INNOVATIVE DESIGN OF PHOTOELECTROCHEMICAL CELLS FOR WATER SPLITTING: SCALE-UP THROUGH NUMBERING-UP AND INTEGRATION INTO A PANEL

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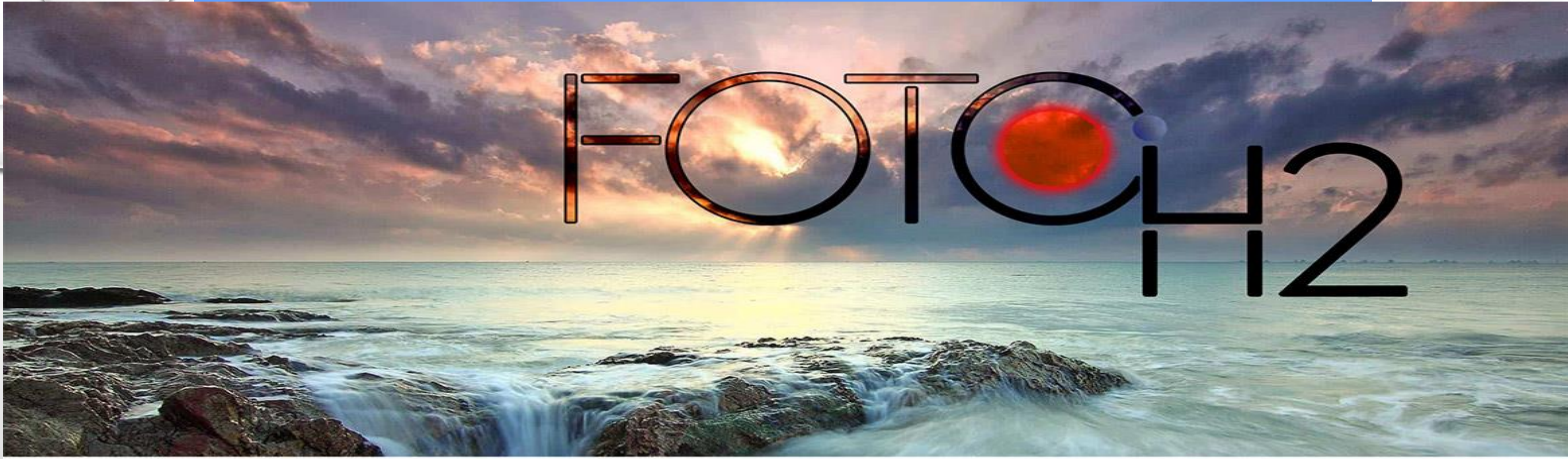

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FOTOH2 CONCEPT

FotoH2 shall develop a highly efficient **<u>tandem photoelectrolysis</u>** cell and PANEL for solar H_2 production, based on **durable** and **cost-effective** advanced materials and interfaces. The following specific breakthroughs are targeted:

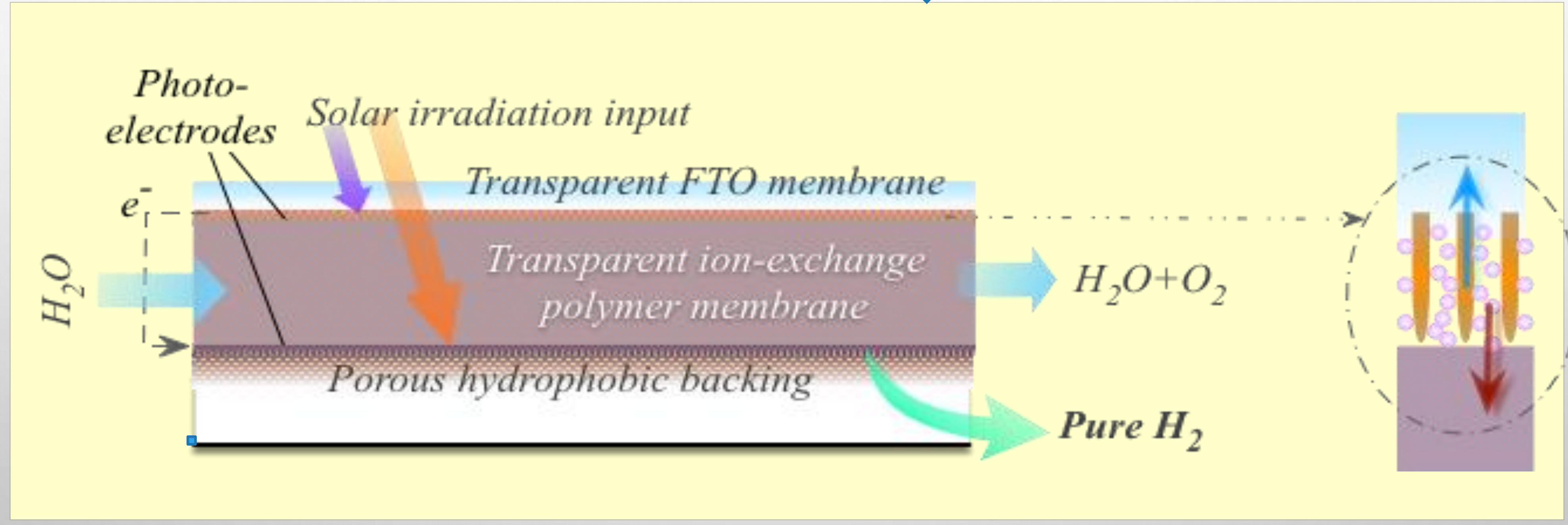
- Developing cost-effective advanced photoelectrode materials
- Achieving long-lasting cells for solar H_2 production
- Simple flow-cell design
- INPUT: PURE WATER
- Production of pure H_2 in the output stream
- High Solar-to-Hydrogen conversion efficiency

FOTOH2 CONCEPT

TWO-PHOTOELECTRODE SYSTEMS

PARALLEL CONFIGURATION

TANDEM CONFIGURATION



Electrodes should have complementary light absorption
Electrolyte should have minimum light absorption and resistance
Separator should avoid crossover of the electrolysis products → PEMs
Good scalability: flat configuration → PEMs

ELECTRODE MATERIALS

PHOTOELECTRODE REQUERIMENTS

- **Narrow band gap** (efficient light absorption).
- Adequate **band edge locations** for water reduction and oxidation reactions.
- High **chemical stability** in the dark and under illumination.
- **Good charge transport a**cross the semiconductor bulk.
- **Low overpotentials** for water oxidation and reduction reactions.

For the viability of a practical device:

- **Low cost reagents** for electrode synthesis.
- **Low cost** and **scalable synthesis route**.
- Materials composed of **Earth abundant elements**.
- **Non-toxic** and **environmental friendly** materials.

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ELECTRODE MATERIALS

1^{st} PEC cell

1972

Fujishima and Honda cell

Electrochemical Photolysis of Water at a Semiconductor Electrode

ALTHOUGH the possibility of water photolysis has been investigated by many workers, a useful method has only now been developed. Because water is transparent to visible light it cannot be decomposed directly, but only by radiation with wavelengths shorter than 190 nm (ref. 1).

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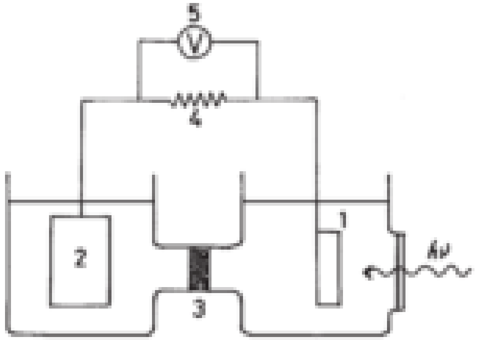

Fig. 2 Electrochemical cell in which the TiO_2 electrode is connected with a platinum electrode (see text). The surface area of the platinum black electrode used was approximately 30 cm^2.

photoanodes

n-TiO_2

n-$BiVO_4$

n-WO_3

n-hematite

Wide band gap
High stability

Wide band gap
Limited stability

photocathodes

p-Cu_2O

p-CuO

High photocurrents
Narrow band gap
Low stability

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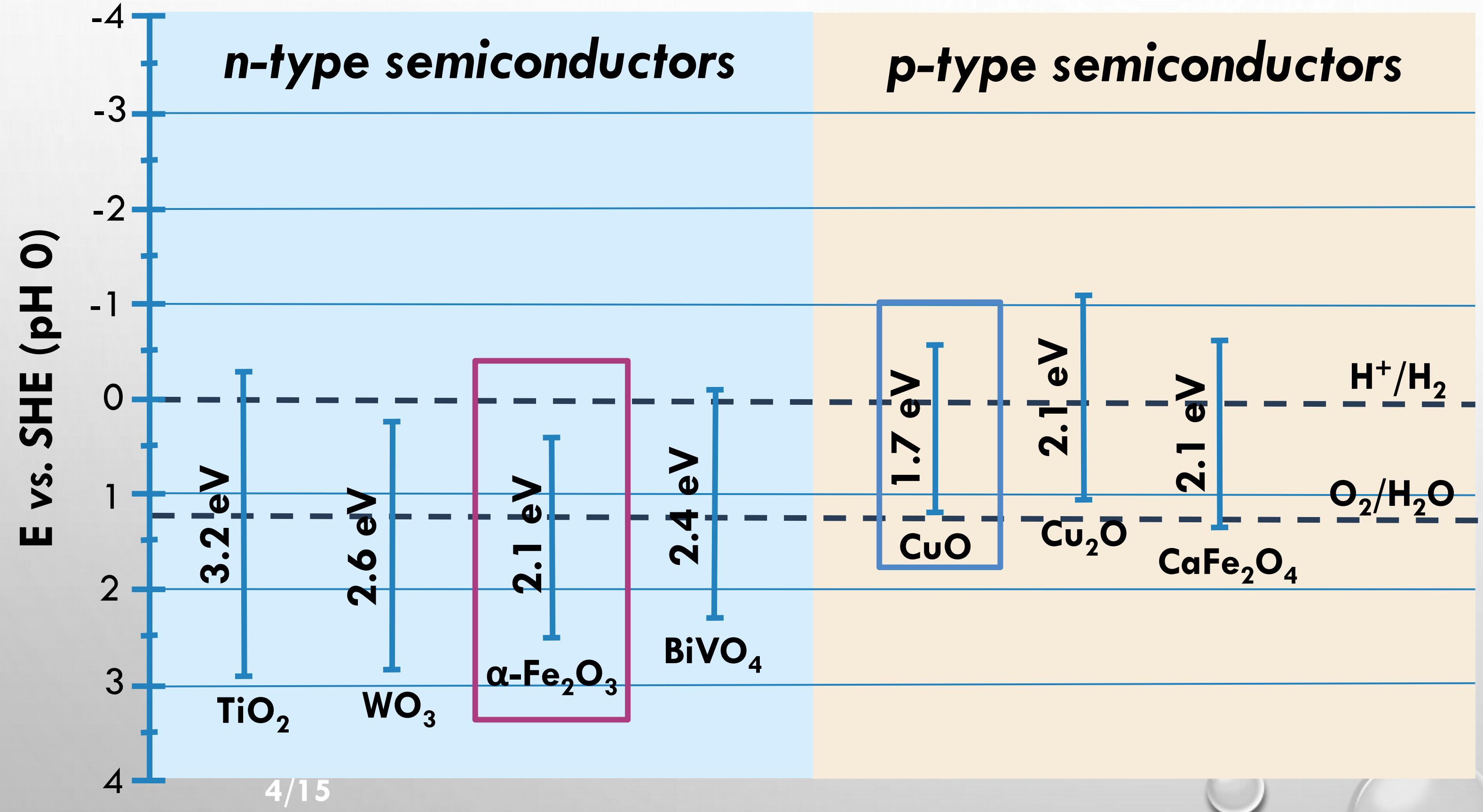
PEC CELL

- Among all the potential candidates, which to choose?



α-Fe_2O_3

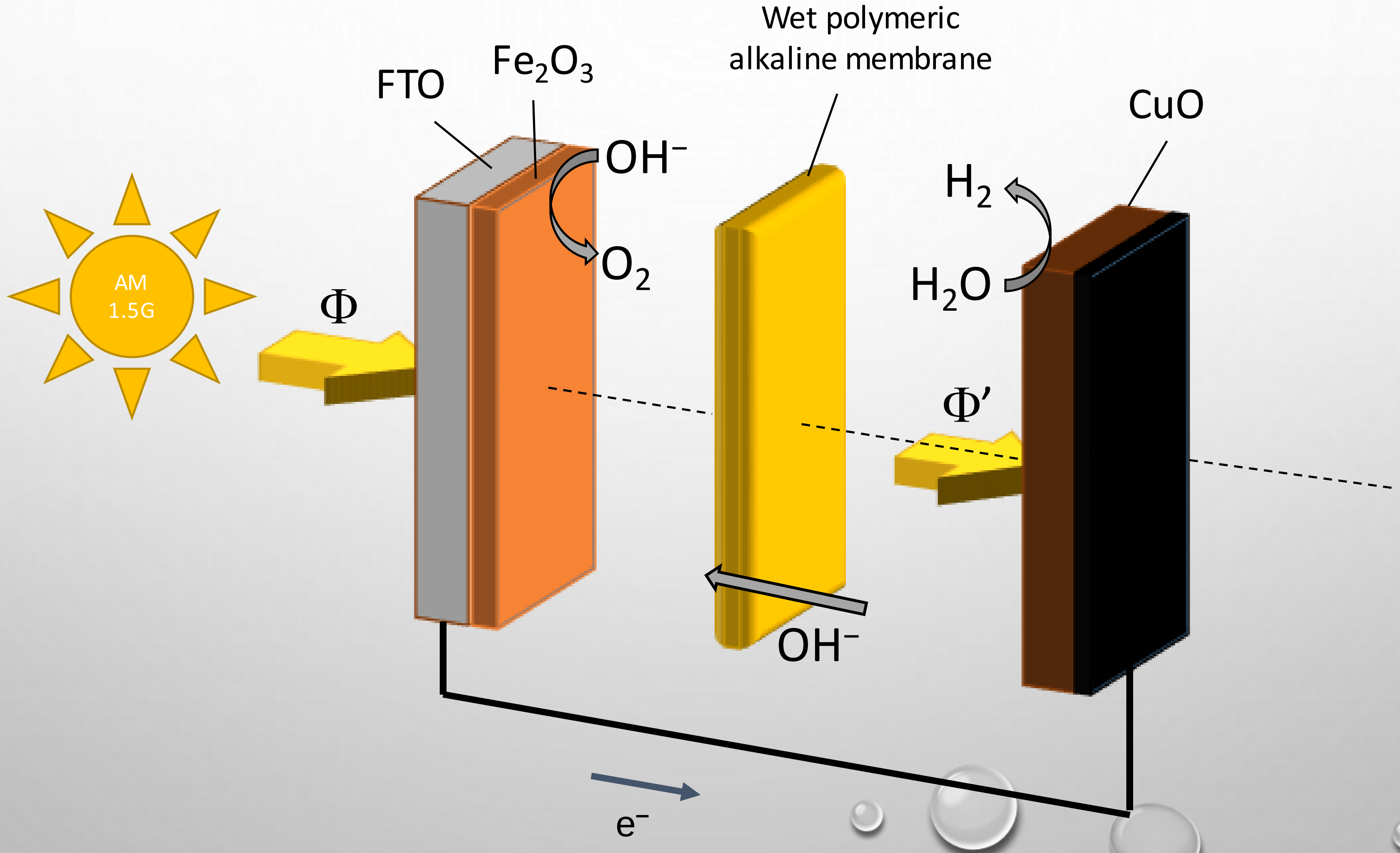
- Efficient light harvesting ✓
- Low cost ✓
- High stability ✓
- High recombination rate ✗

CuO

- Efficient light harvesting ✓
- Low cost ✓
- Low toxicity ✓
- Unstable ✗

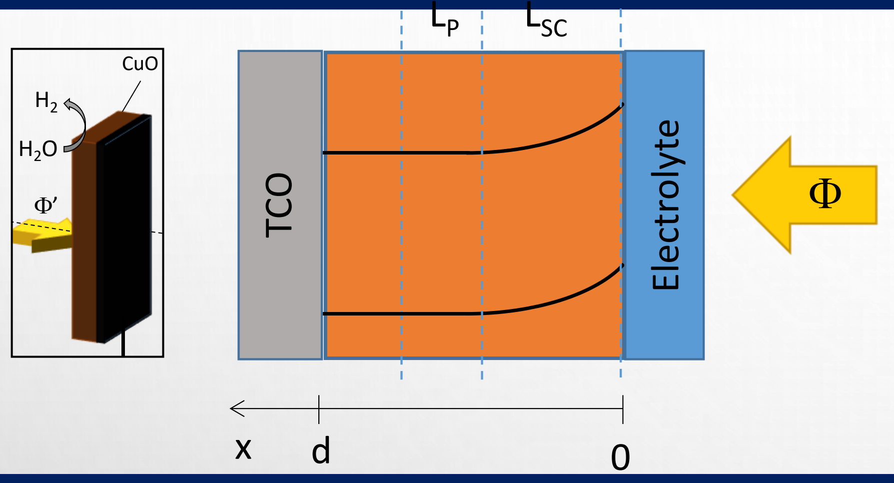
PEC CELL

Theoretical validation of the FOTOH2 concept

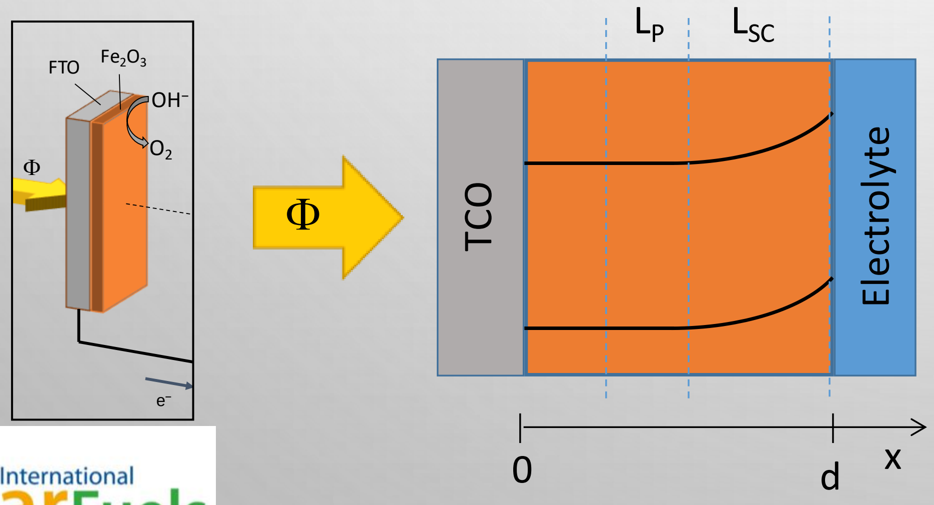


PEC CELL

MODEL FOR **FRONT** ILLUMINATION (PHOTOCATHODE)



MODEL FOR **BACK** ILLUMINATION (PHOTOANODE)



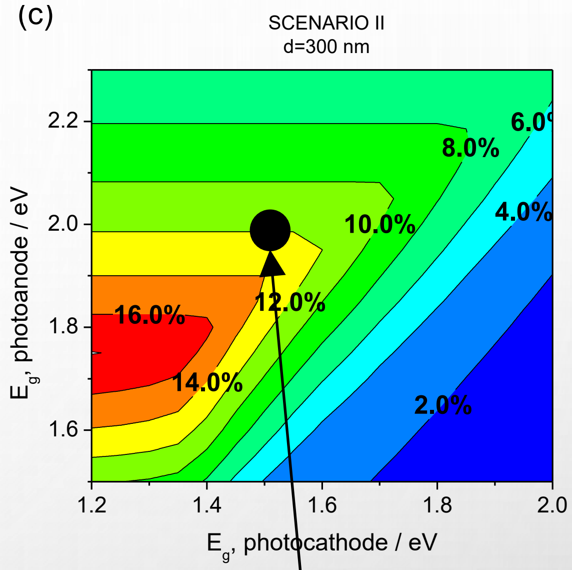
IMPROVEMENTS RESPECT TO THE ORIGINAL GÄRTNER MODEL:

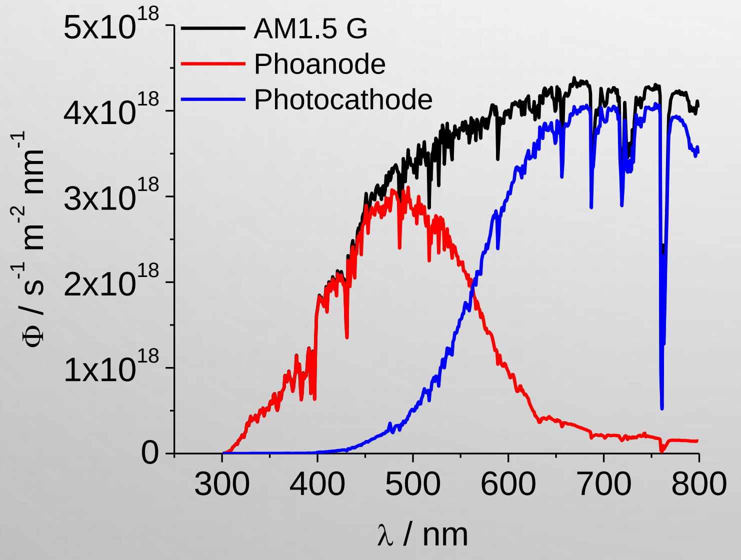
a) Polychromatic light: AM 1.5G (instead of monochromatic light)
b) Kinetic model (recombination and charge transfer rate constants)
c) Absorption coefficients as a function of the wavelength (Tauc relationships)

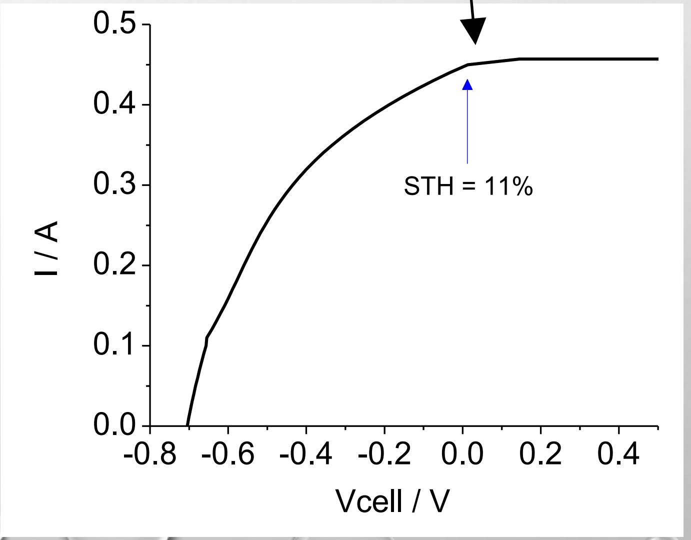
PEC CELL

TANDEM CELL: HEMATITE-CuO

PHOTOANODE		PHOTOCATHODE		MEMBRANE	
E_{fb} / V vs RHE	0.3	E_{fb} / V vs RHE	1	σ / S cm^{-1}	0.1
ε_{hem}	80	ε_{CuO}	115	L / µm	50
L_p / nm	5	L_n / nm	50	A / cm^2	50
A / cm^2	50	A / cm^2	50		
N_D / cm^{-3}	10^{17}	N_A / cm^{-3}	10^{17}	R (Ω)	0.001
d / mm	0.150	d / mm	2		





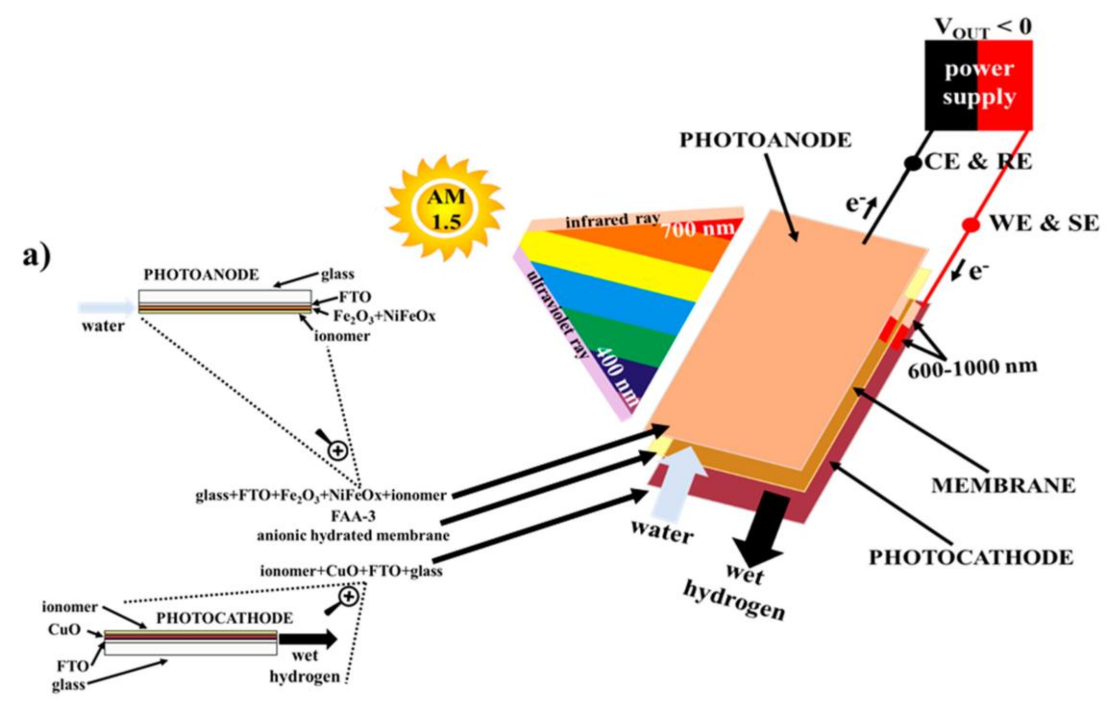


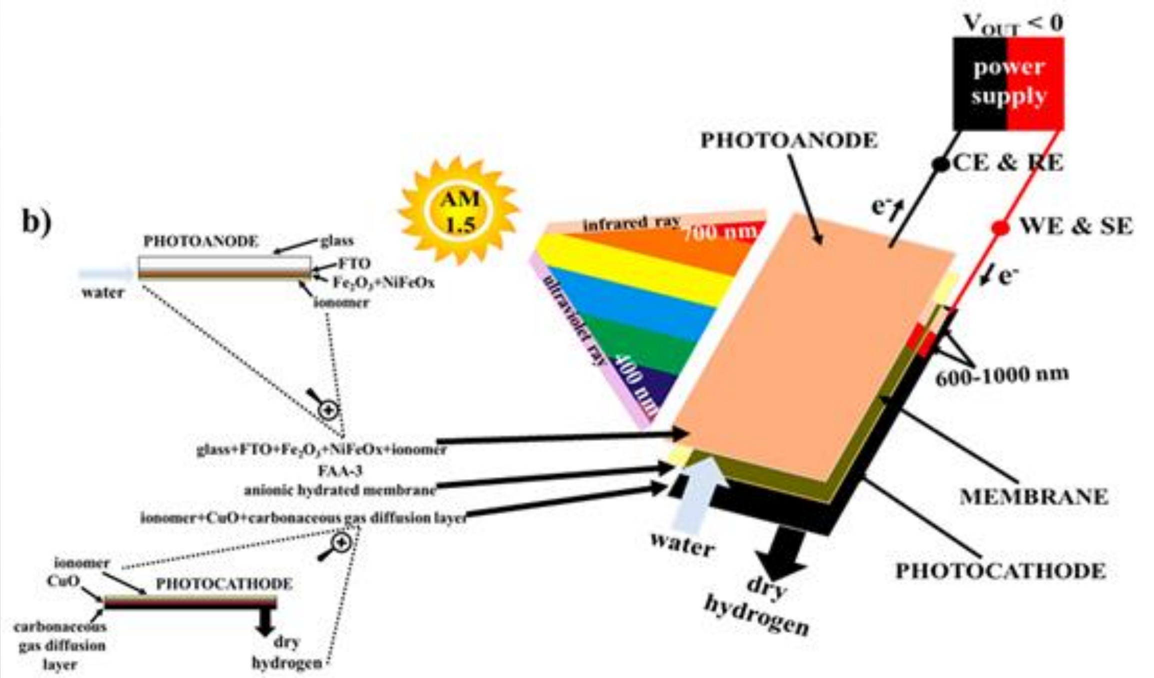
PEC CELL

- Electrolyte should have minimum light absorption and resistance
- Separator should avoid crossover of the electrolysis products
- Good scalability: flat configuration

→ POLYMER ELECTROLYTE MEMBRANE

FTO-SUPPORTED PHOTOCATHODE → PHOTOCATHODE SUPPORTED ON CARBONACEOUS GAS DIFFUSION LAYER → DRY HYDROGEN

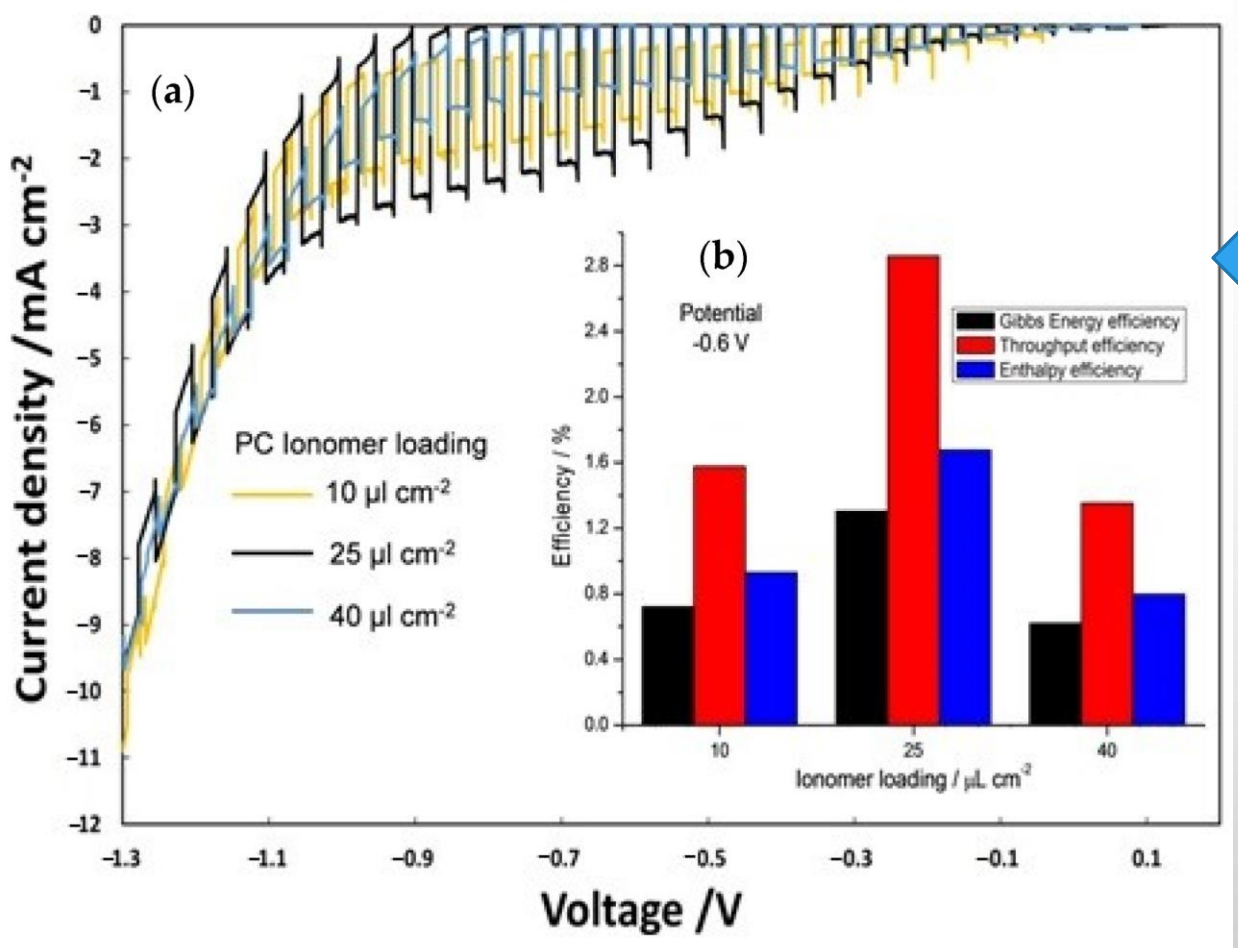




Catalysts **2020**, *10*(11), 1319

PEC CELL

MEMBRANE ELECTRODE ASSEMBLY



- Fumasep membrane (FAA3-50 from Fumatech)
- Thickness of 50 µm
- Based on a brominated polysulfone backbone with quaternary ammonium side chain groups

EFFECT OF THE IONOMER DISPERSION LOADING

Enthalpy efficiency $\eta_{Enth} = I_p\,(\Delta H/nF - E_{bias})/P_{in} = I_p\,(E_{tn} - E_{bias})/P_{in}$

Gibbs Energy efficiency $\eta = I_p\,(\Delta G/nF - E_{bias})/P_{in} = I_p\,(E_{rev} - E_{bias})/P_{in}$

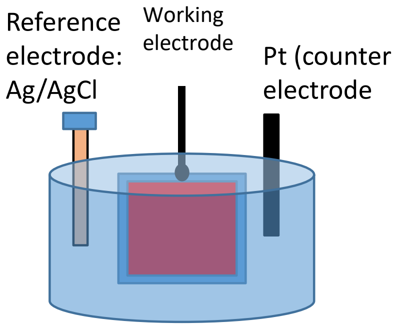
Throughput efficiency $\eta_{throughput} = I_p\,(\Delta H/nF)\,/(P_{in} + I_p\,E_{bias}) = I_p\,E_{tn}/(P_{in} + I_p\,E_{bias})$

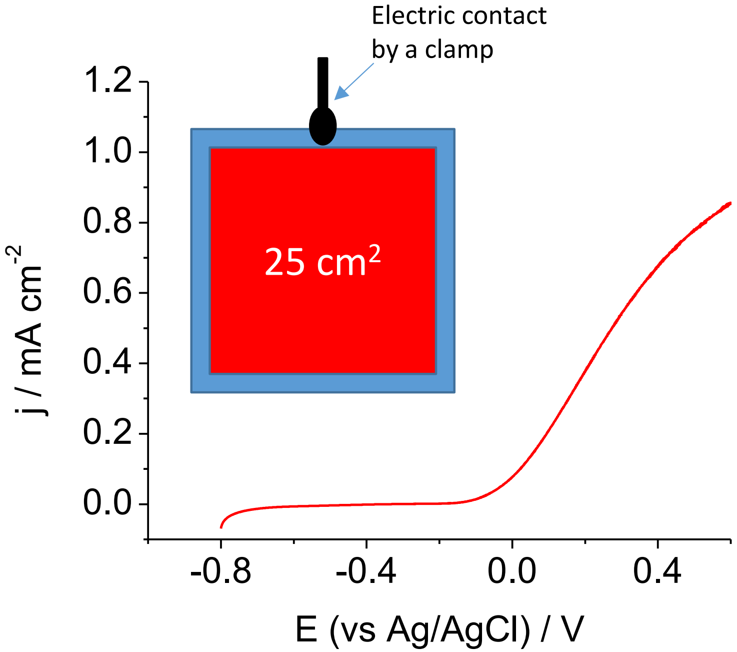
$E_{tn} = 1.48$ V, $E_{rev} = 1.23$ V, $E_{bias} \equiv$ V, $P_{in} \equiv$ mW cm^{-2} and $I_p = I_{light} - I_{dark} \equiv$ mA cm^{-2}.

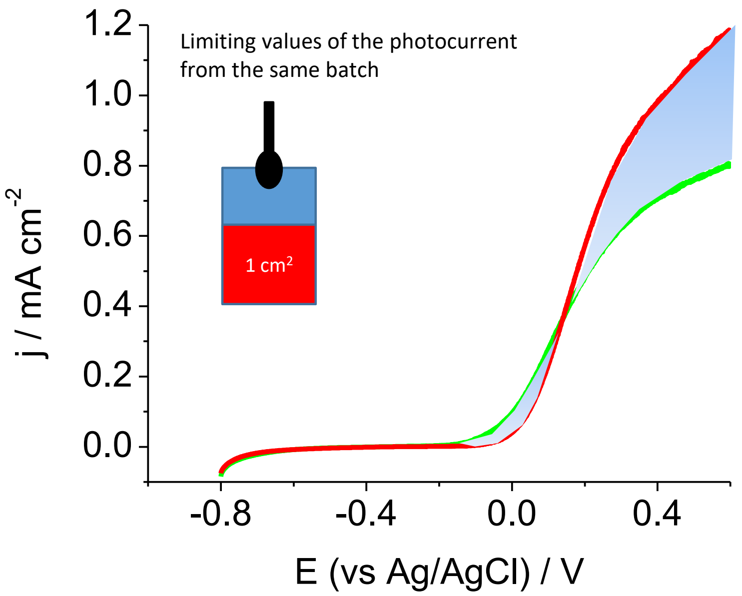
Polymers **2020**, *12*(12), 2991

TOWARDS A PANEL

EFFECT OF THE FTO CONDUCTIVITY IN THE 25 cm^2 HEMATITE PHOTOANODE

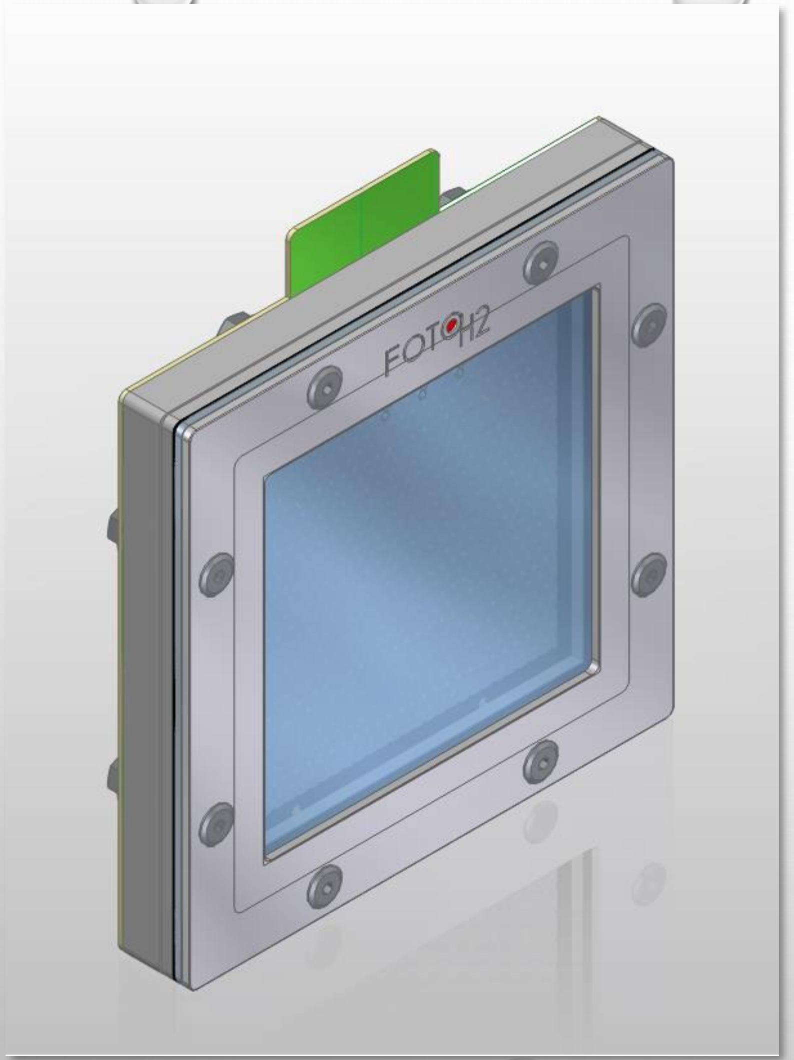


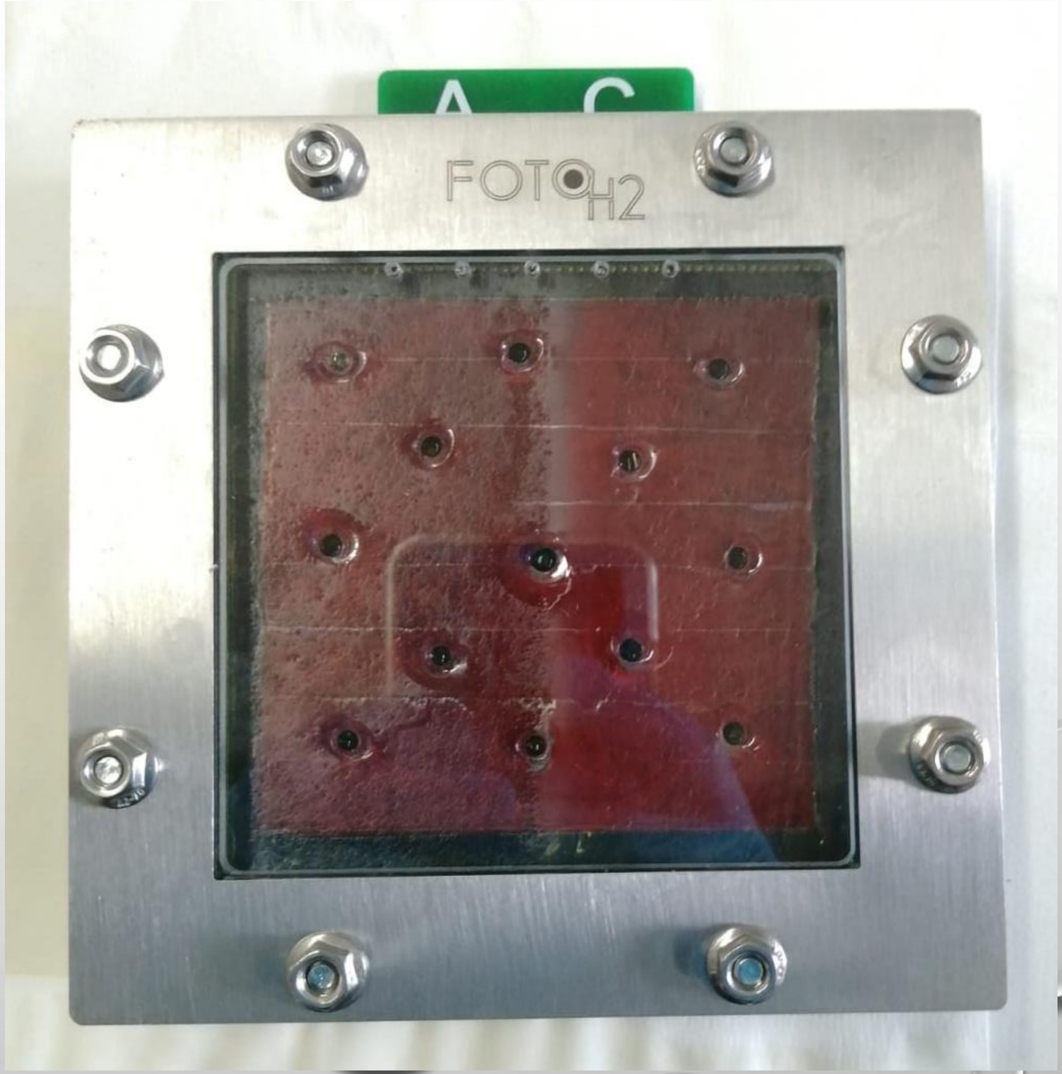




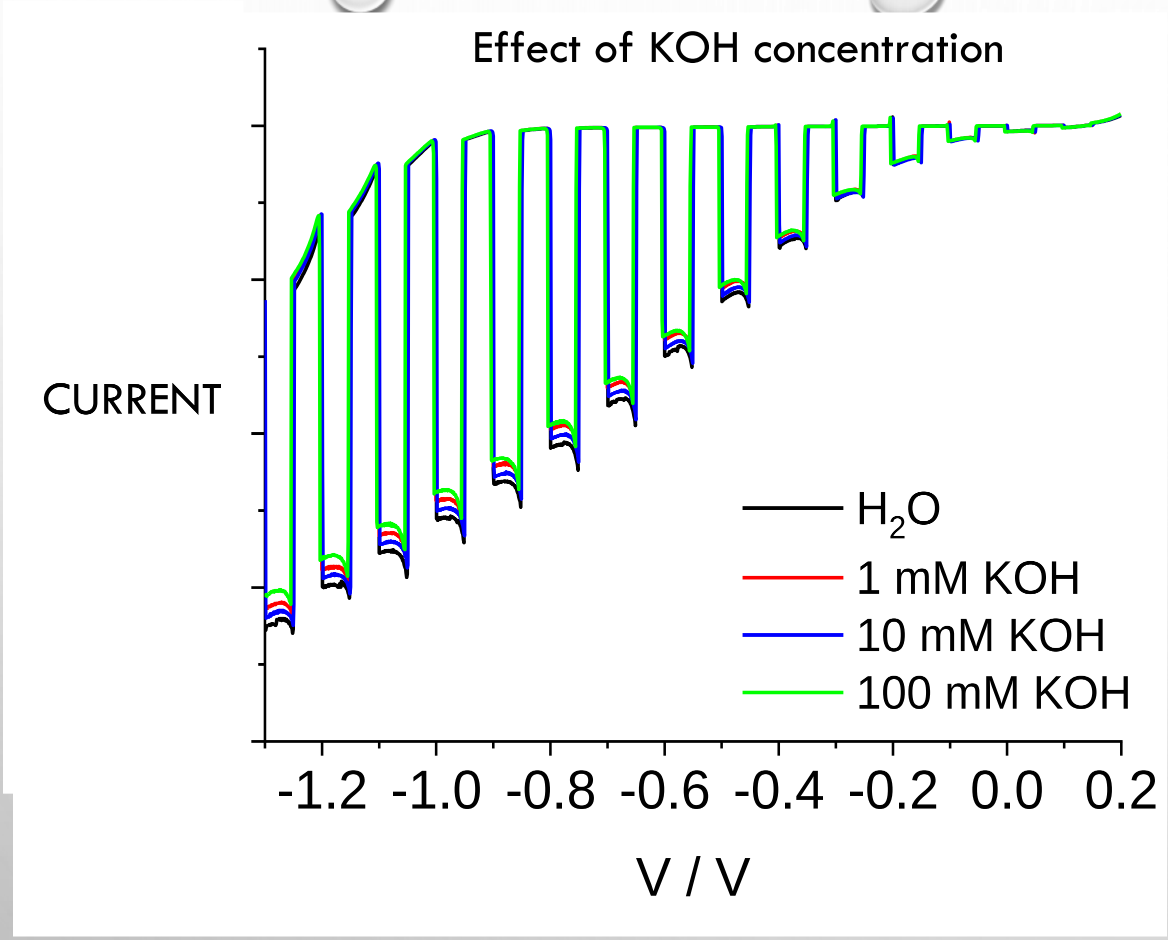
Conductivity of the glass is not the main limitation of the photocurrent.

SCALING-UP THE PEC CELL





SCALING-UP THE PEC CELL



KOH concentration does not affect tandem cell photoresponse

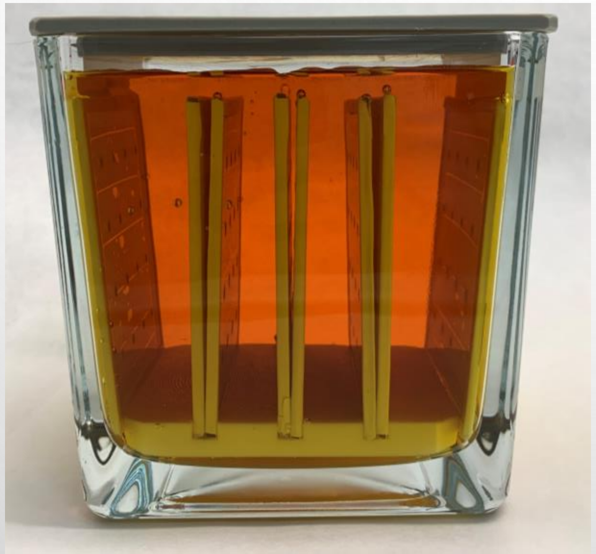
All measurements in this presentation are done in N_2-purged water

TOWARDS A PANEL

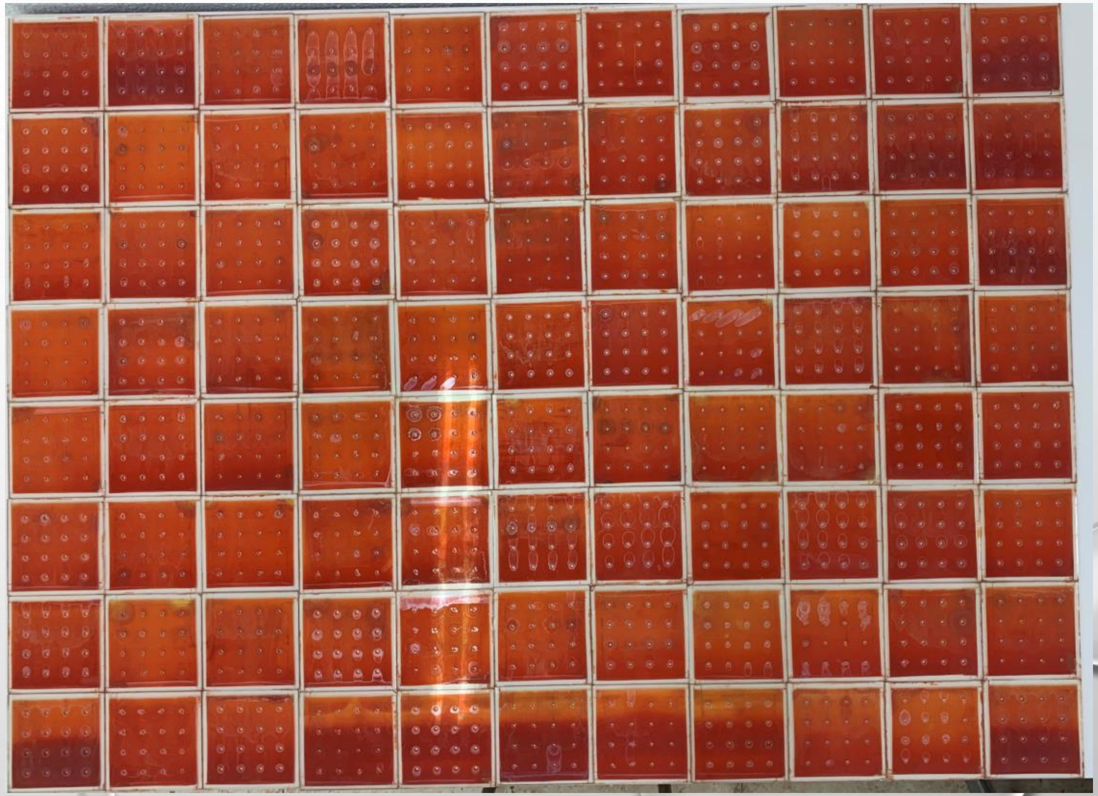
Up to 4 electrodes at once

Up to 8 electrodes at once

First reactor design

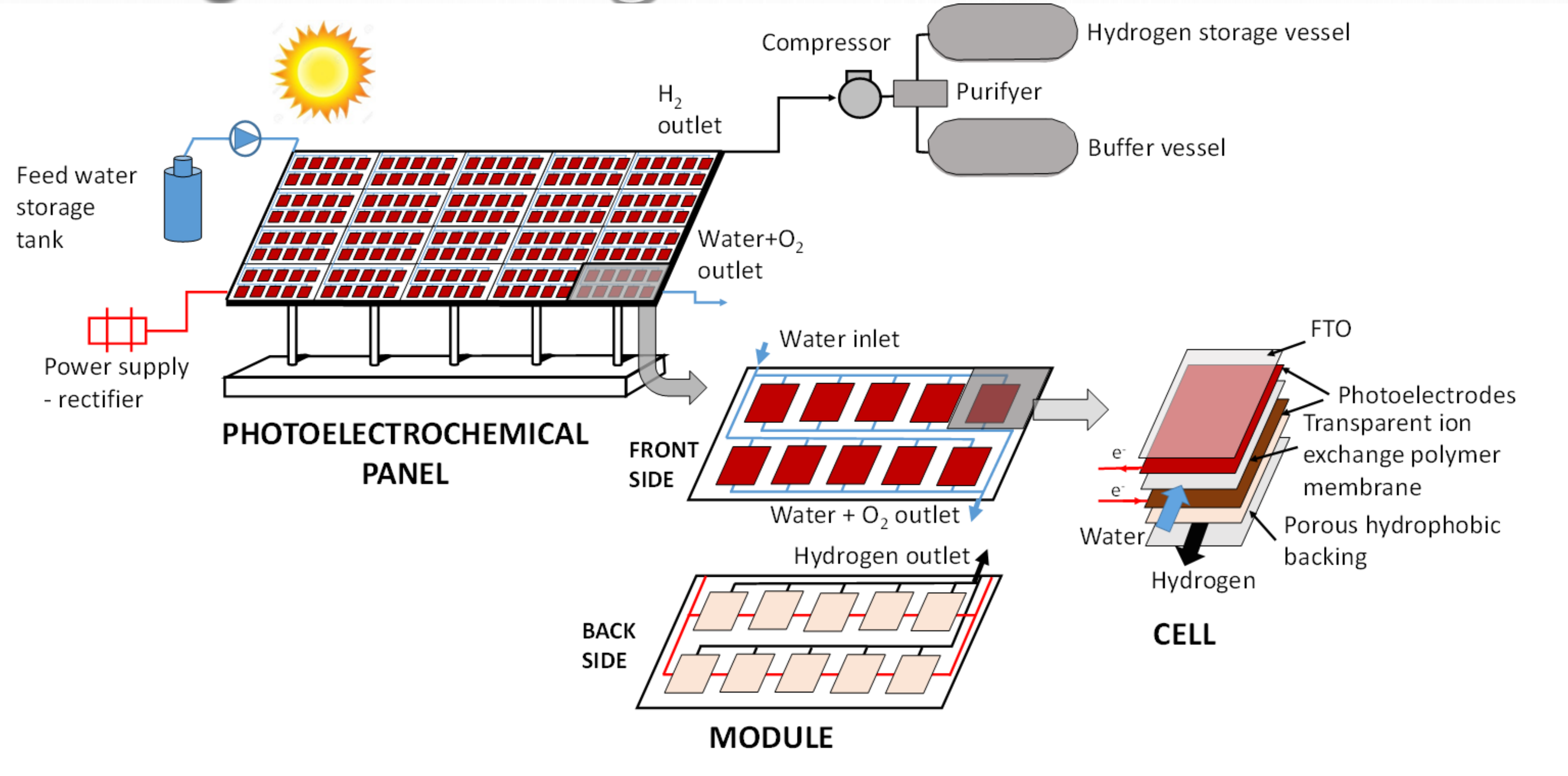


Final reactor design



Synthetized hematite electrodes

TOWARDS A PANEL



CONCLUSIONS

- **EFFICIENT OXIDE/POLYMER ELECTROLYTE MEMBRANE CONFIGURATION**
- **GOOD SCALABILITY OF HEMATITE ELECTRODES**
- **INTERFACE PHOTOELECTRODE/PEM DESIGNED FOR MINIMIZING CHARGE TRANSFER RESISTANCE**
- **FLAT CELL CONFIGURATION FED WITH WATER**
- **NOVEL CELL, MODULE AND ANCILLARY EQUIPMENT DESIGN**

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