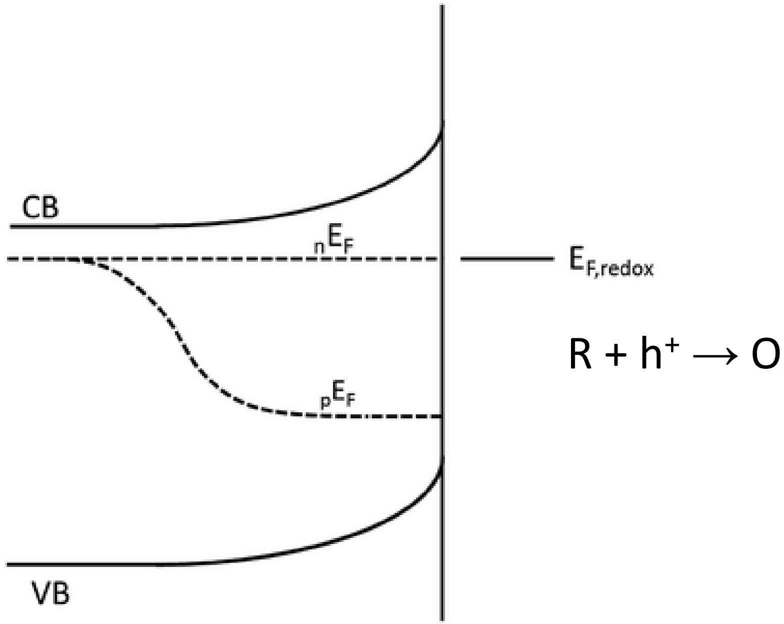


Quasi Fermi level for electron

$$ {}_{\mathrm{n}}E_{\mathrm{F}} = E_{\mathrm{c}} + k_{\mathrm{B}}T\ln\frac{n}{N_{\mathrm{c}}} $$

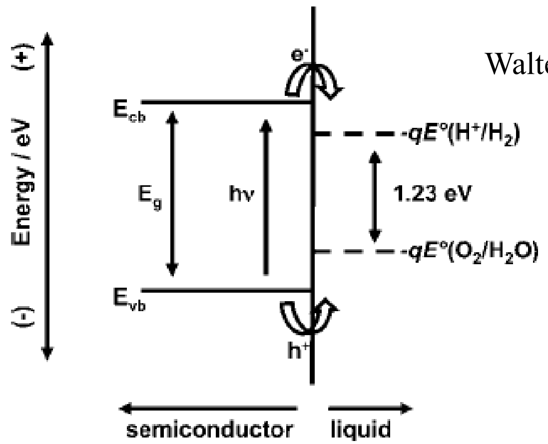
and holes

$$ {}_{\mathrm{p}}E_{\mathrm{F}} = E_{\mathrm{v}} - k_{\mathrm{B}}T\ln\frac{p}{N_{\mathrm{v}}} $$



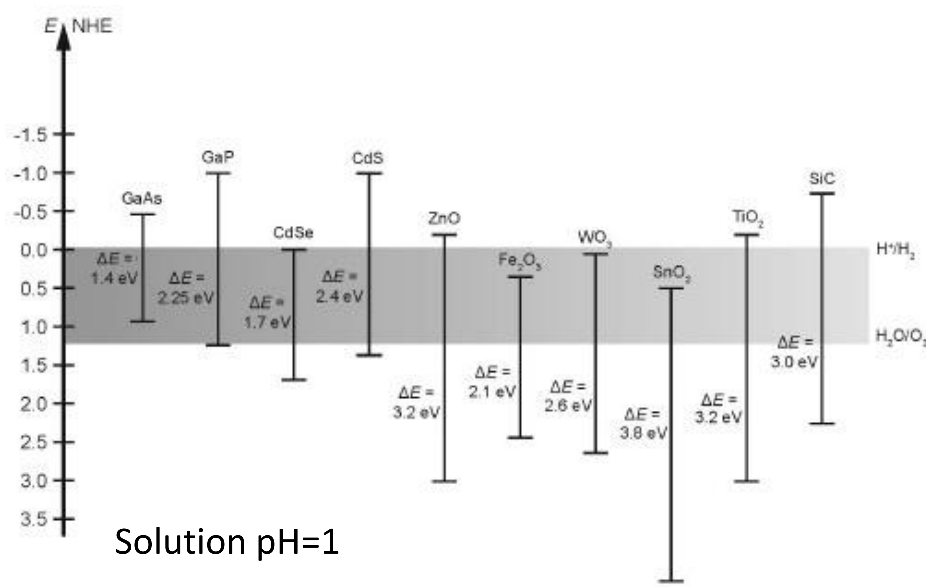
Photoelectrochemistry

- Band gap and band position of photoelectrode material must match reaction potentials:



Walter et al., 2006

- Example materials:

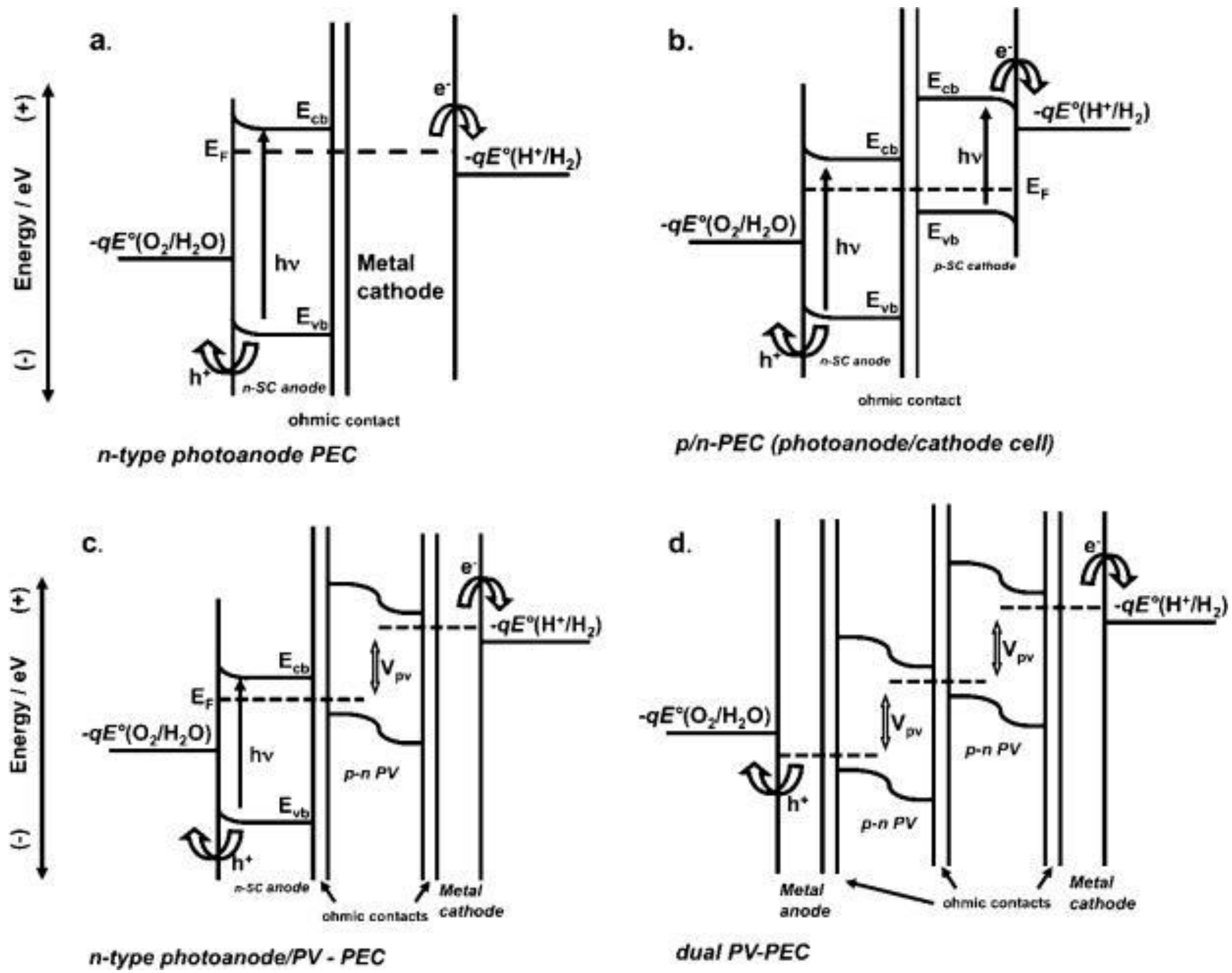


Photoelectrochemistry

- Stringent material requirements:
  - band gap size
  - suitable band edge position
  - high chemical stability in the dark and under illumination, as well as
    under highly acidic or base conditions
  - efficient charge transport in the semiconductor
  - selective and efficient electrochemical reactions
  - earth-abundance and low costs

- Various possible architectures that relax requirements:

Walter et al., 2006



Photoelectrochemistry

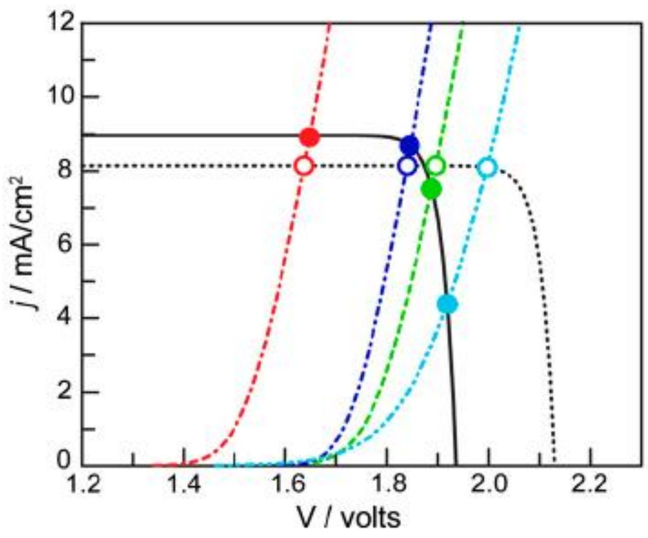
- Calculations:
  - Photoactive material(s) will show diode-like current-potential behavior:

$$i = i_L - i_0\left(\exp\left(\frac{qV}{kT}\right)-1\right)$$

  - Electrochemical system shows losses:
    - Reaction overpotentials
    - Ohmic losses
    - Concentration losses

$$E = E_0 + \eta_a + \eta_c + iR_{sol} + E_{mem} + E_{conc} > E_0$$

  - Electrochemical load curve will show electrolyzer like load curve
  - Intersection between both is operating point



Surendranath et al., 2012

Photoelectrochemistry

- Calculations:
  - Electrochemical system shows losses:
    - Reaction overpotentials
      - E.g. via Tafel equations:

Tafel slope

$$\eta_{\mathrm{a}} = a_1 \log\left(\frac{i}{i_{0\mathrm{a}}}\right) \qquad \eta_{\mathrm{c}} = a_2 \log\left(\frac{i}{i_{0\mathrm{c}}}\right)$$

Exchange current density

      - Or Buttler-Volmer:

$$i_{\mathrm{R}} = i_{0\mathrm{a/c}}\left[\exp\left(\frac{\alpha_{\mathrm{a}} F\left(\Phi_{\mathrm{s}} - \Phi_{\mathrm{l}} - E_0\right)}{RT}\right) - \exp\left(\frac{\alpha_{\mathrm{c}} F\left(\Phi_{\mathrm{s}} - \Phi_{\mathrm{l}} - E_0\right)}{RT}\right)\right]$$

    - Ohmic losses account for resistances in electrolyte, membrane, and solid conductor:

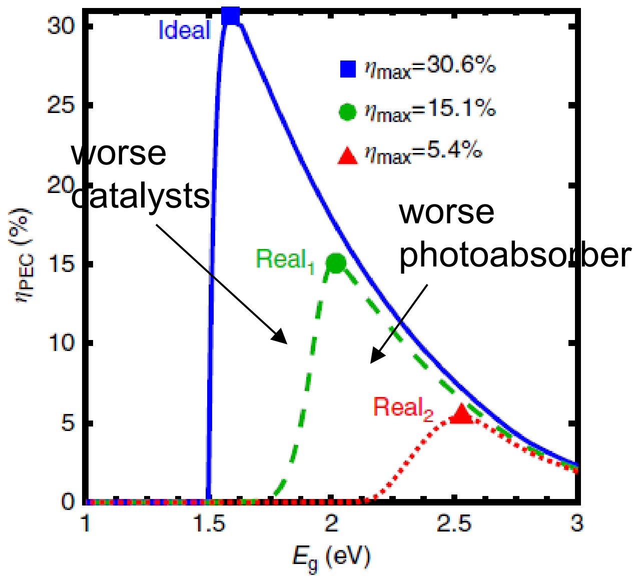
$$\Delta V_{\mathrm{ohm}} = i \rho_{\mathrm{sol}} l$$

Characteristic ion and electron path length

resistivity

Theoretical efficiency limits

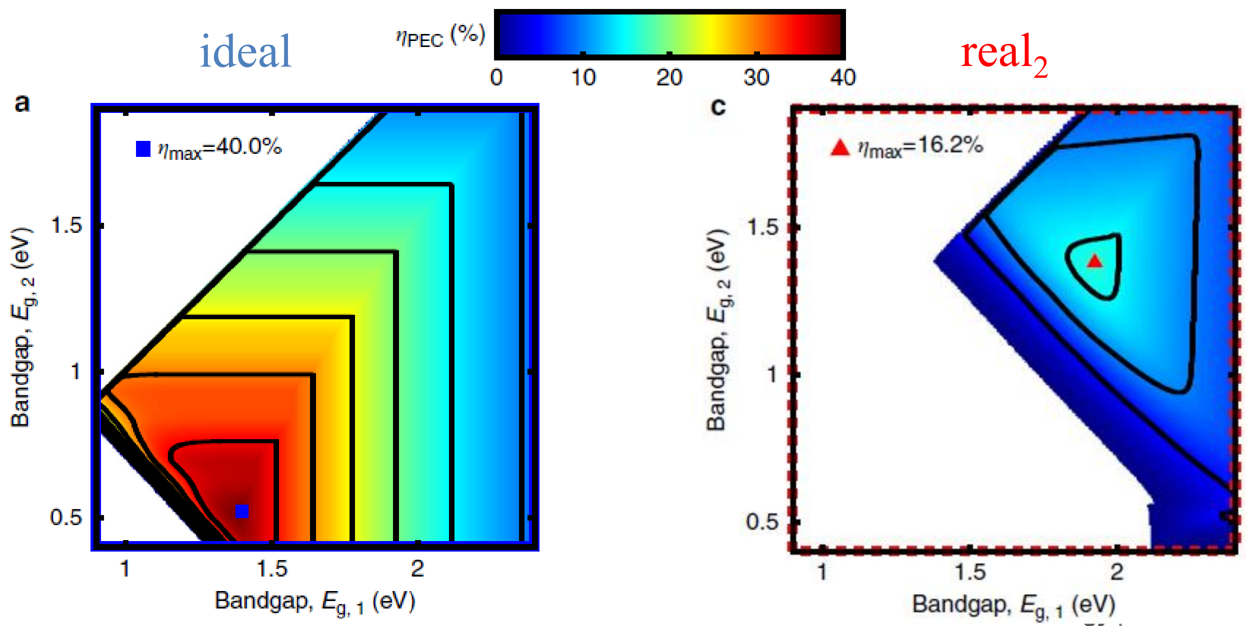
– Single cell



Fountaine et al., Nature Com., 7, 2016

Rocheleau et al., E&F, 12, 1998
Winkler et al., PNAS, 110, 2013
Hu et al., EES, 6, 2013
Seitz et al., ChemSusChem, 7, 2014
Haussener et al., EES, 6, 2018

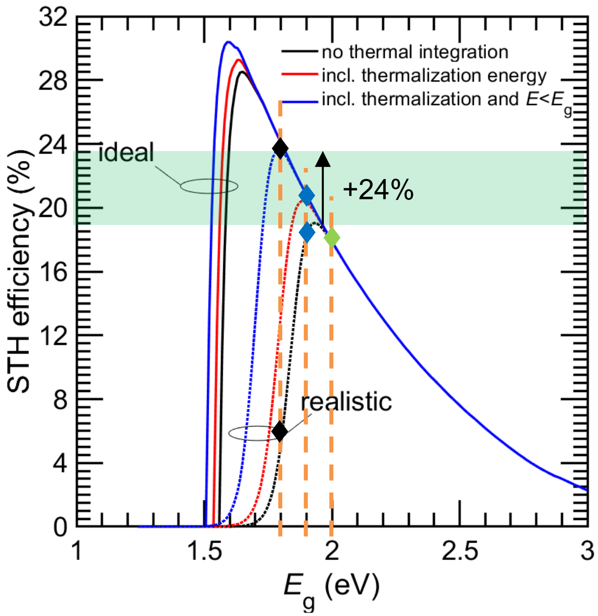
– Dual cell

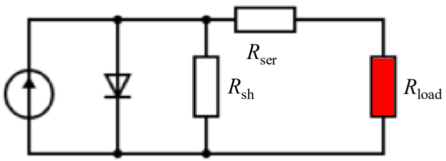


Thermal Integration

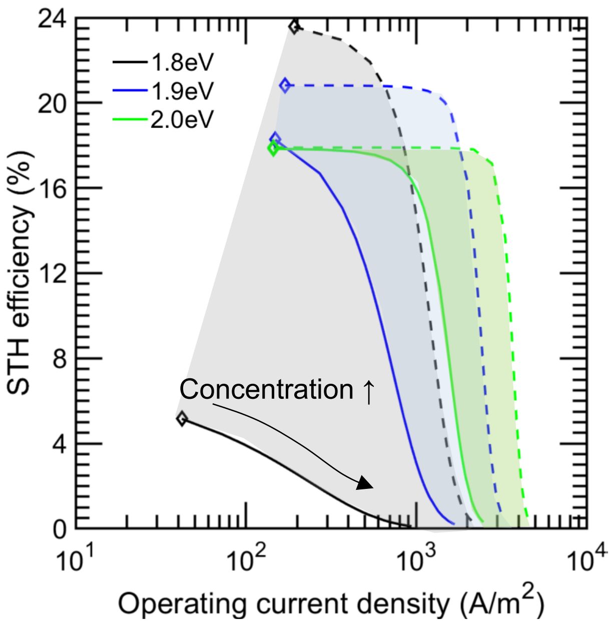
- Engineering to go beyond the perceived limits:

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





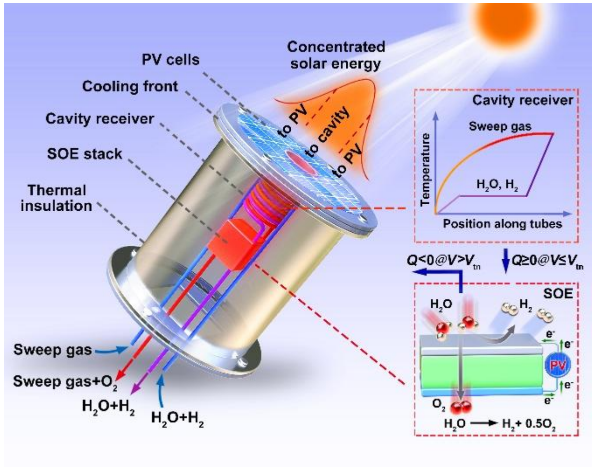
Solid lines: no thermal integration
Dashed lines: with thermal integration

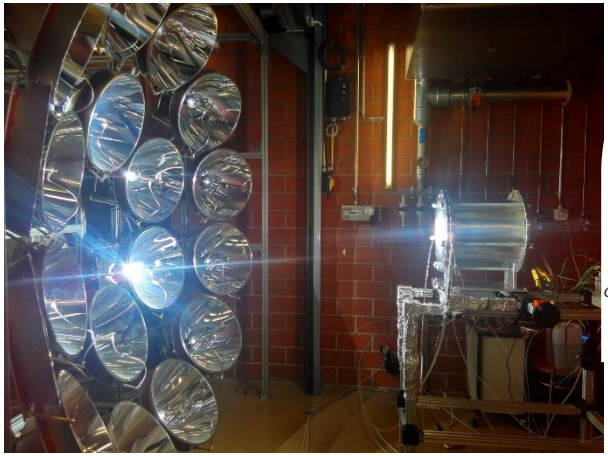


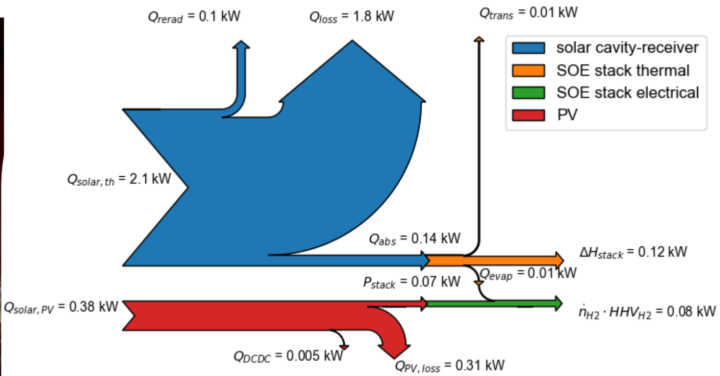
High electrochemical and power densities enabled by thermal integration

Pushing the thermal integration

- PV driven high-temperature electrolysis



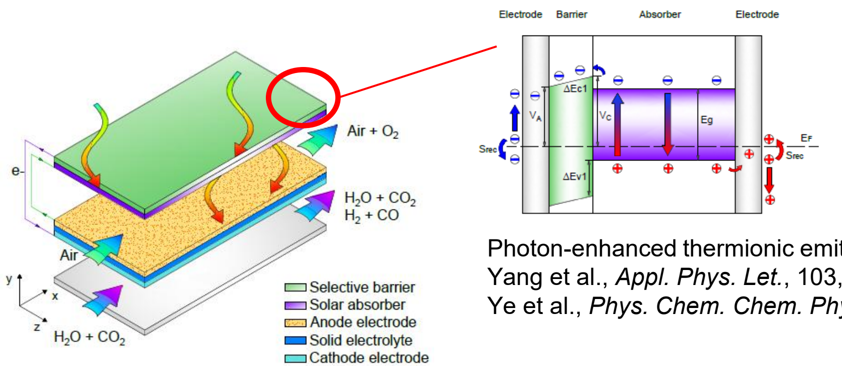




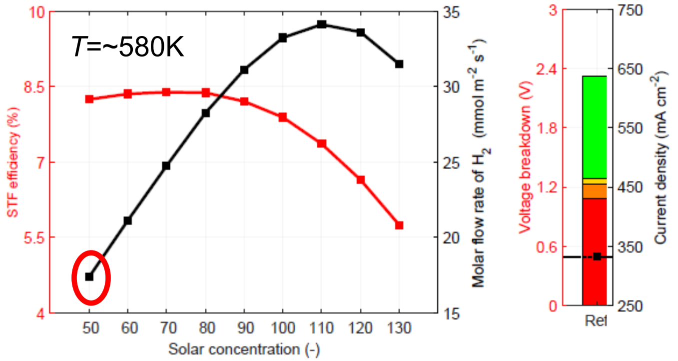
η_{STH} = 3.3%, $T_{stack} \approx$ 973 K

Lin, Suter, Diethelm, Van herle, Haussener, *Joule*, 10.1016/j.joule.2022.07.013, 2022.

- High-temperature PEC



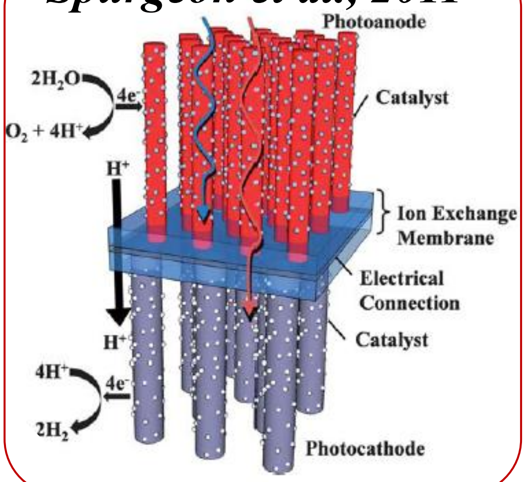
Photon-enhanced thermionic emitter:
Yang et al., *Appl. Phys. Let.*, 103, 2013
Ye et al., *Phys. Chem. Chem. Phys.*, 15, 2013



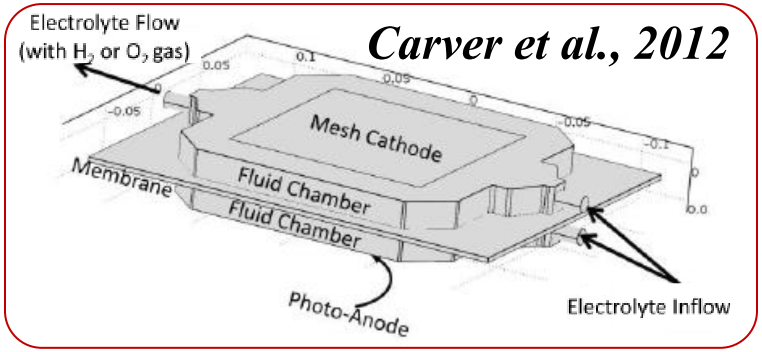
Photoelectrochemistry

- Proposed devices

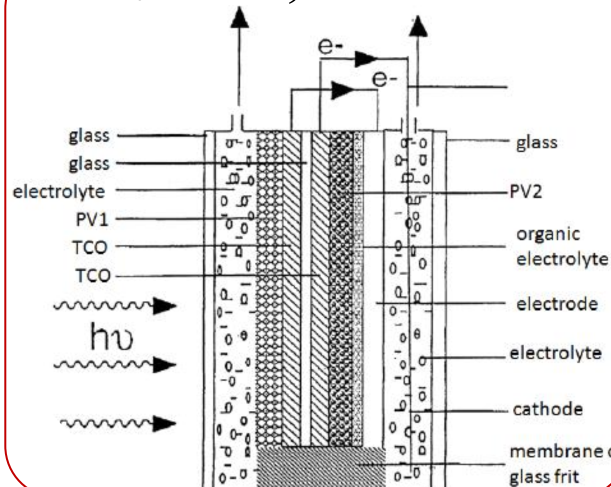
Spurgeon et al., 2011



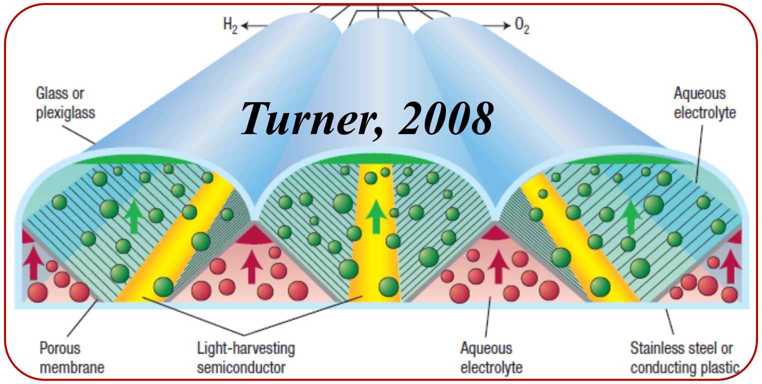
Carver et al., 2012



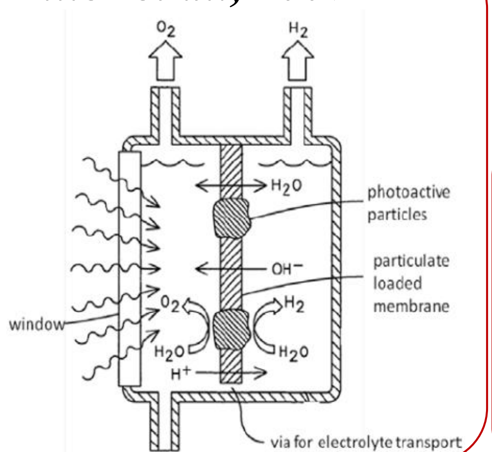
Grätzel et al., 2007



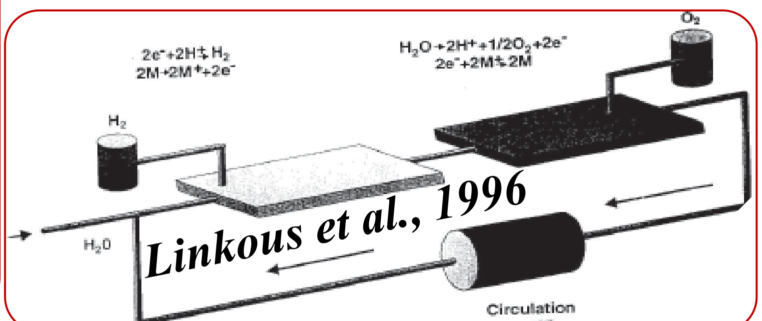
Turner, 2008



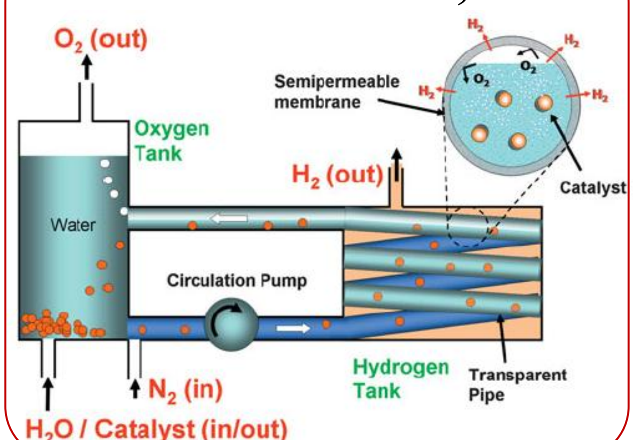
Miller et al., 2007



Linkous et al., 1996

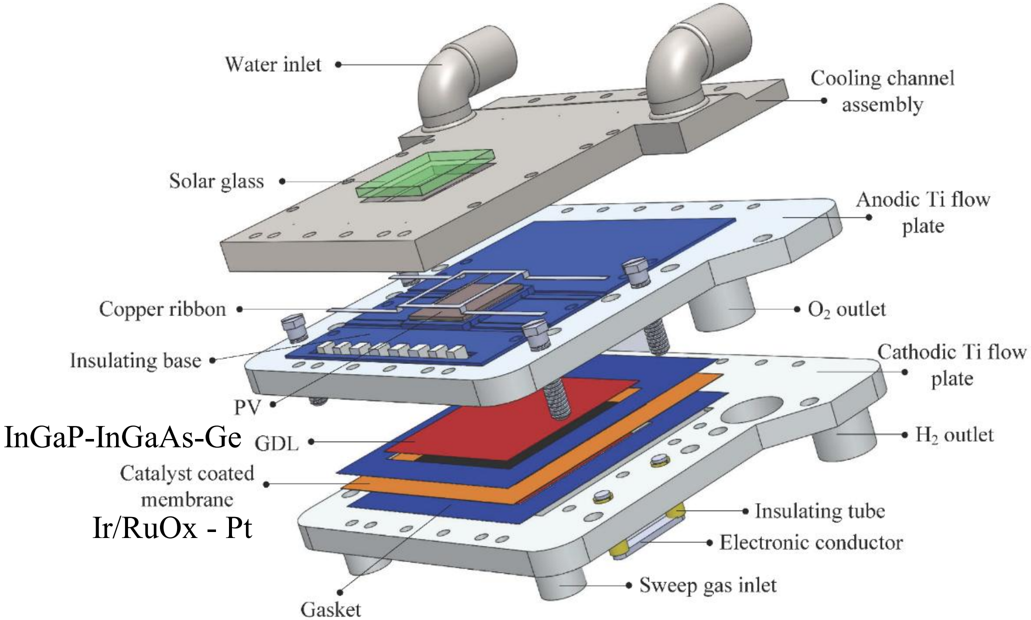


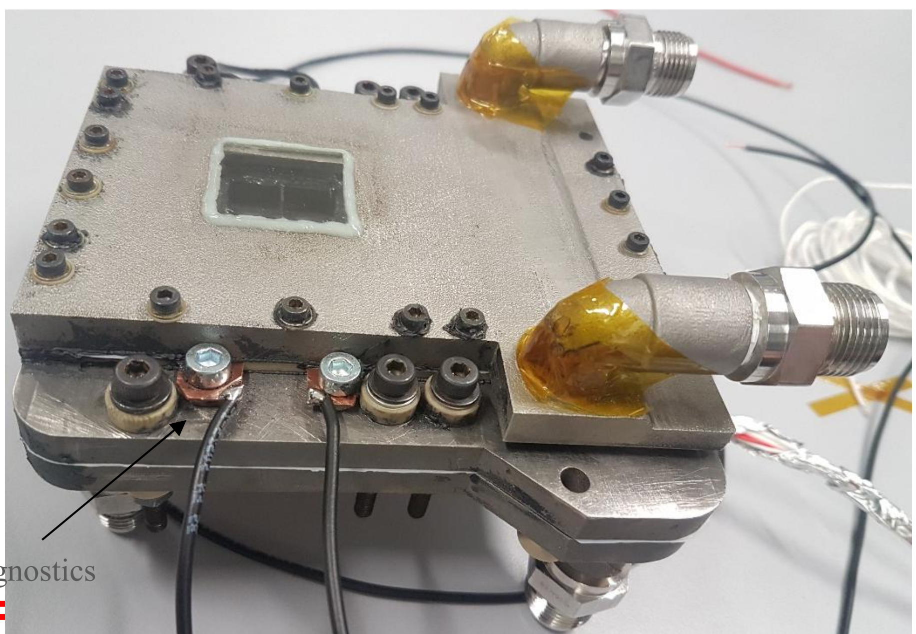
Parkinson et al., 2011

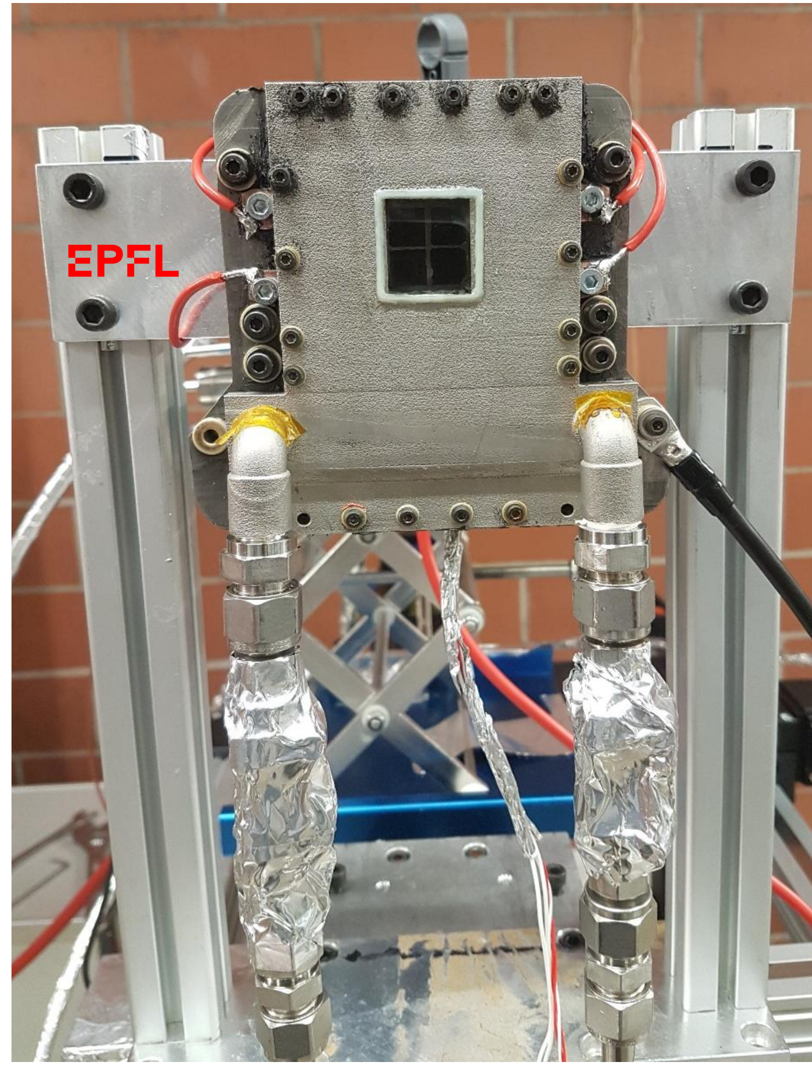


Photoelectrochemistry

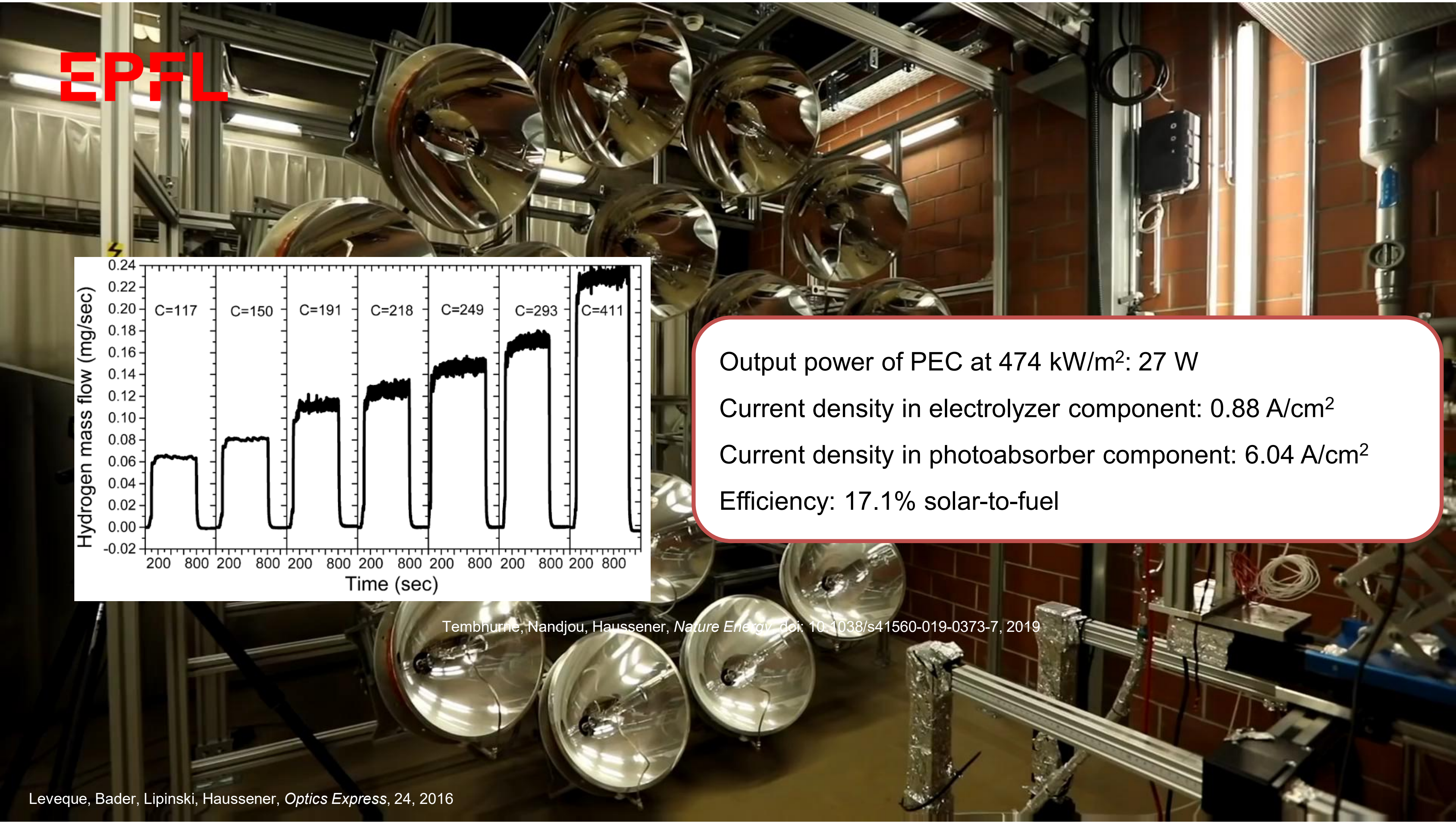
US Patent 62/376923
EP Patent 16020308.9







CPEC device realization



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

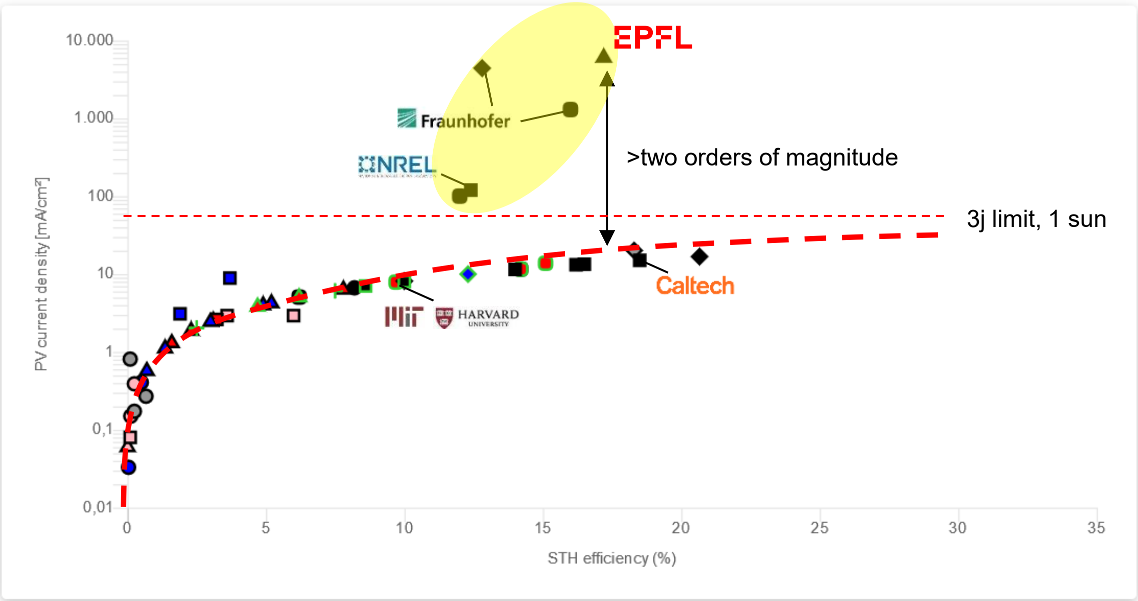
Tembhurne, Nandjou, Haussener, *Nature Energy*, doi: 10.1038/s41560-019-0373-7, 2019

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

Comparison

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

SolarFuelsDB



Concentrated irradiation
AND
Thermal management

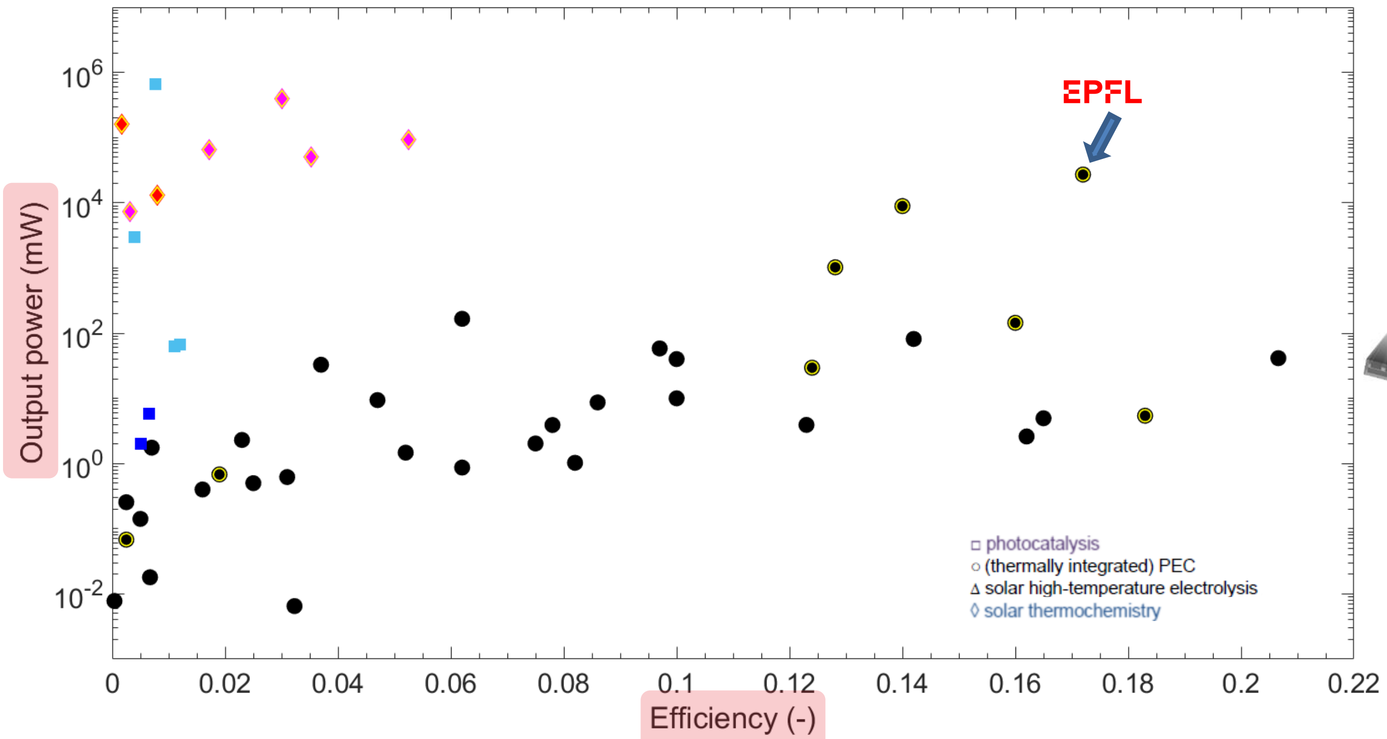
w/o multi-module demonstrations
w/o multiple electrolyzer demonstrations

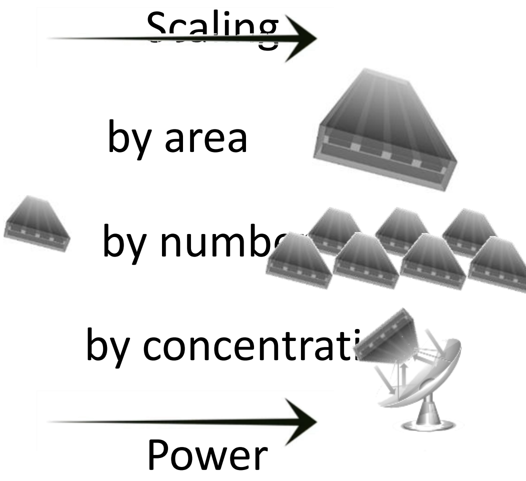
LEGEND			
Fill color - PV / photoabsorber material	Boundary color - EC material	Symbol shape - PV / photoabsorber and EC configuration	
All III-V	Rare metal-based (expensive)	○ 2J, integrated PVs and catalyst	+ 3J, integrated PVs and catalyst
Partial III-V	Abundant (cheap)	□ 2J, integrated PVs, wired 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

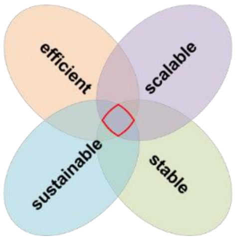


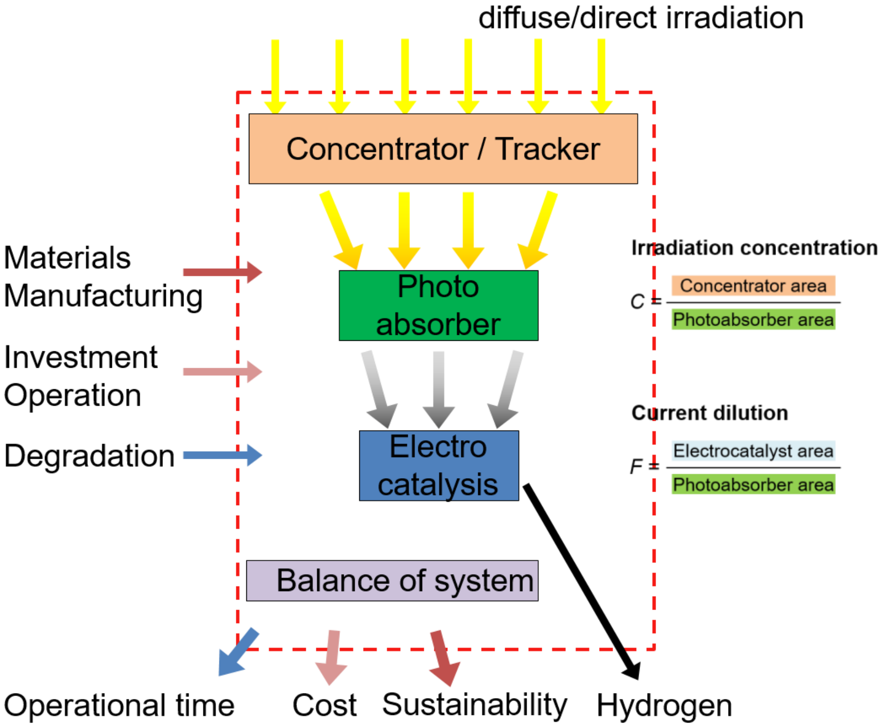


Tembhurne, Nandjou, Haussener, *Nature Energy*, doi: 10.1038/s41560-019-0373-7, 2019

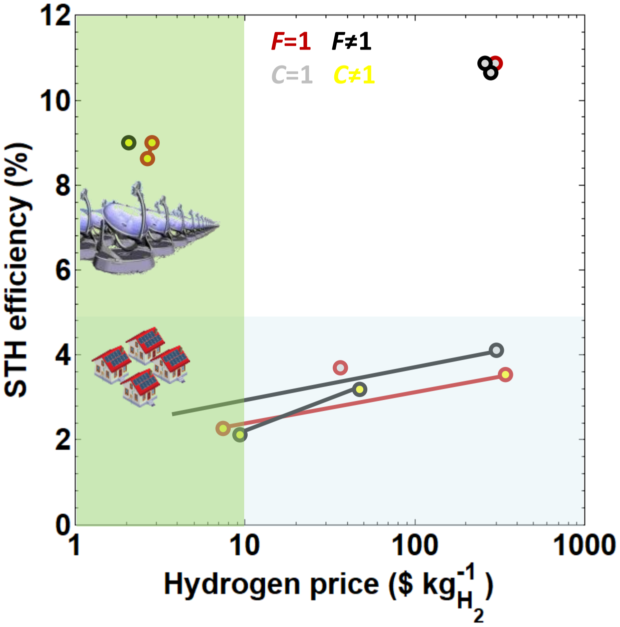
Techno-Economics and LCA

- Promising device design groups





(0D performance model)

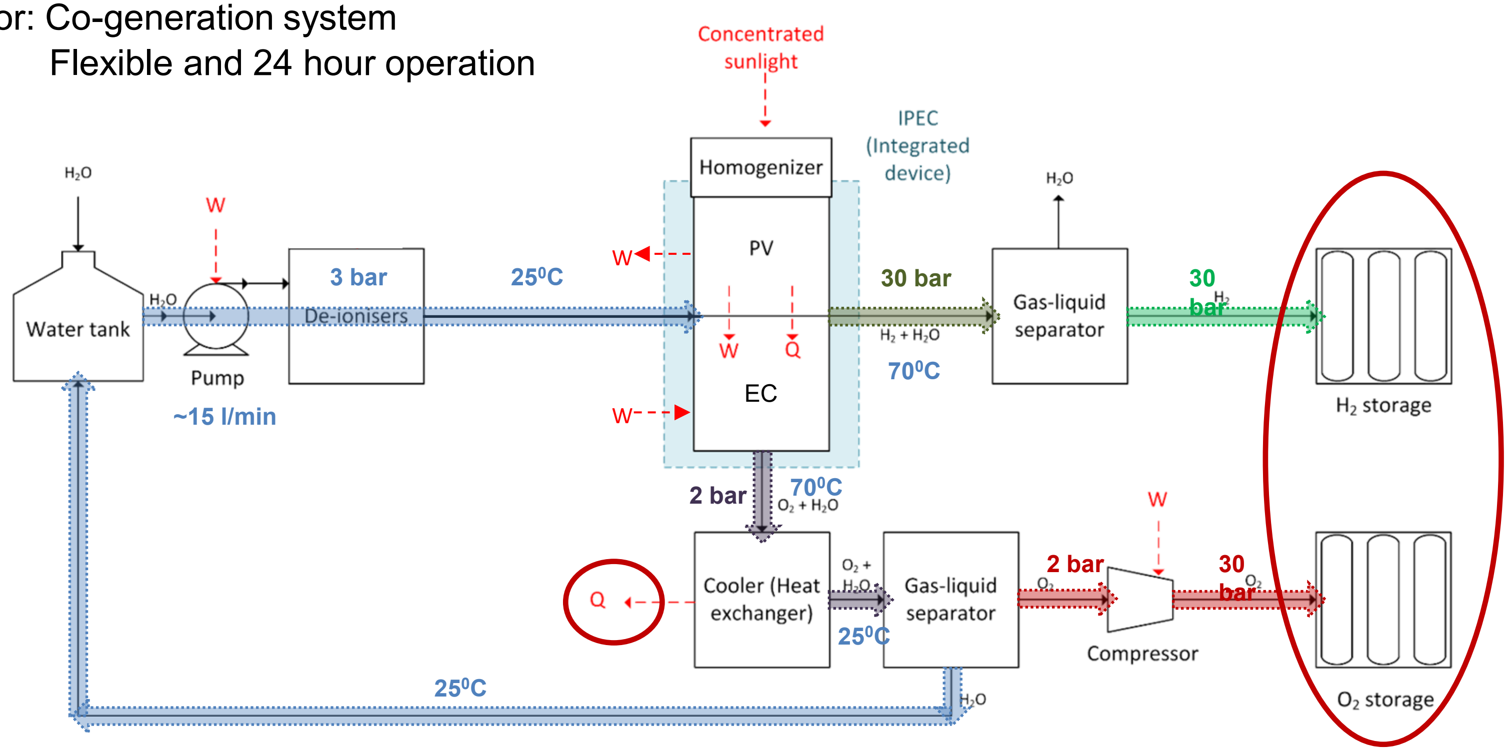


Dumortier, Tembhurne, Haussener, *Energy Environ Sci*, 8, 2015; http://specdo.epfl.ch


EPFL
~0.5kg H_2/day, kW-scale, long-term, on-sun demonstration

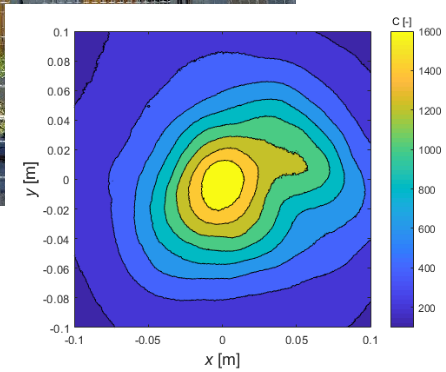
System Process Flow Diagram

Potential for: Co-generation system
Flexible and 24 hour operation



Tembhurne, Holmes-Gentle, Suter, Haussener, Nature Energy, 2023

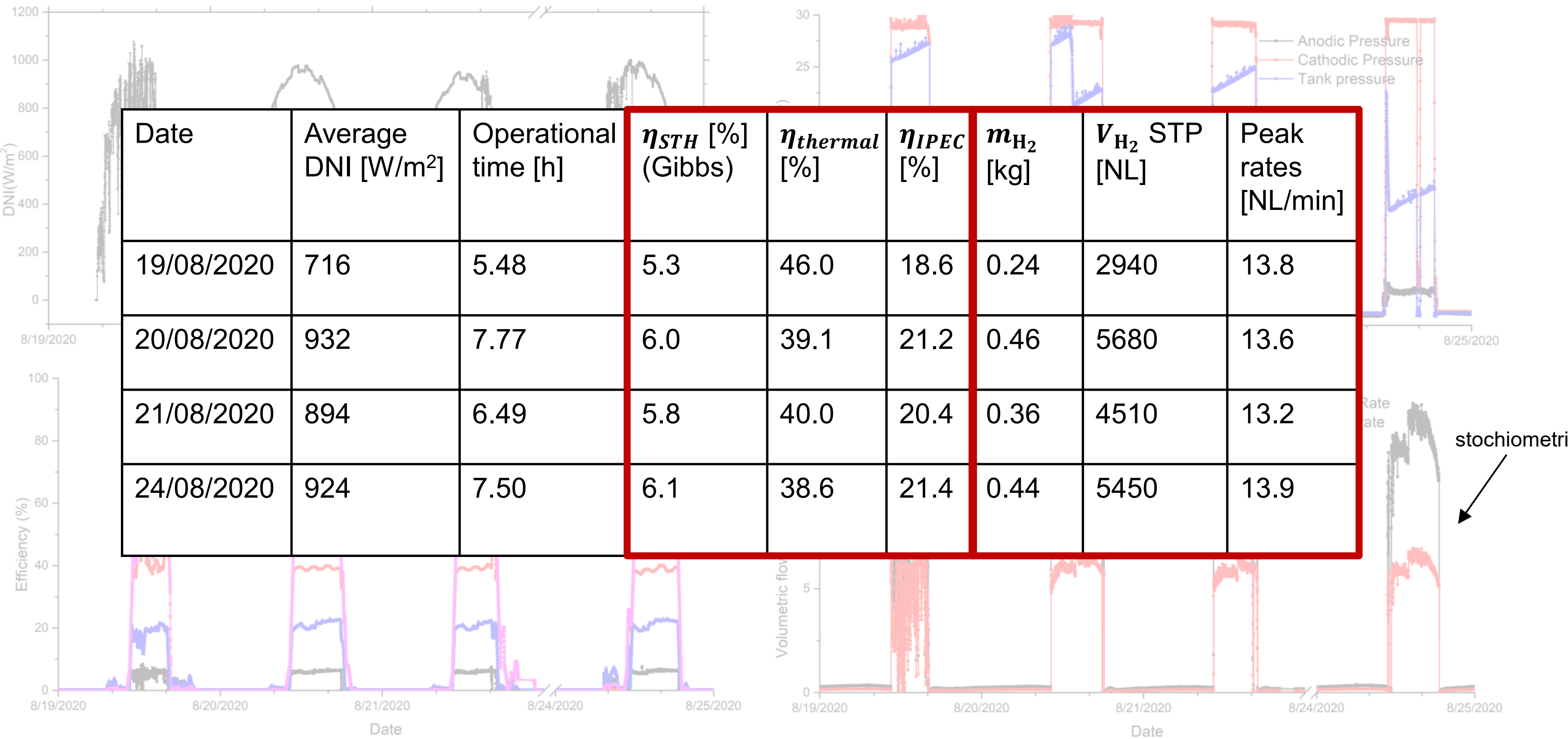
Reactor and System in Operation



Tembhurne, Holmes-Gentle, Suter, Haussener, Nature Energy, 2023

Integrated System Test

- Full operation over multiple days in varying meteorological conditions

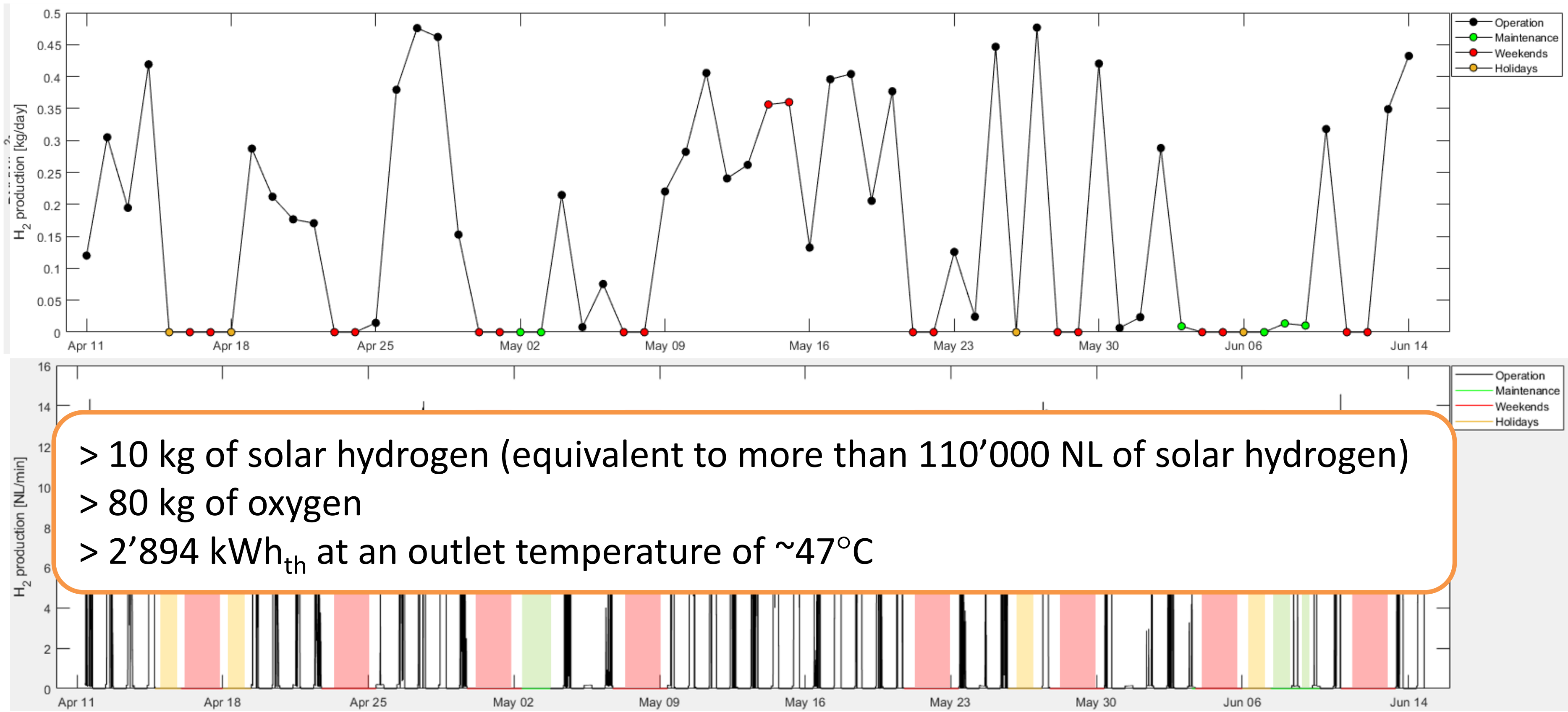


Date	Average DNI [W/m^2]	Operational time [h]	η_{STH} [%] (Gibbs)	$\eta_{thermal}$ [%]	η_{IPEC} [%]	m_{H_2} [kg]	V_{H_2} STP [NL]	Peak rates [NL/min]
19/08/2020	716	5.48	5.3	46.0	18.6	0.24	2940	13.8
20/08/2020	932	7.77	6.0	39.1	21.2	0.46	5680	13.6
21/08/2020	894	6.49	5.8	40.0	20.4	0.36	4510	13.2
24/08/2020	924	7.50	6.1	38.6	21.4	0.44	5450	13.9

Tembhurne, Holmes-Gentle, Suter, Haussener, Nature Energy, 2023

Durability

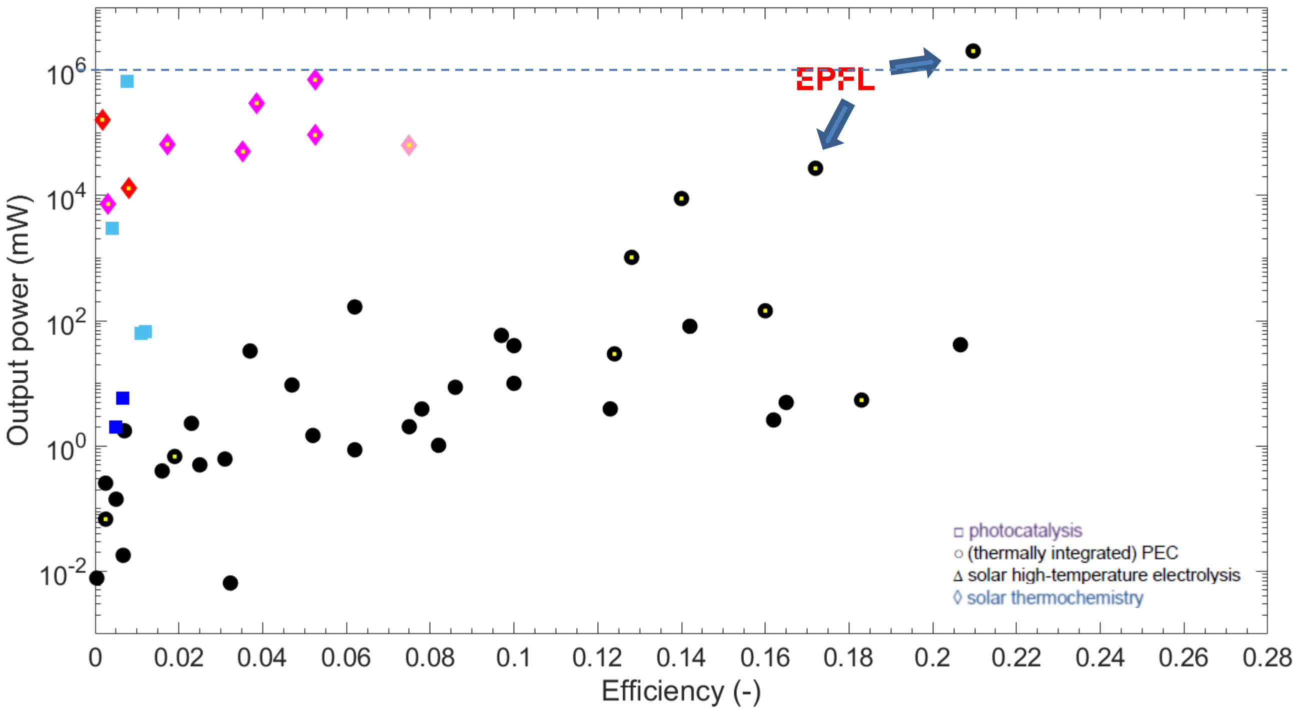
- Long term operation:



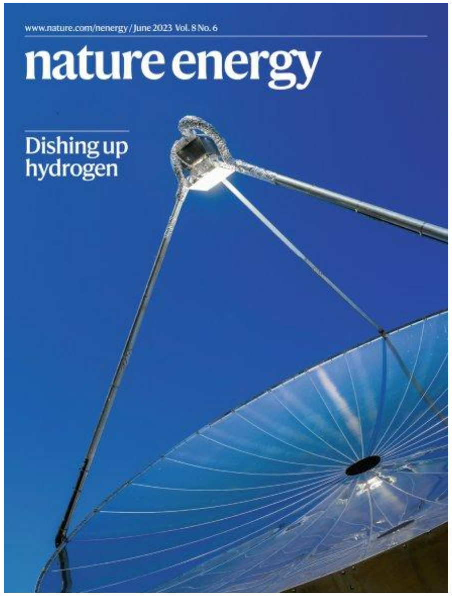
> 10 kg of solar hydrogen (equivalent to more than 110’000 NL of solar hydrogen)
> 80 kg of oxygen
> 2’894 kWh_{th} at an outlet temperature of ~47°C

Armas, Mutrux, Holmes-Gentle, Rezai, Giordano, Tembhurne, Haussener, in preparation, 2024

Comparison



SolarFuelsDB



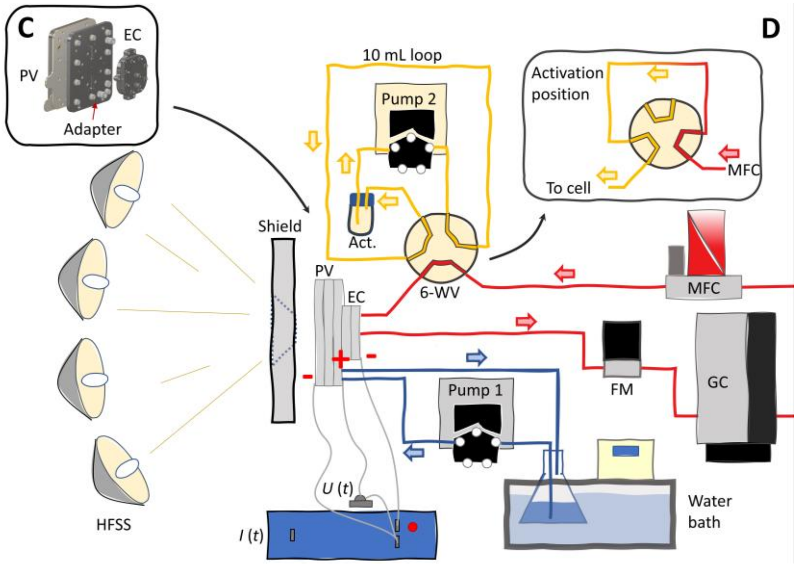
Tembhurne, Holmes-Gentle, Suter, Haussener, *Nature Energy*, 10.1038/s41560-023-01247-2, 2023

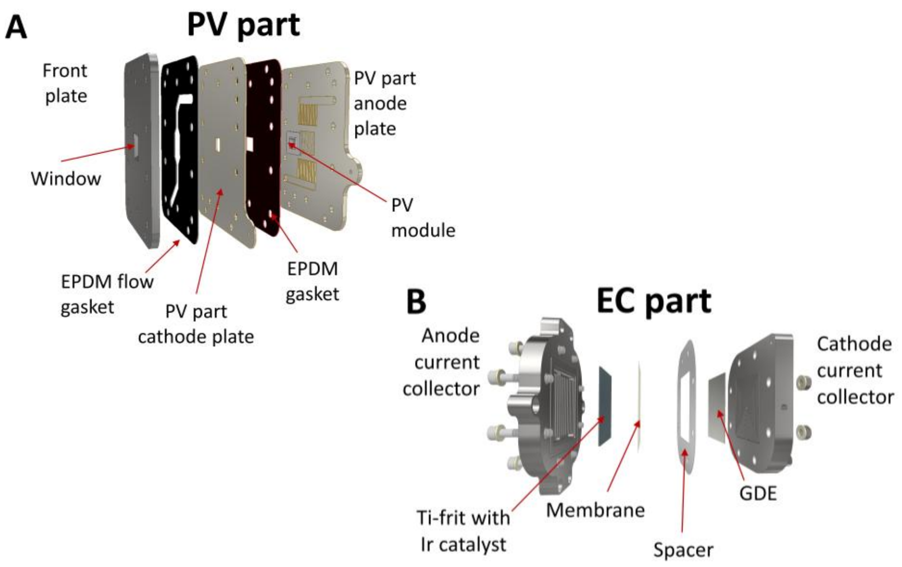
Scaling?


EPFL
SoHHytec
SOLAR FUEL, THE SMARTER WAY
http:\\www.sohhytec.com
Industry
Steel production
Fertilizer production …
Fuel/Mobility
Electricity/(Seasonal) storage

Alternative Chemistry

- 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

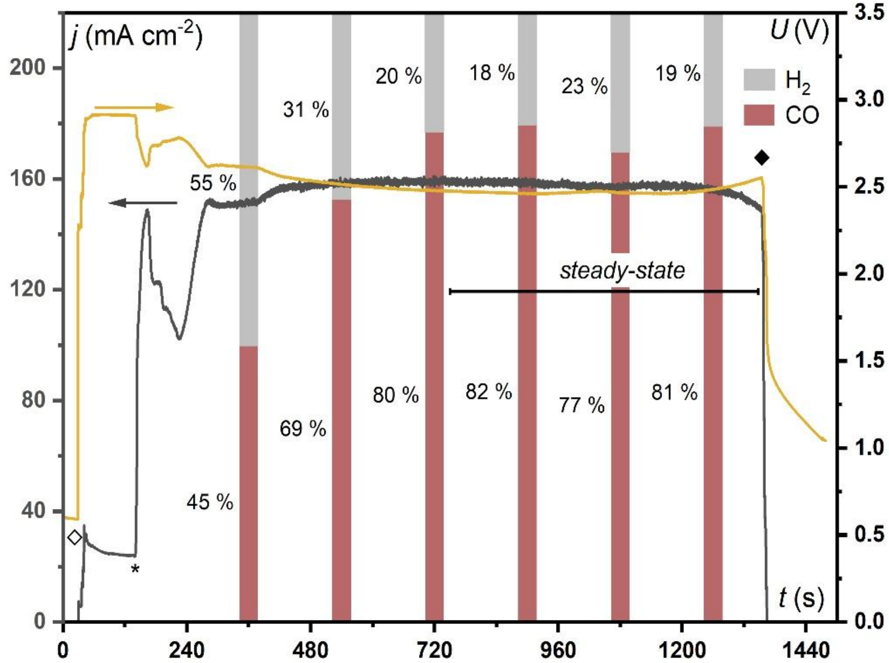




Boutin, Patel, Kecsenovity, Suter, Janaky, Haussener, *Advanced Energy Materials*. doi:: 10.1002/aenm.202200585, 2022

CO_2 Reduction with Concentrated Light

- Typical experimental run



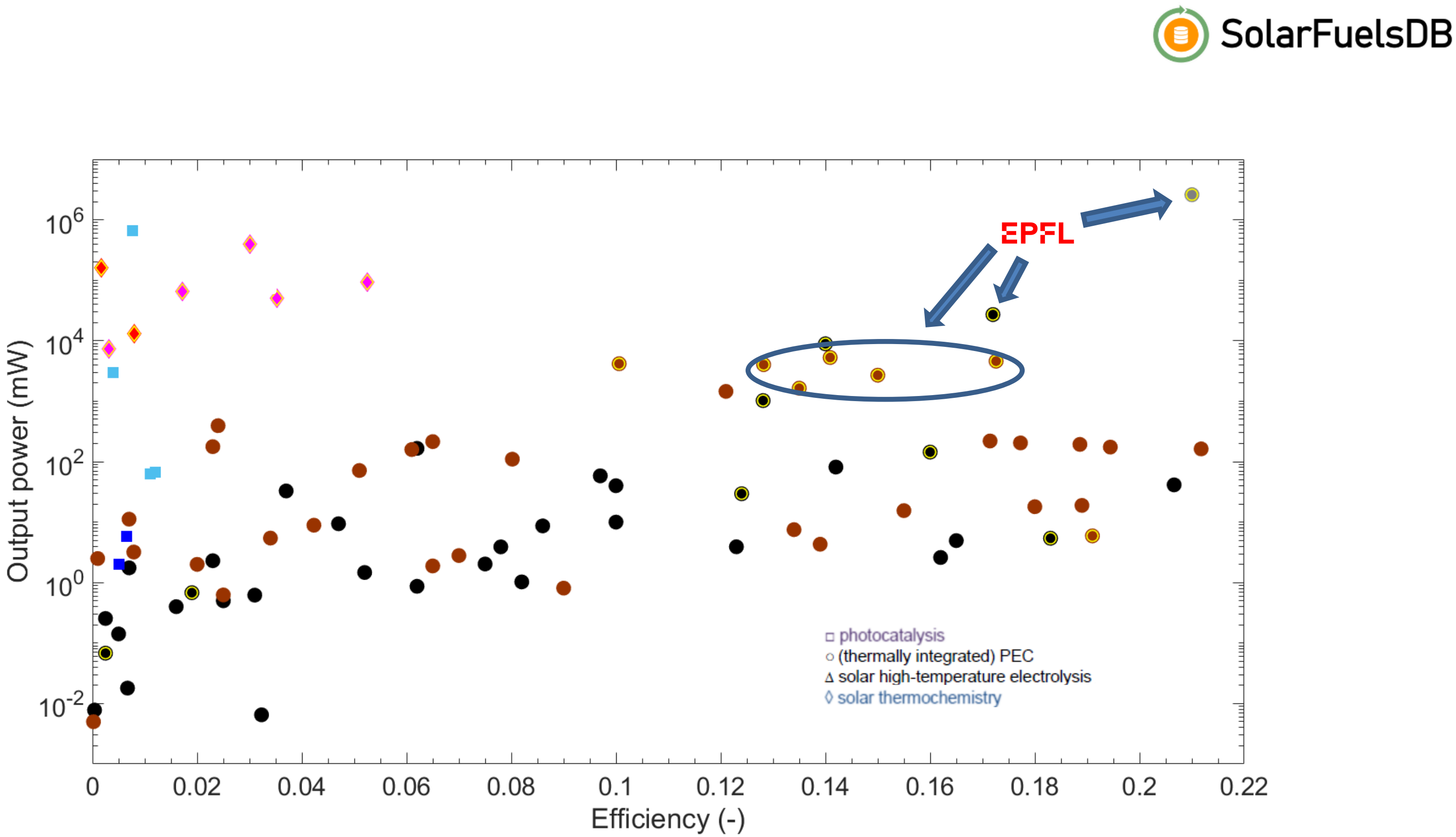
Typical 20 min experiment at 341 suns with the integrated PEC cell.

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.

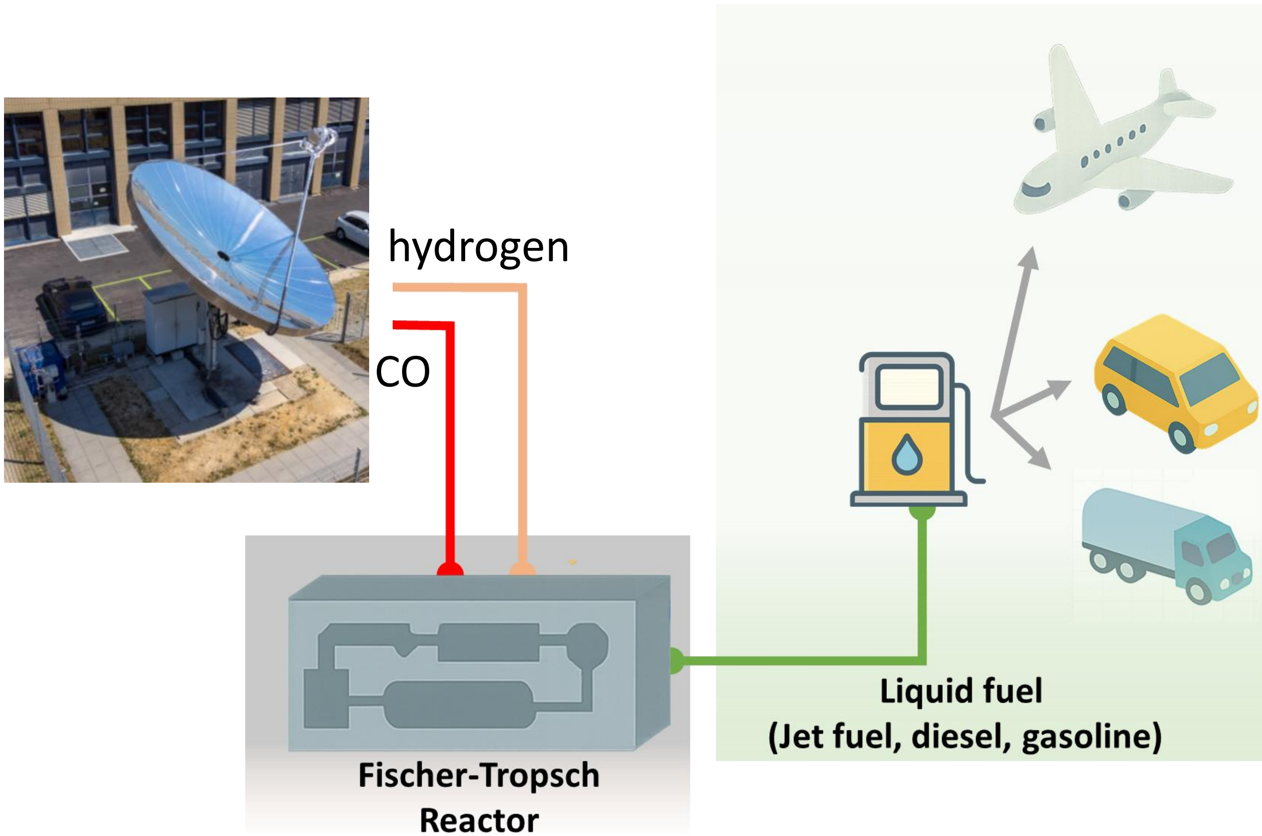
Boutin, Patel, Kecsenovity, Suter, Janaky, Haussener, *Advanced Energy Materials*. doi:: 10.1002/aenm.202200585, 2022

Comparison



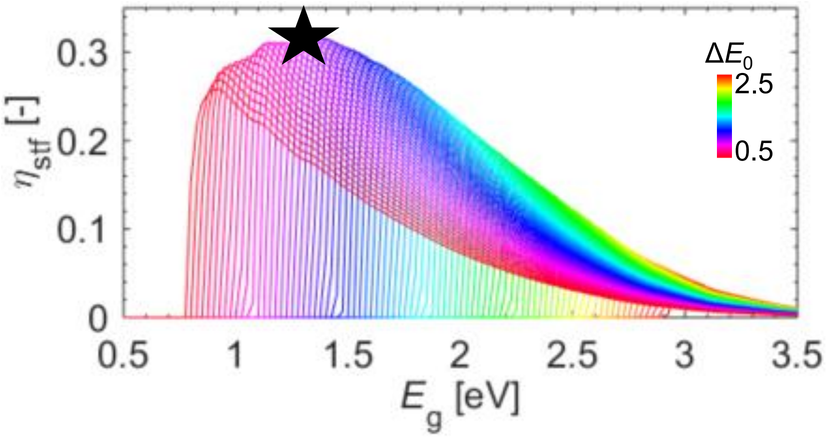
SolarFuelsDB
EPFL
Output power (mW)
Efficiency (-)
□ photocatalysis
○ (thermally integrated) PEC
Δ solar high-temperature electrolysis
◊ solar thermochemistry

From Hydrogen to Synthesis Gas and Beyond

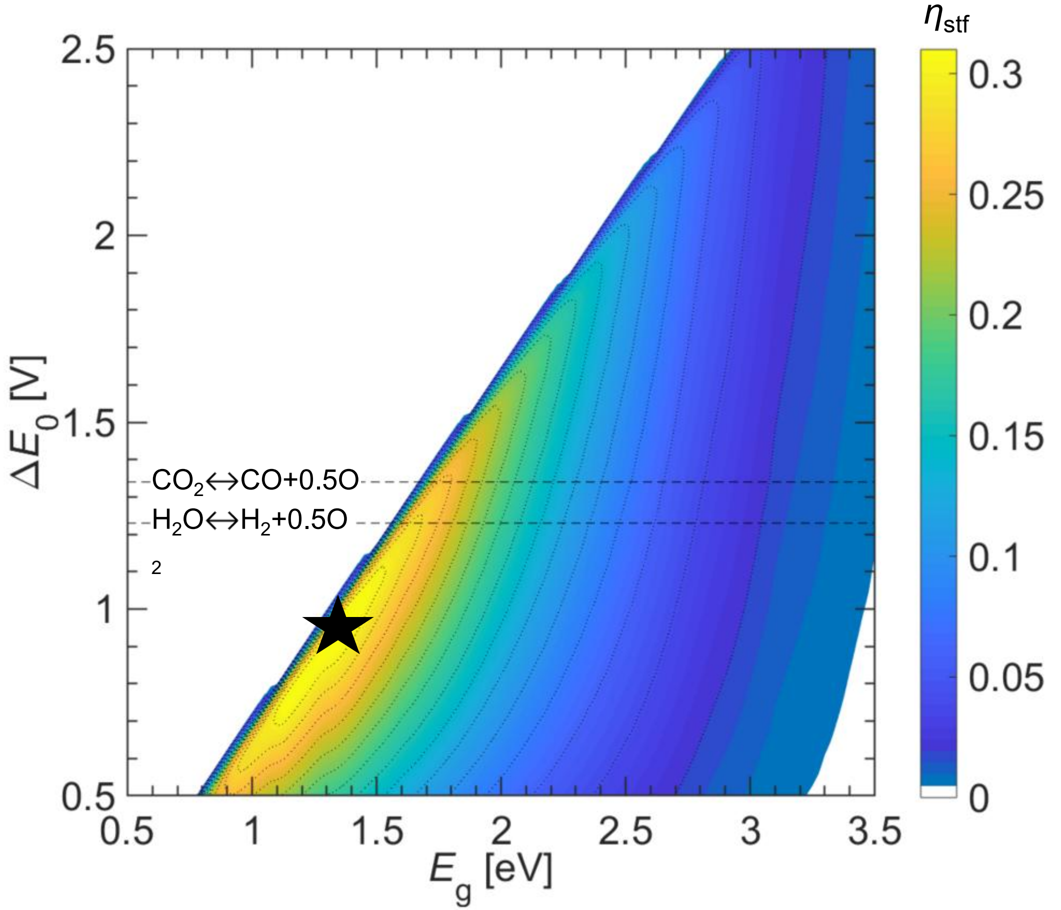


Beyond water splitting or CO_2 reduction

- Which reactions are interesting?
- Limiting efficiencies:



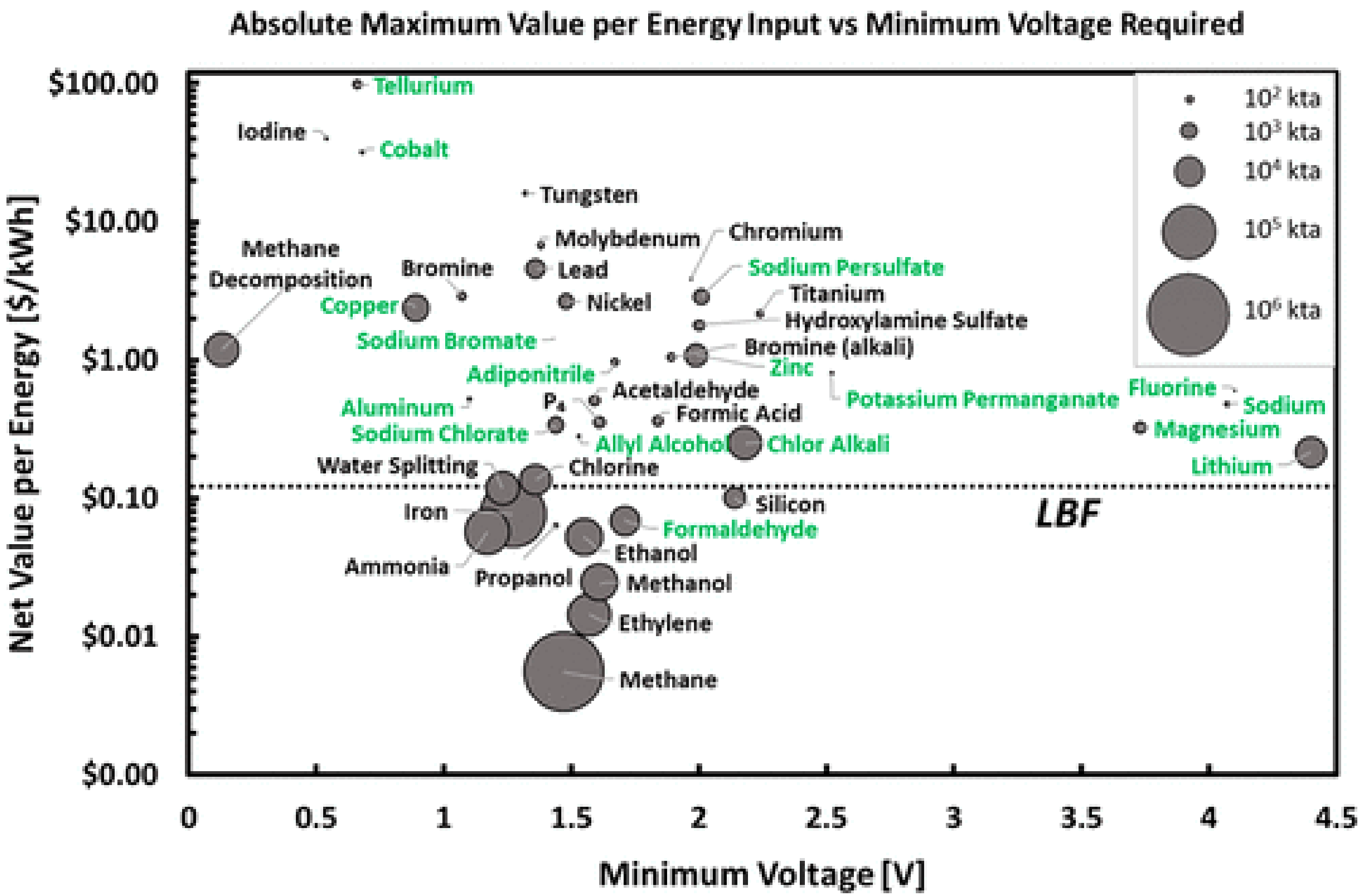
Global maxima:
η_{STF} = 32% at E_g=1.35eV and ΔE_0=0.96V



Haussener, Suter, Gutierrez Perez, Solar fuel devices: Multi-scale modeling and device design guidelines, Chapter, Springer, 2020

Solar materials

- (Photo)electrochemical:

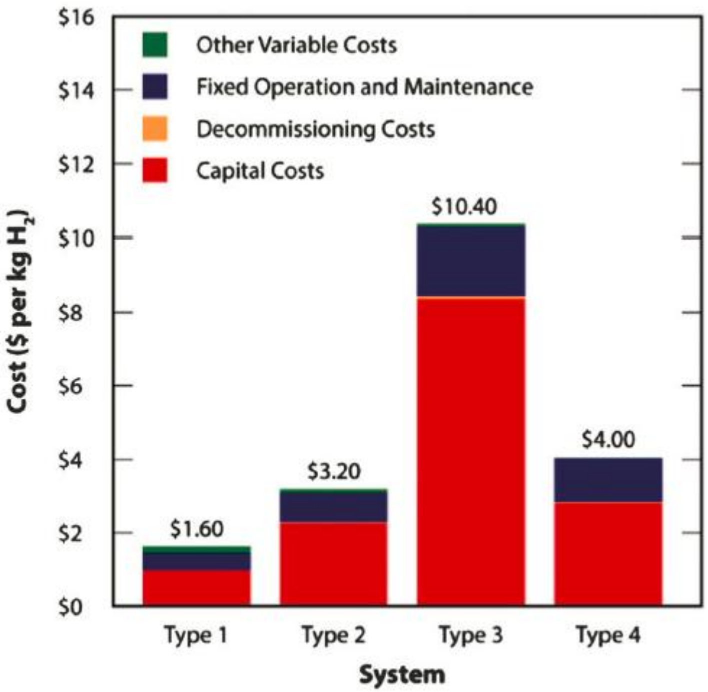


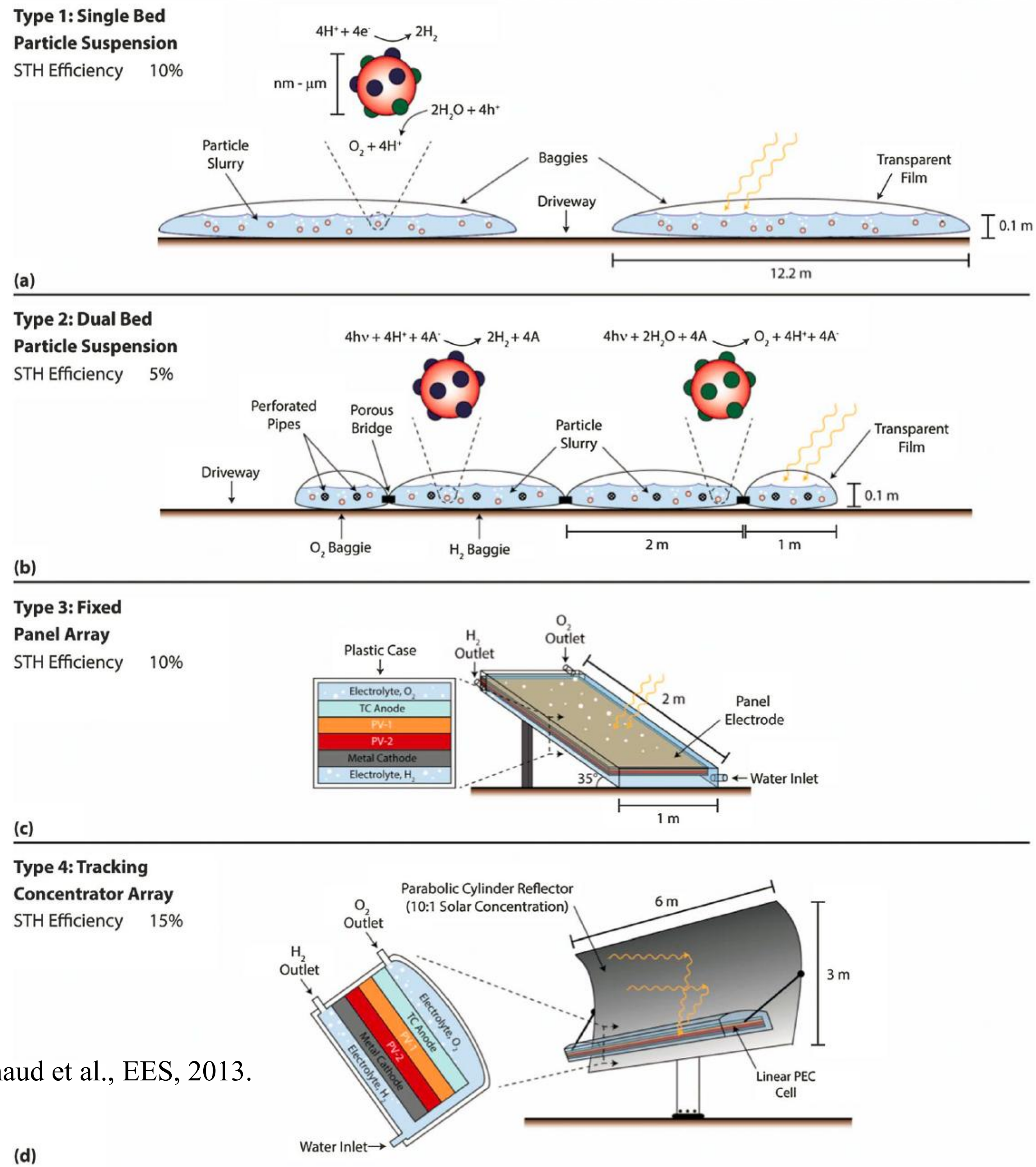
Maximum net value per energy input (log scale) plotted versus minimum voltage required for all electrochemical processes or electrochemical equivalents of thermochemical processes. For each point, the width of the circle corresponds to the relative market size. Processes highlighted in green are conducted electrochemically in industry, to any appreciable extent. The lower bound of feasibility (LBF) is plotted as the horizontal dashed line

Palmer et al., Technoeconomics of Commodity Chemical Production Using Sunlight, ACS Sustainable Chemistry & Engineering, 2018

Photoelectrochemistry and Photocatalysis

- Proposed devices

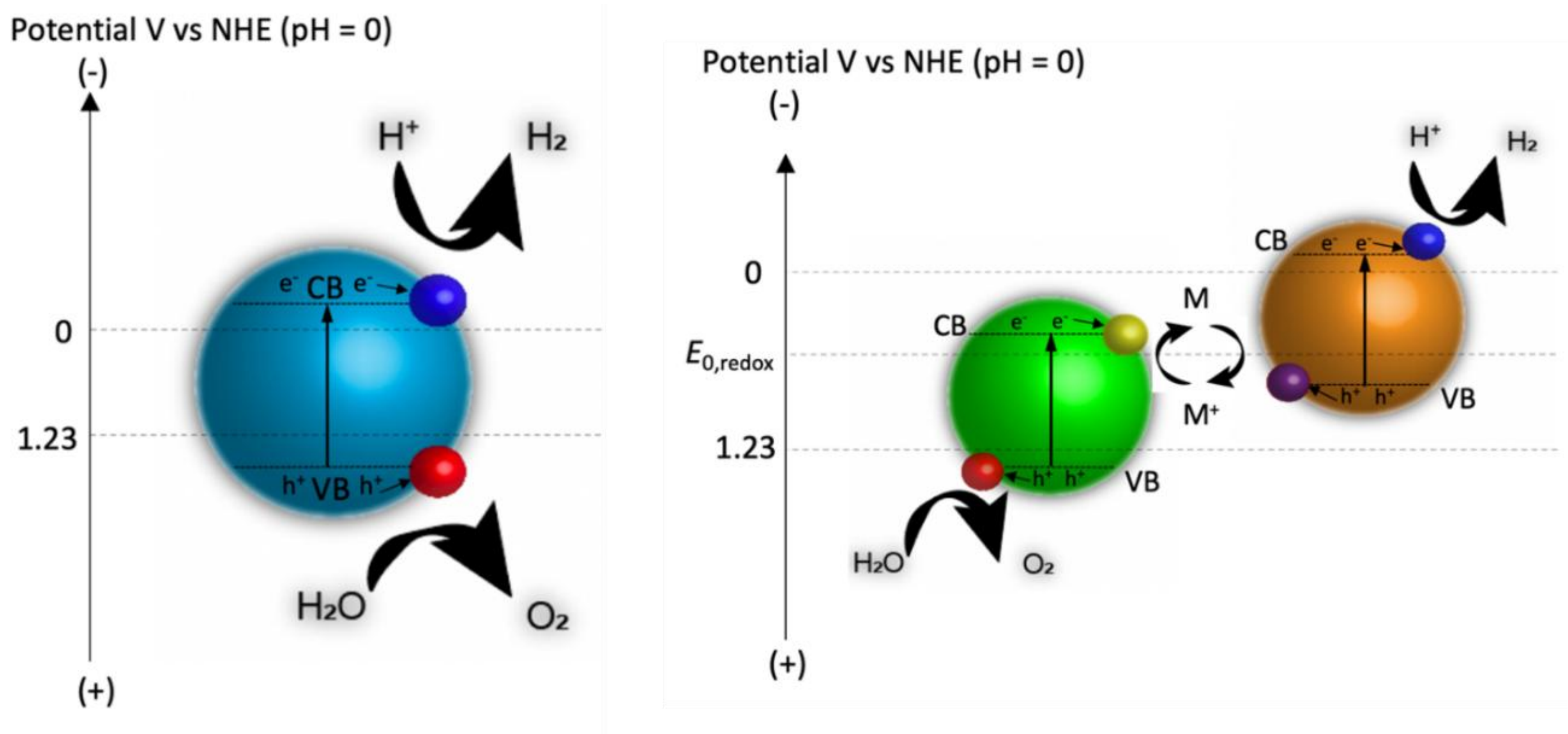




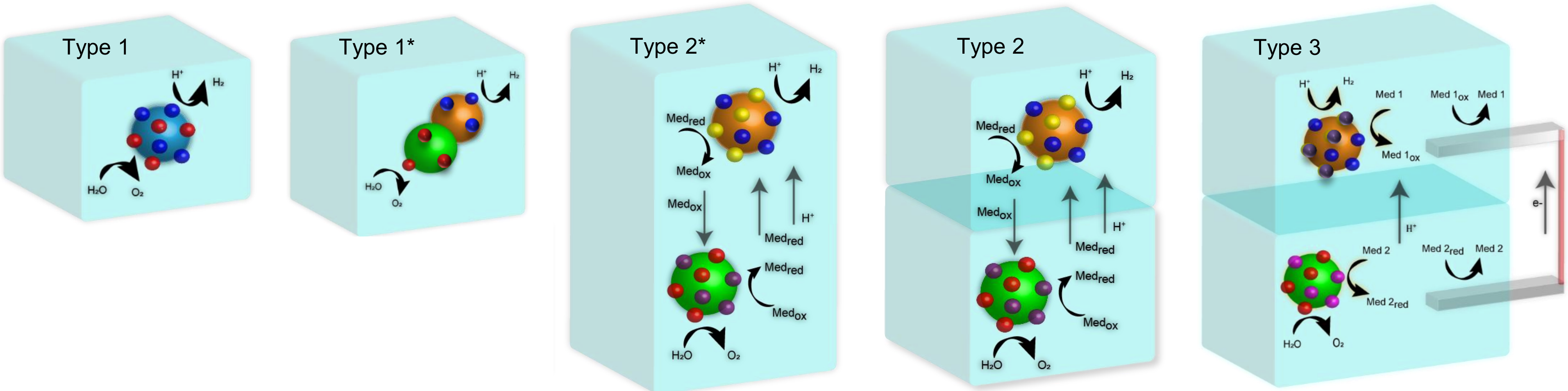
Pinaud et al., EES, 2013.

Photocatalysis

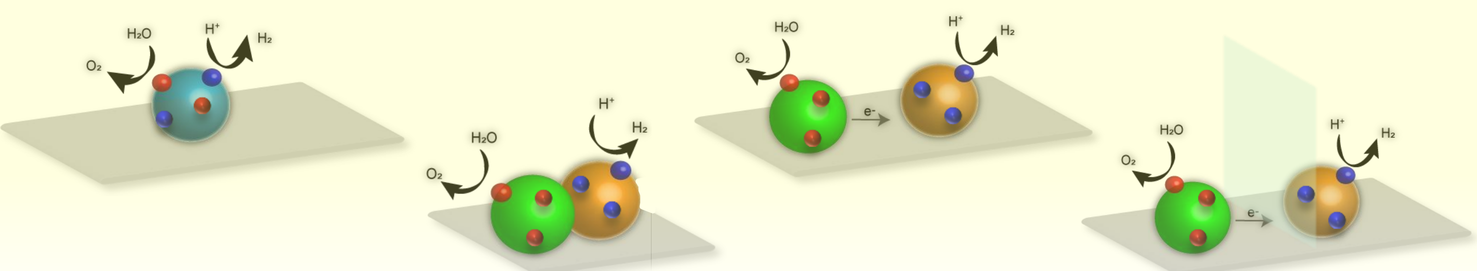
- Working principle



Potential Design Options

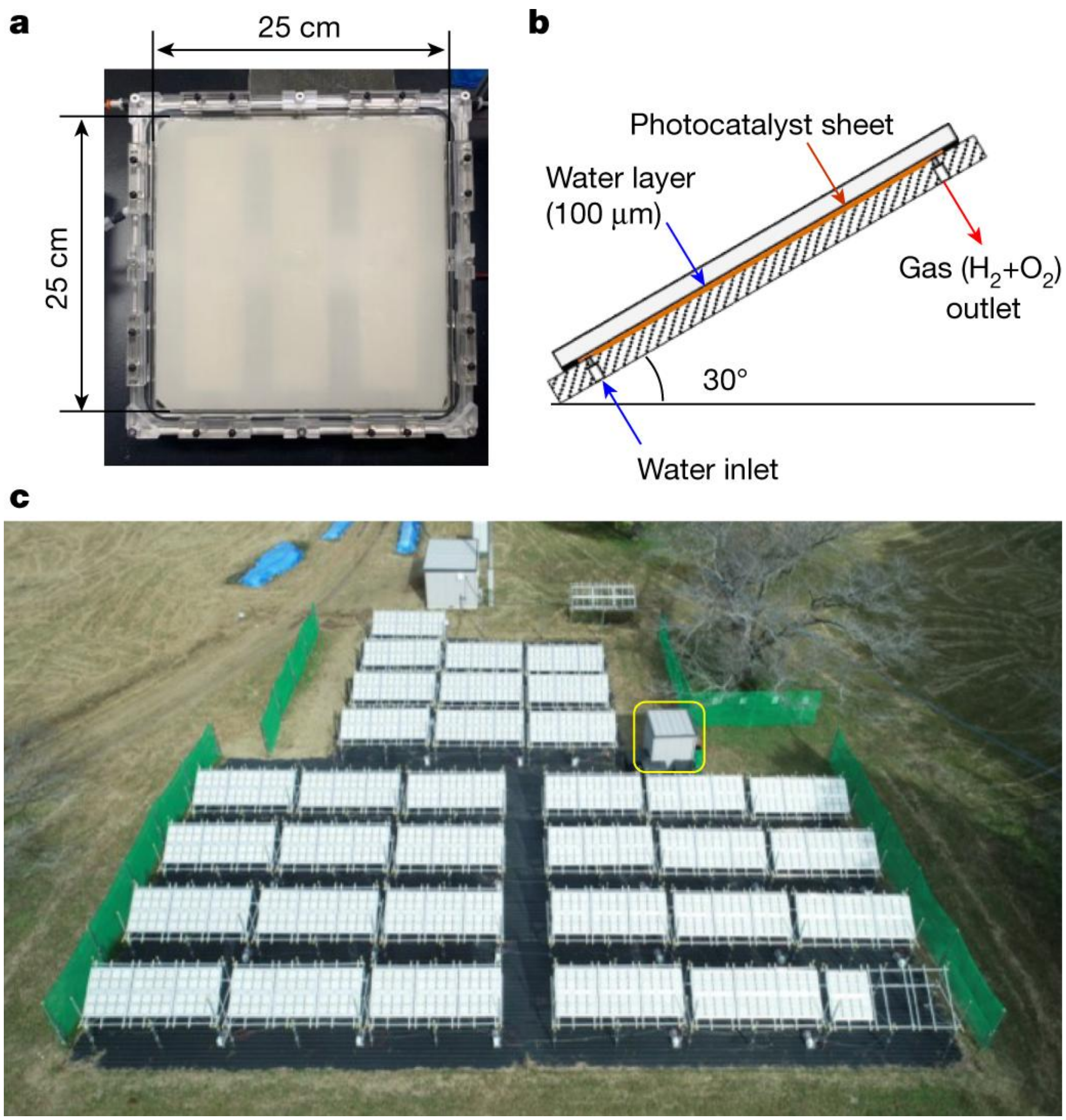


Catalyst sheets version



Savant et al., Chem. Sci., 10.1039/d1sc01504d, 2021

Large-scale Photocatalystic Hydrogen Demo



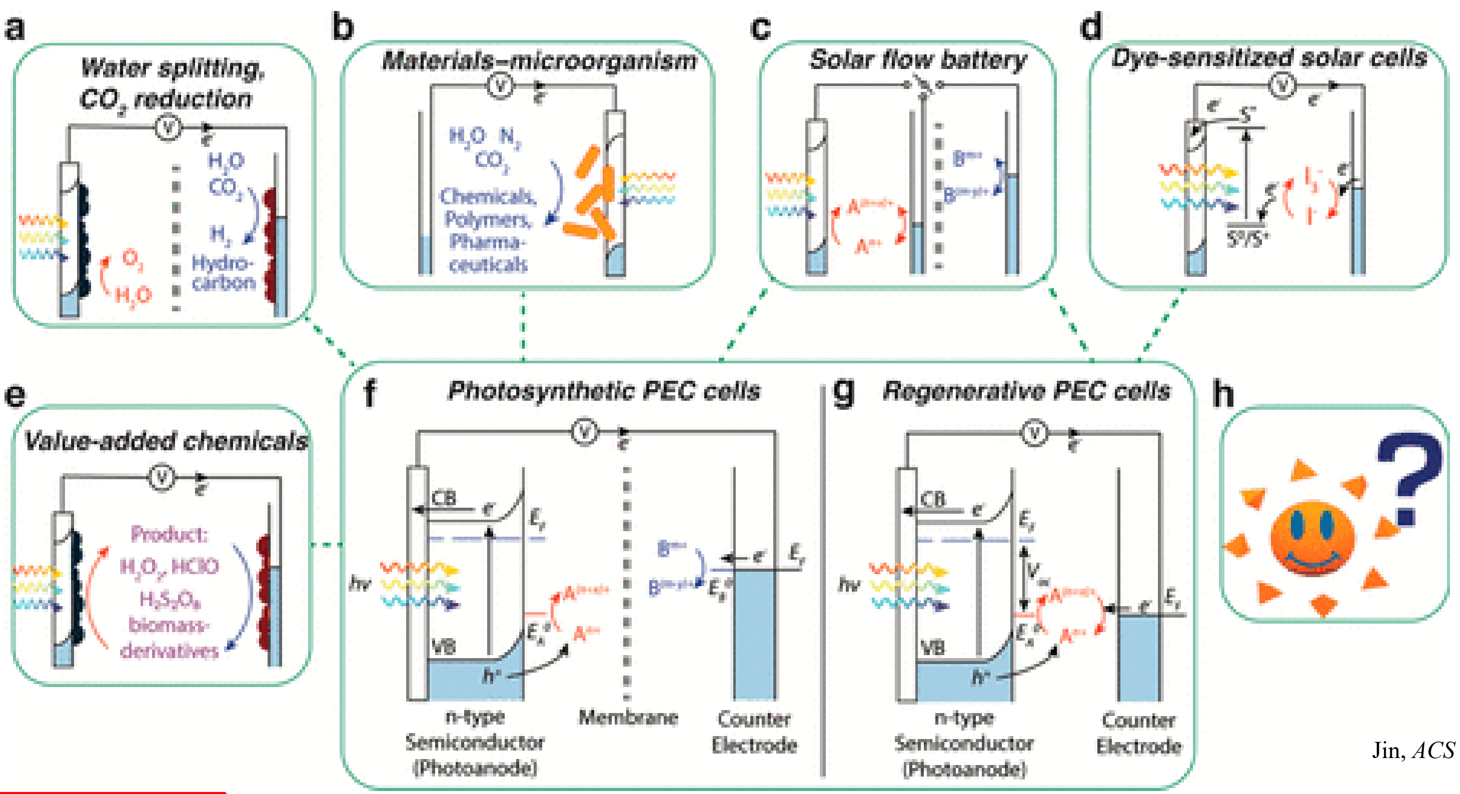
aluminium-doped strontium titanate particulate photocatalyst, with a maximum STH of 0.76%

Nishiyama et al., Nature, 2021

Other photo-driven chemistry

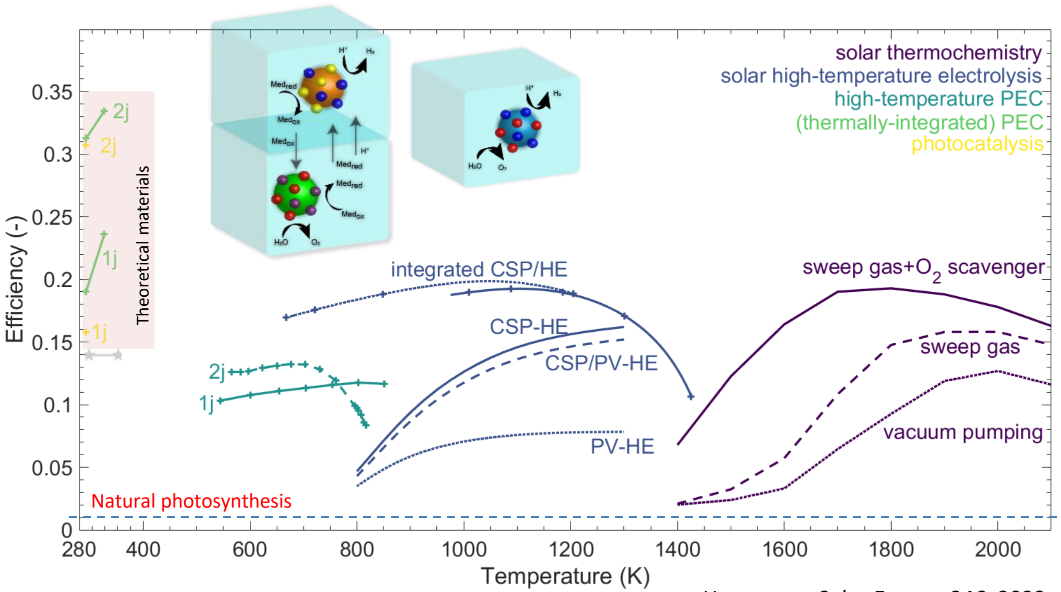
- Photo-electro-chemistry – more than fuels:
  - Oxidation of organic matter

  (water treatment, air cleaning, medical disinfection, …)
  - Photo-electrochemical nitrogen reduction
  - Photo-driven flowbatteries (I_3^-/I^-,VO_2^+/VO^{2+}…)

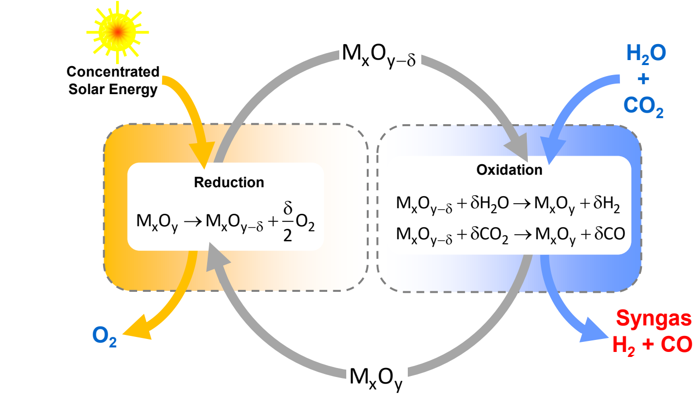


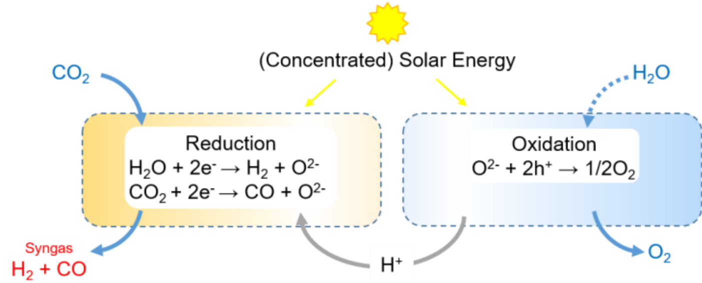
Jin, *ACS Energy Letters*, 3, 2018

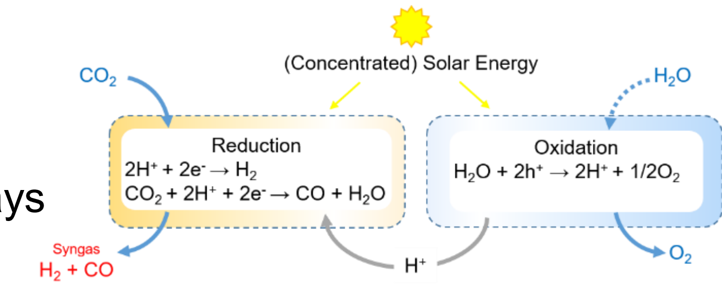
Theoretical Efficiency Limits



Haussener, *Solar Energy*, 246, 2022







- Comparison:
  - Similar achievable STF efficiency for all technical pathways
  - Lower temperature requirements for HTE
  - Less stringent requirement for heat recovery in HTE
  - No requirement for p_{O2} at OER (1 Pa for TC, Air for HTE)
  - But significant, unsolved thermo-mechanical material challenges for HTE
  - For PEC: Low temperature, but corrosive environments, instability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