



# Hydrogen generation with polymer electrolyte membranes water photoelectrolyzers: from materials selection to device construction

**Roberto Gómez**

Departament de Química-Física i Institut Universitari d'Electroquímica.  
Universitat d'Alacant. Alacant, Spain



# FOTCH<sub>2</sub>



This project has received funding from the European Union's  
Horizon2020 Framework Programme under grant agreement no 760930



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 Consiglio Nazionale  
delle Ricerche

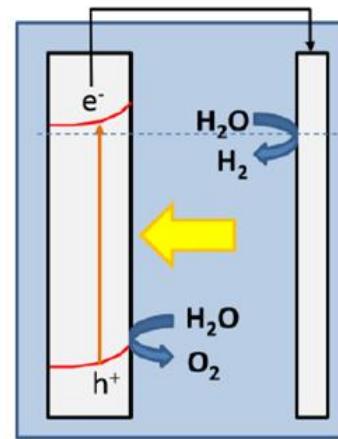


**FotoH2** shall develop a highly efficient tandem photoelectrolysis cell for solar H<sub>2</sub> production, based on **durable** and **cost-effective** advanced materials and interfaces. The following specific breakthroughs are targeted:

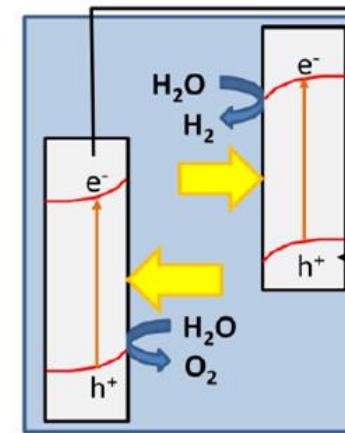
- Developing cost-effective advanced photoelectrode materials
- Achieving long-lasting cells for solar H<sub>2</sub> production
- Simple flow-cell design
- Production of pure H<sub>2</sub> in the output stream
- High Solar-to-Hydrogen conversion efficiency

# Cell architecture

One photoelectrode



Two photoelectrodes



Simple cell design

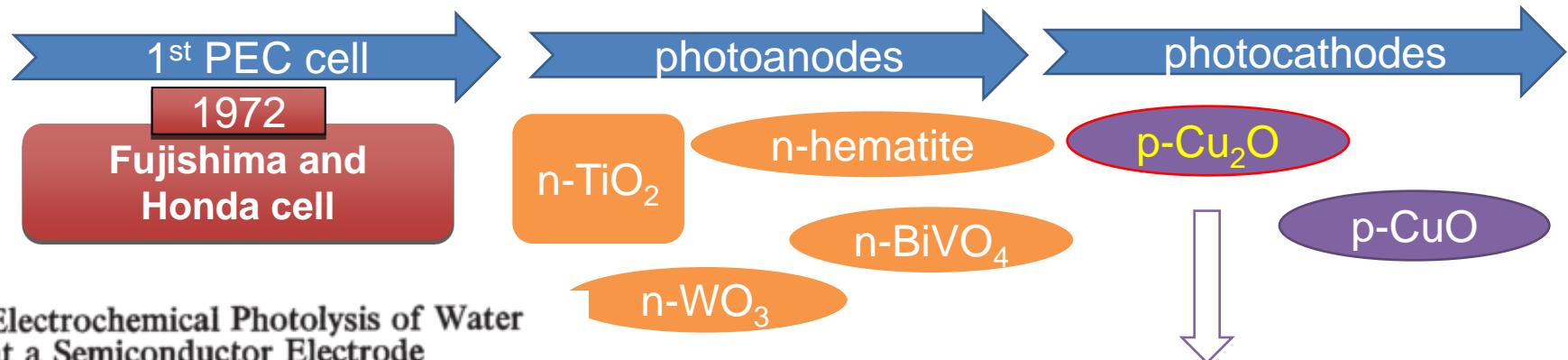
Flexibility in materials selection  
Higher efficiencies (TANDEM)

## 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** across 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.



### 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).

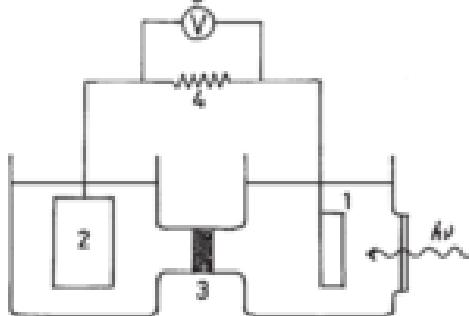


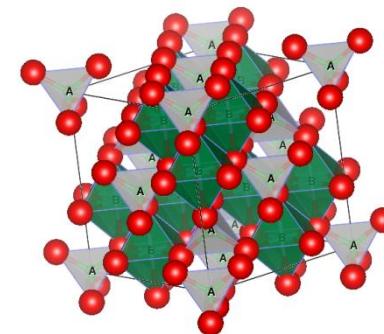
Fig. 2. Electrochemical cell in which the TiO<sub>2</sub> electrode is connected with a platinum electrode (see text). The surface area of the platinum black electrode used was approximately 30 cm<sup>2</sup>.

High photocurrents  
Narrow band gap  
Low stability X

## TERNARY METAL OXIDES AS PHOTOCATHODES

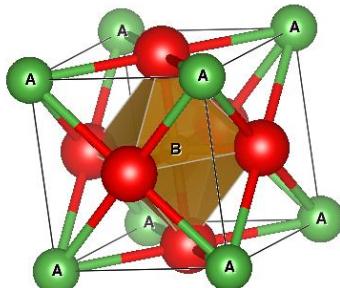
SPINELS:  $AB_2O_4$ 

$CaFe_2O_4$   
 $CuBi_2O_4$   
 $ZnRh_2O_4$



## PEROVSKITES:

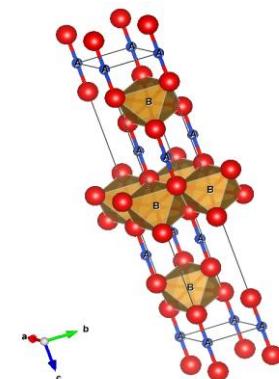
$ABO_3$   
 $LaFeO_3$   
 $CuNbO_3$



**GROUPS**

## DELAFOSSITES:

$ABO_2$   
 $CuFeO_2$   
 $CuCrO_2$   
 $CuRhO_2$



## OTHERS

$CuNb_3O_8$   
 $Cu_3Ta_7O_{19}$   
 $Fe_{0.84}CrAl_{0.16}O_3$   
 $La_2CuO_4$

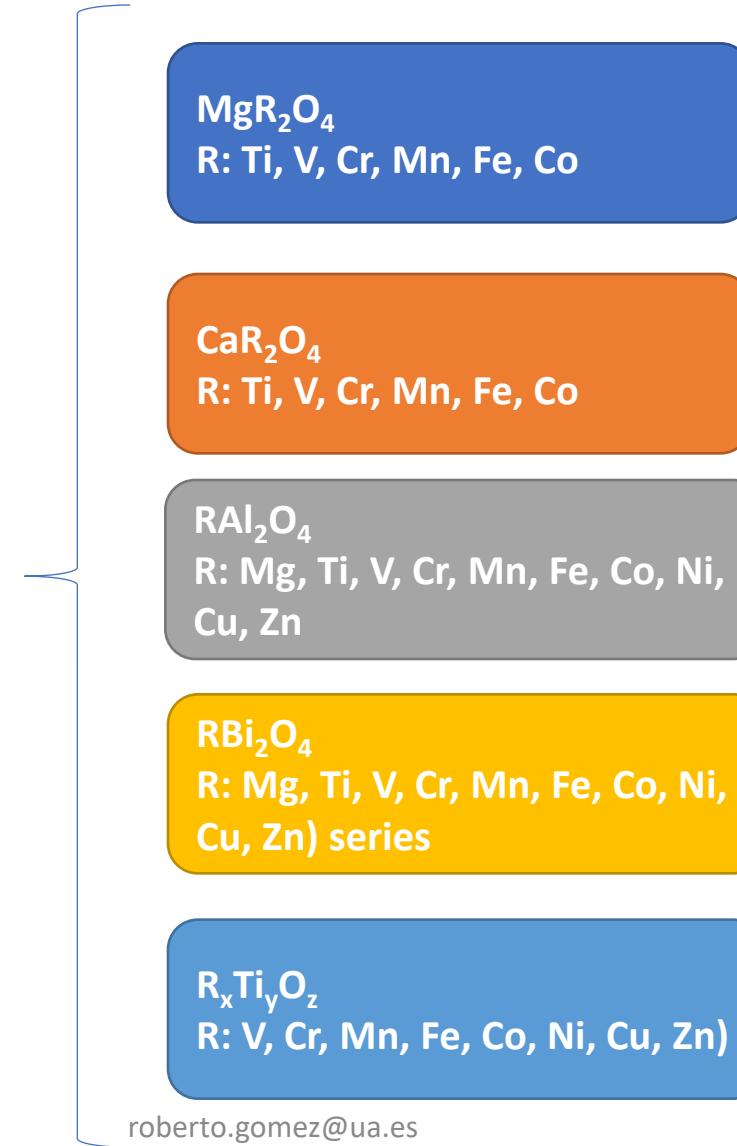
### METHODOLOGY:

1. Bibliographic search: To know which materials were already well characterized (experimentally and theoretically) with consistent results from different research groups. The computational screening was applied to those materials with either no data or disagreeing data reported.

### 2. Screening methodology:

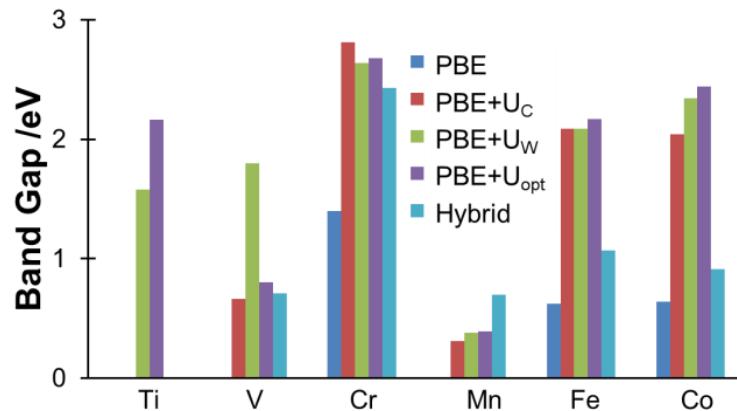
Density Functional  
Theory (DFT) based  
calculations

- Phase 1: Obtainment of reliable estimates of the **band gaps**. Those materials having either too low or too high band gap values were discarded.
- Phase 2: Evaluation of **transport properties** (carrier mobilities).

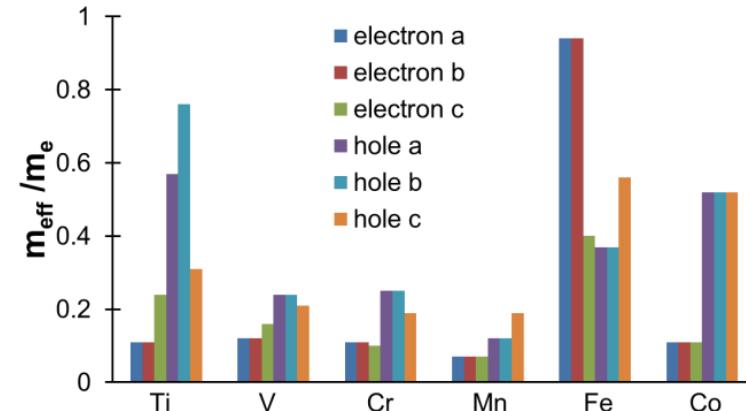
COMPUTATIONAL (DFT)  
SCREENED MATERIALS

## An example of computational screening: Mg spinels

Phase 1: band gap determination



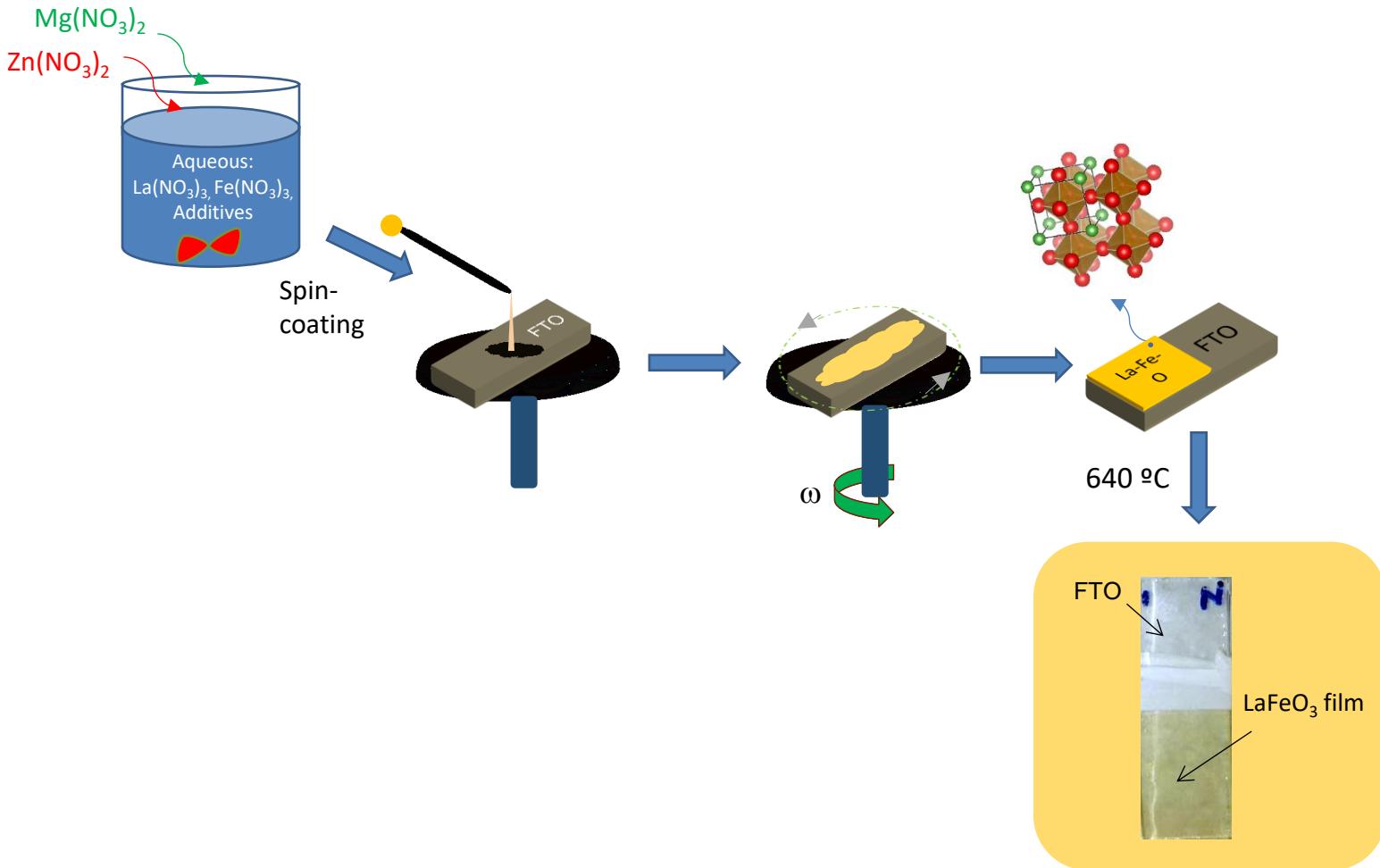
Phase 2: carrier mobility determination



Not reported synthesis

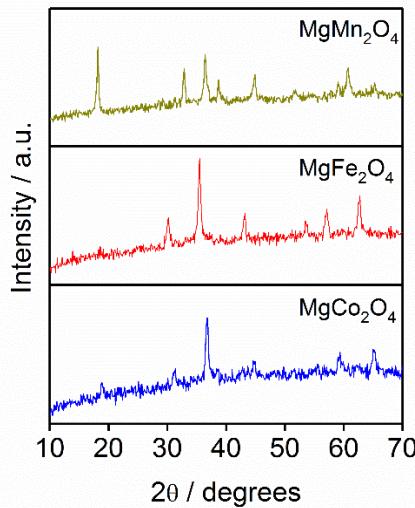
$\tau=1 \cdot 10^{-15}$ s	electron $\mu / \text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$			hole $\mu / \text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$			Gap / eV	Gap type	Observations
	a direction	b direction	c direction	a direction	b direction	c direction			
MgTi <sub>2</sub> O <sub>4</sub>	15.98	15.98	7.43	3.06	2.31	5.74	2.15	I	OS rare and low mob.
MgV <sub>2</sub> O <sub>4</sub>	14.61	14.61	10.67	7.24	7.24	8.49	0.82	I	low mob.
MgCr <sub>2</sub> O <sub>4</sub>	16.73	16.73	17.92	7.05	7.05	9.11	2.68	D	Gap too high
* MgMn <sub>2</sub> O <sub>4</sub>	25.22	25.22	24.66	14.79	14.79	9.05	0.39	D	Gap too low
* MgFe <sub>2</sub> O <sub>4</sub>	1.87	1.87	4.43	4.81	4.81	3.12	2.17	I	low mob.
* MgCo <sub>2</sub> O <sub>4</sub>	16.67	16.67	16.67	3.37	3.37	3.37	2.44	I	low mob.

## ➤ Electrode fabrication

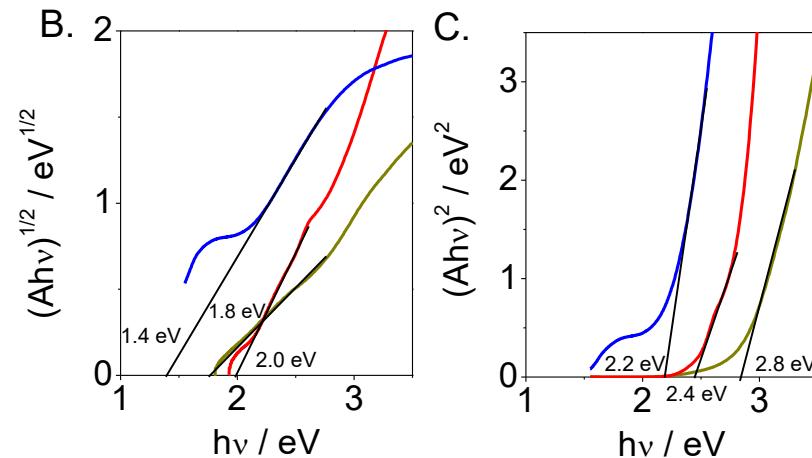


Benchmarking → Laboratory testing

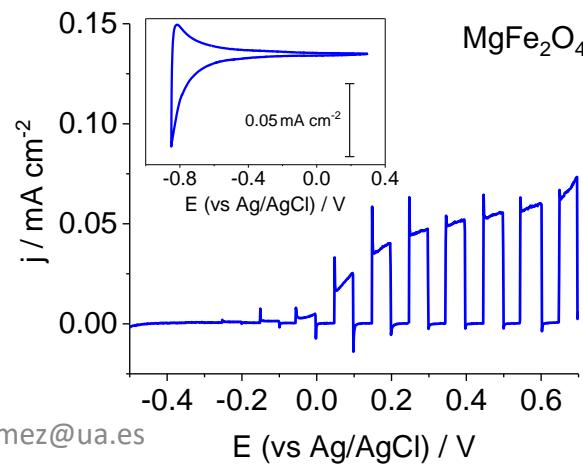
## □ X-ray diffractogram



## □ UV-visible spectra: TAUC PLOTS

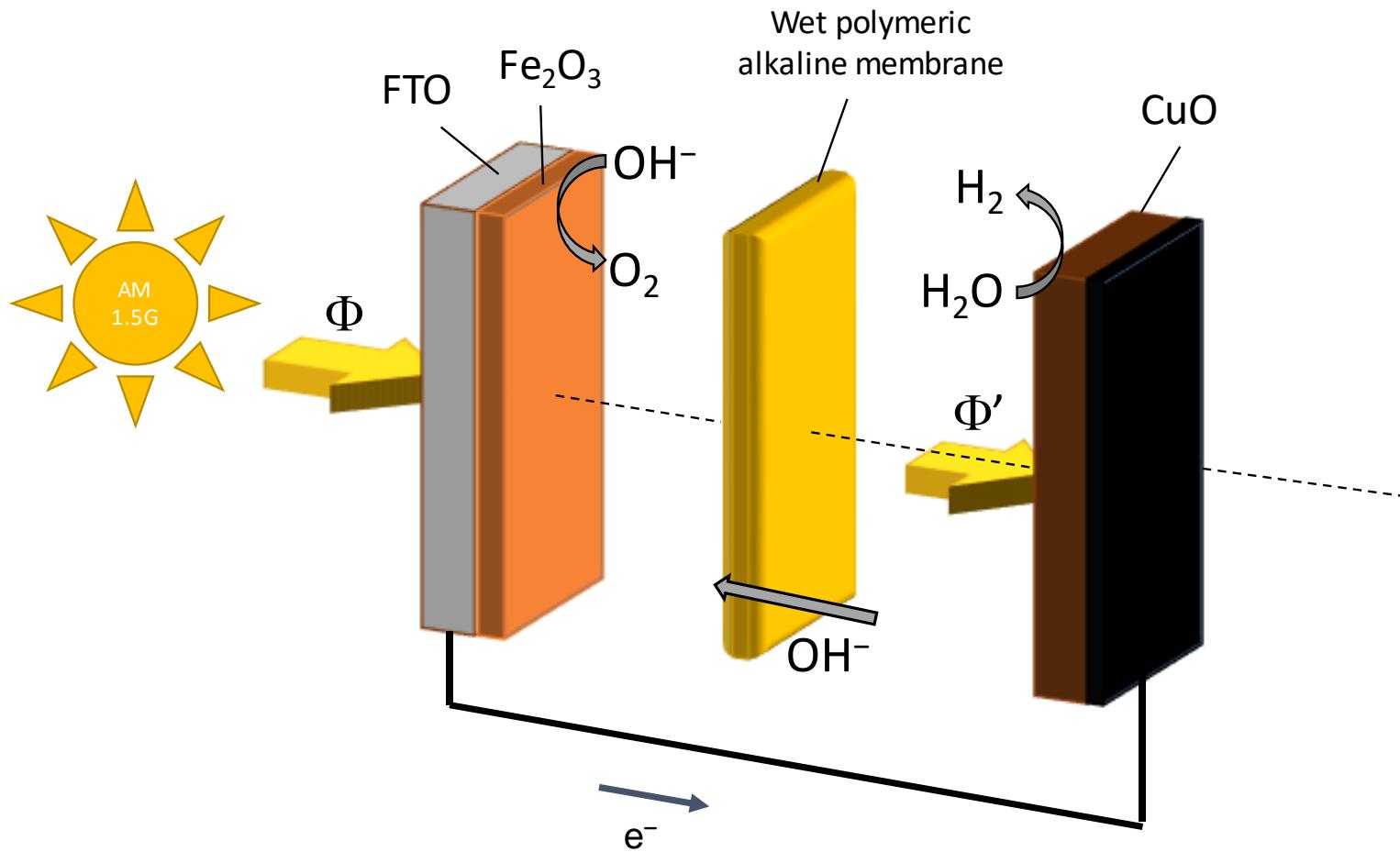


## □ Photoelectrochemical characterization



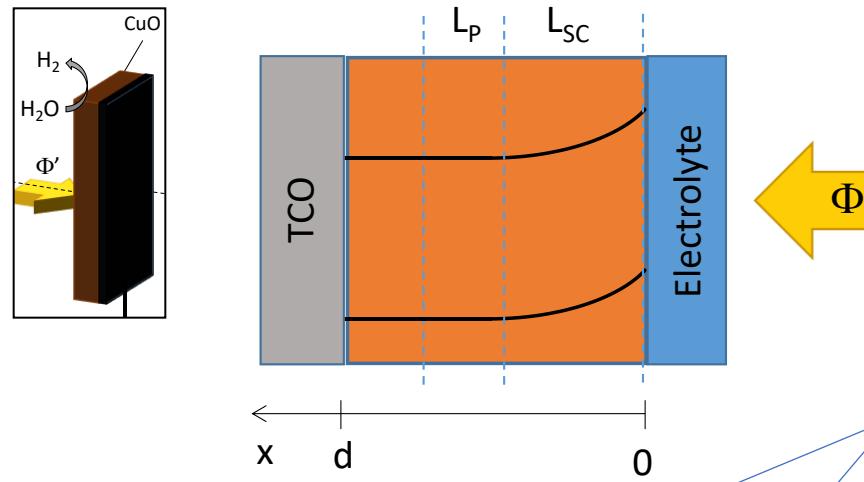
## 2. ANALYTICAL MODEL

Analytical model based on FOTOH2 concept



MODEL FOR FRONT  
ILLUMINATION (PHOTOCATHODE) 

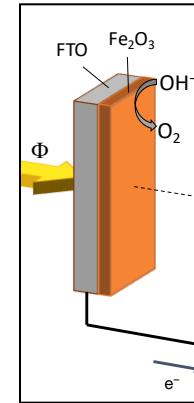
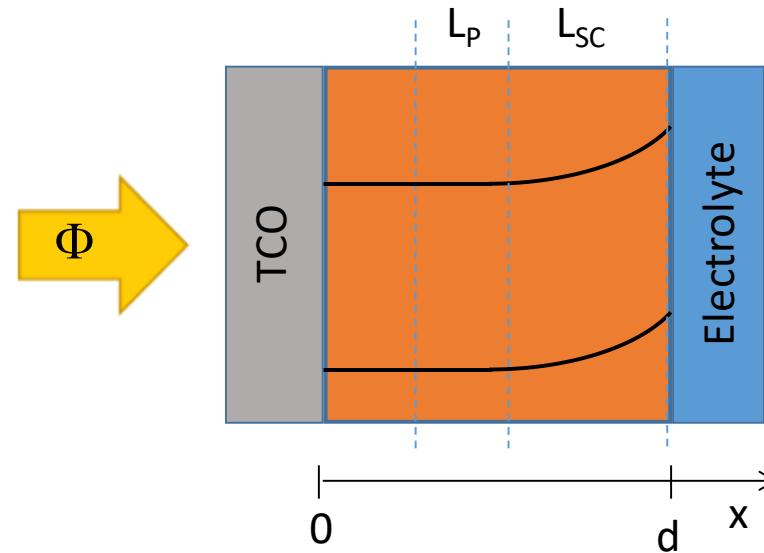
## GÄRTNER MODEL

IMPROVEMENTS RESPECT TO THE  
ORIGINAL 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)

$$j_{ph,cat} = q \frac{k_{trans,cat}}{k_{trans,cat} + k_{rec,cat}} \int_{\lambda_{min}}^{\lambda_{max}} \Phi'(\lambda) \left( 1 - \frac{e^{-\alpha'(\lambda)L_n^{cat}}}{1 + \alpha'(\lambda)L_n} \right) d\lambda$$

## 2. ANALYTICAL MODEL

MODEL FOR BACK ILLUMINATION  
(PHOTOCATHODE)

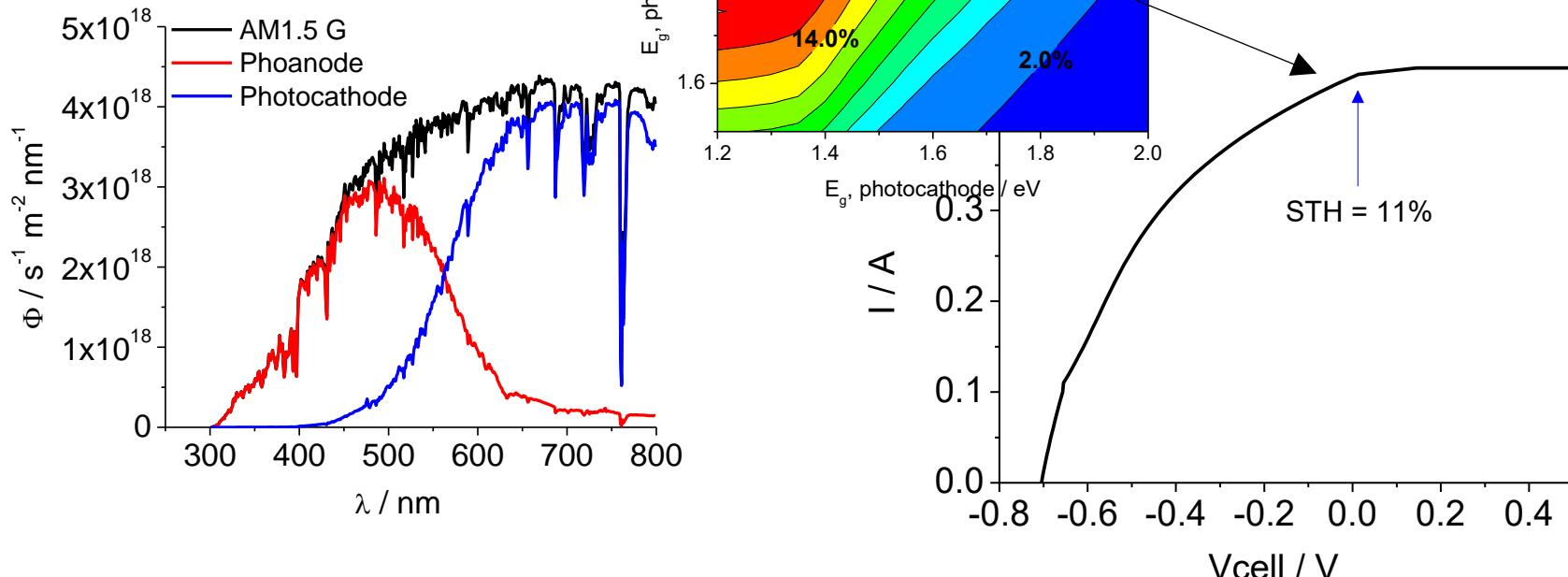
$$j_{TOT} = q \frac{k_{trans,an}}{k_{trans,an} + k_{rec,an}} \int_{\lambda_{min}}^{\lambda_{max}} \Phi(\lambda) \left[ \left( 1 + \delta \left( 1 + \frac{\tanh\left(\frac{d - L_{SC}^{an}}{L_p}\right)}{\alpha(\lambda)L_p} \right) \right) e^{\alpha(\lambda)(dL_{SC}^{an})} \left( \delta \operatorname{sech}\left(\frac{d - L_{SC}^{an}}{L_p}\right) + e^{-\alpha(\lambda)d} \right) \right] d\lambda$$

$$\text{where } \delta = \frac{(\alpha(\lambda)L_p)^2}{1 - (\alpha(\lambda)L_p)^2}$$

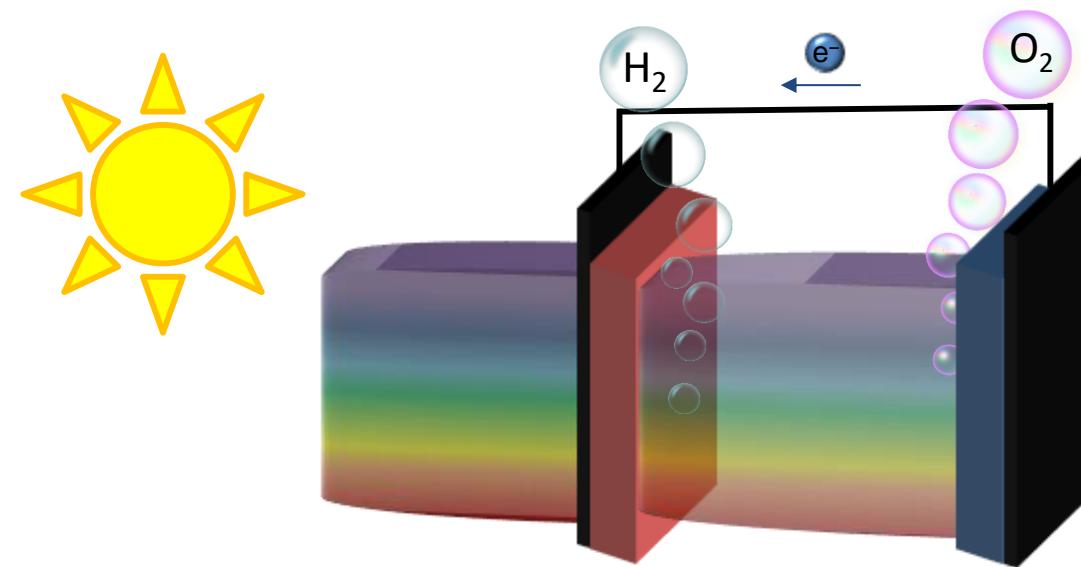
## 2. ANALYTICAL MODEL

### TANDEM CELL: HEMATITE-CuO

PHOTOANODE		PHOTOCATHODE		MEMBRANE	
$E_{fb}$ / V vs RHE	0.3	$E_{fb}$ / V vs RHE	1	$\sigma$ / S cm <sup>-1</sup>	0.1
(c) $\varepsilon_{hem}$	SCENARIO 80 $d=300$ nm	$\varepsilon_{CuO}$	115	$L$ / $\mu$ m	50
$L_p$			50	$A$ / cm <sup>2</sup>	50
$N_p$			50		
$d$			$10^{17}$	$R$ ( $\Omega$ )	0.001
			2		

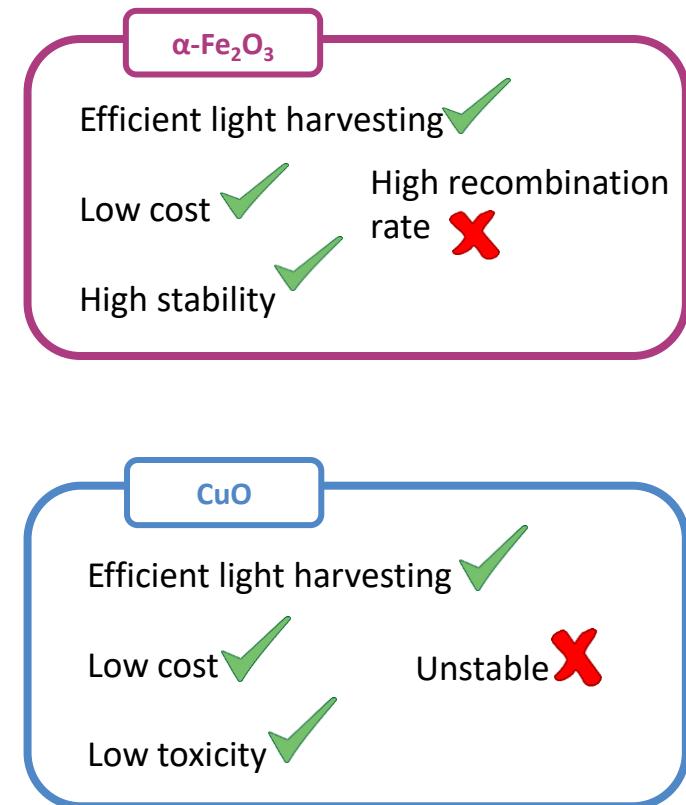
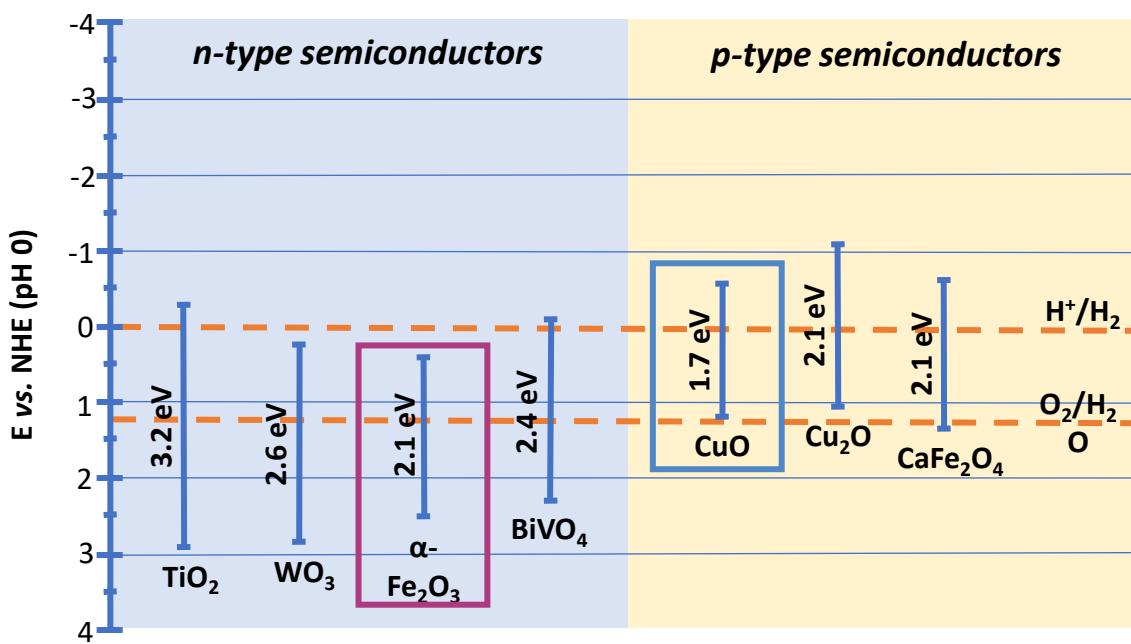


## Toward Tandem Solar Cells for Water Splitting using polymer electrolyte membranes



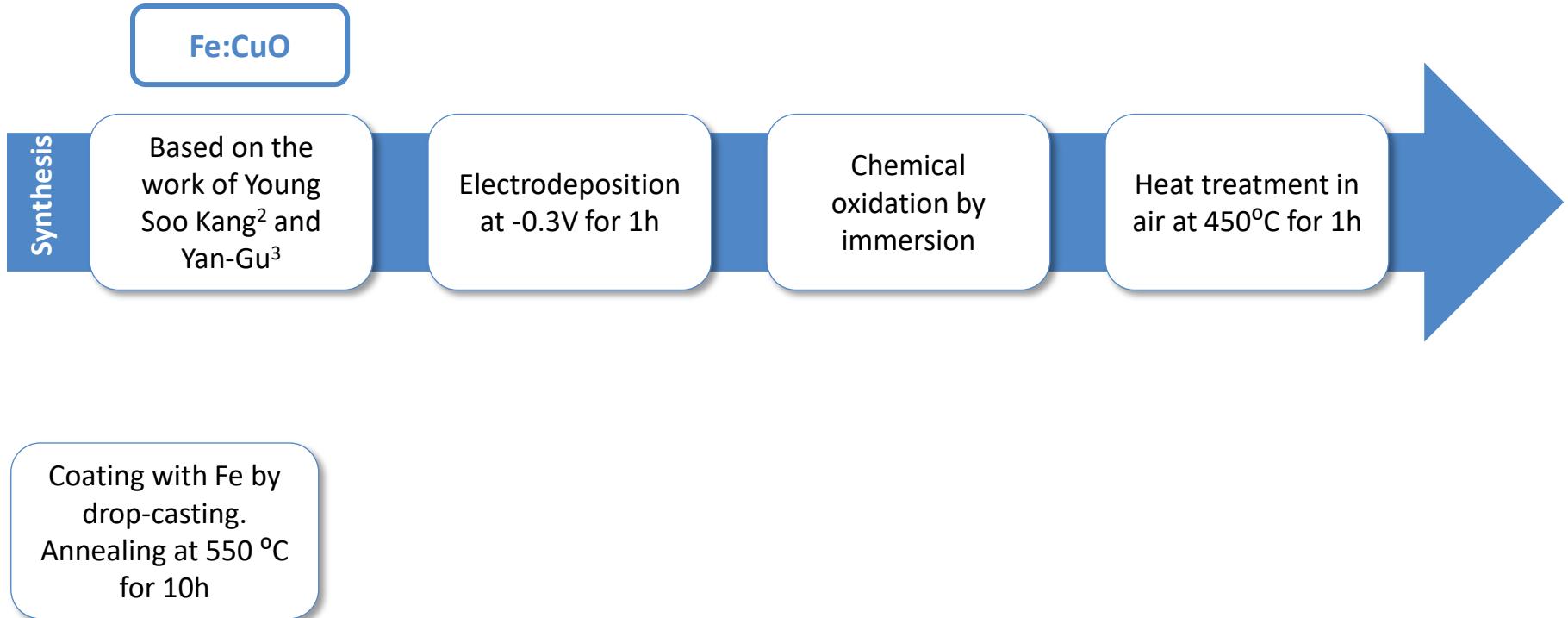
# PEM TANDEM CELL

➤ Among all the potential candidates, which to choose?



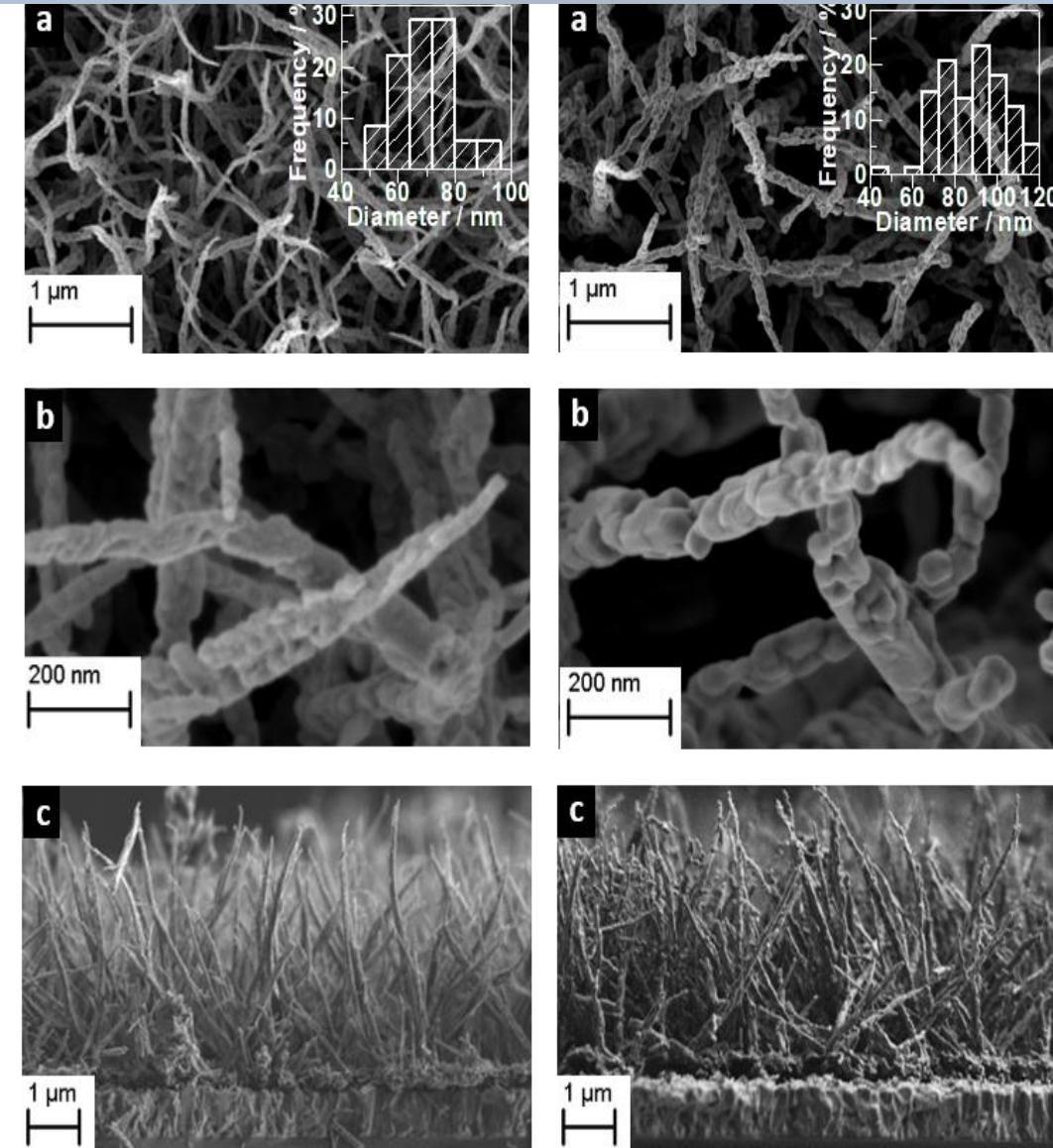


# PEM TANDEM CELL

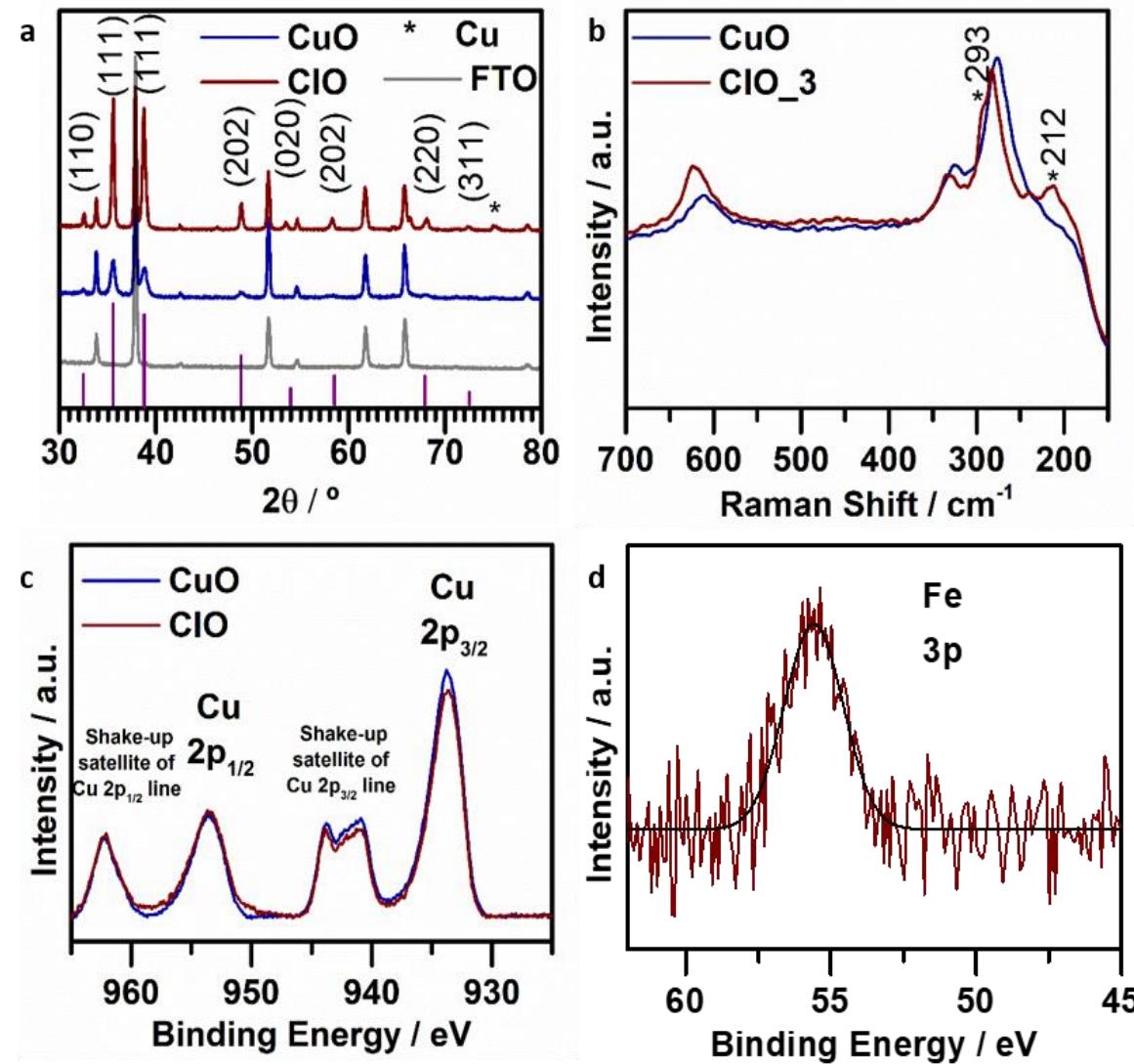


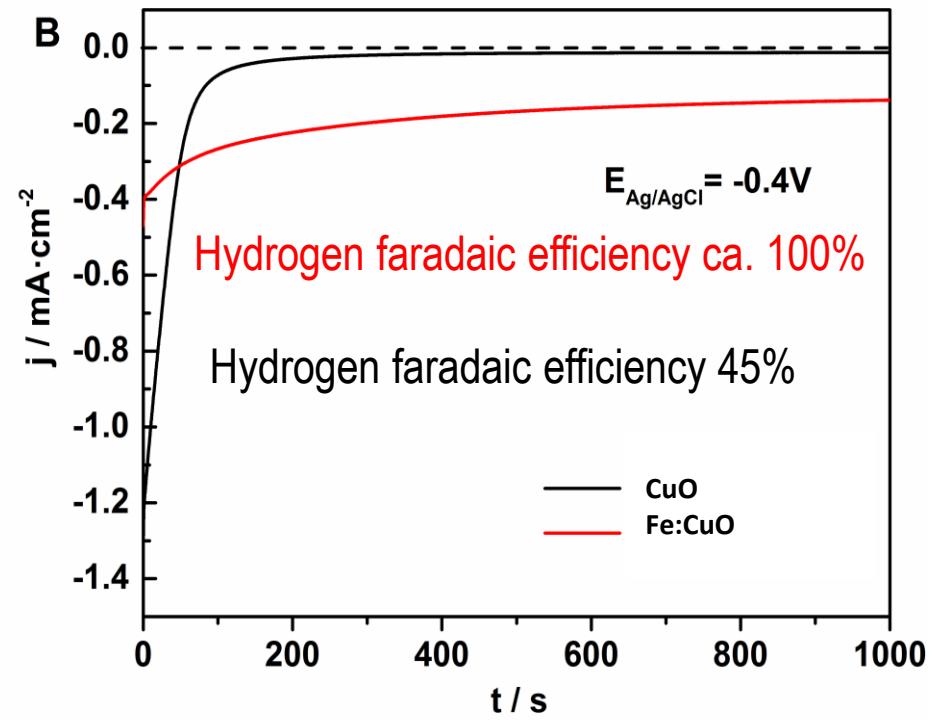
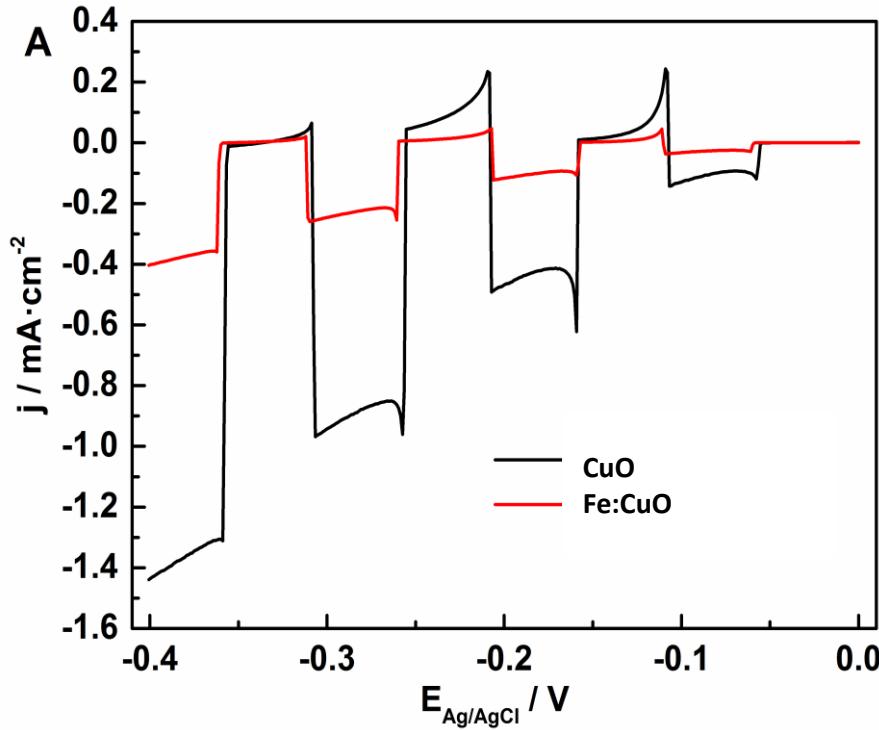
<sup>2</sup> *Electrochim. Acta* 69, 340-344 (2012); <sup>3</sup> *J. Electroanal. Chem* 704, 19-23 (2013)

# PEM TANDEM CELL



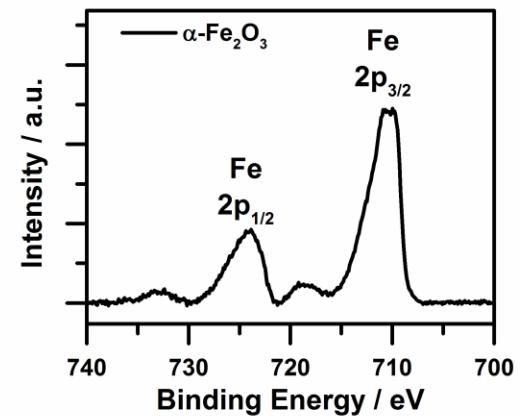
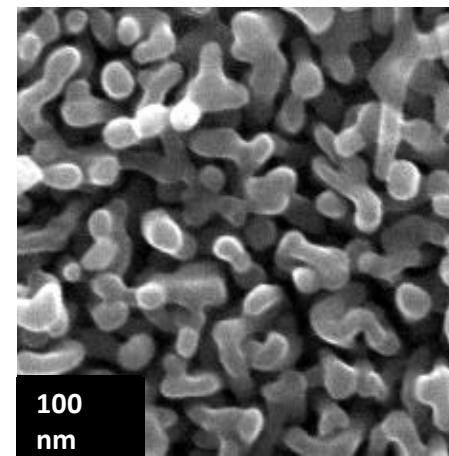
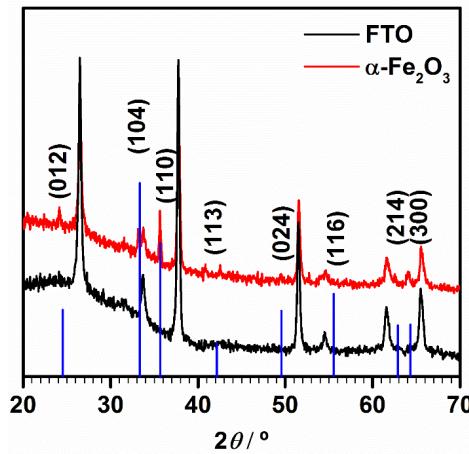
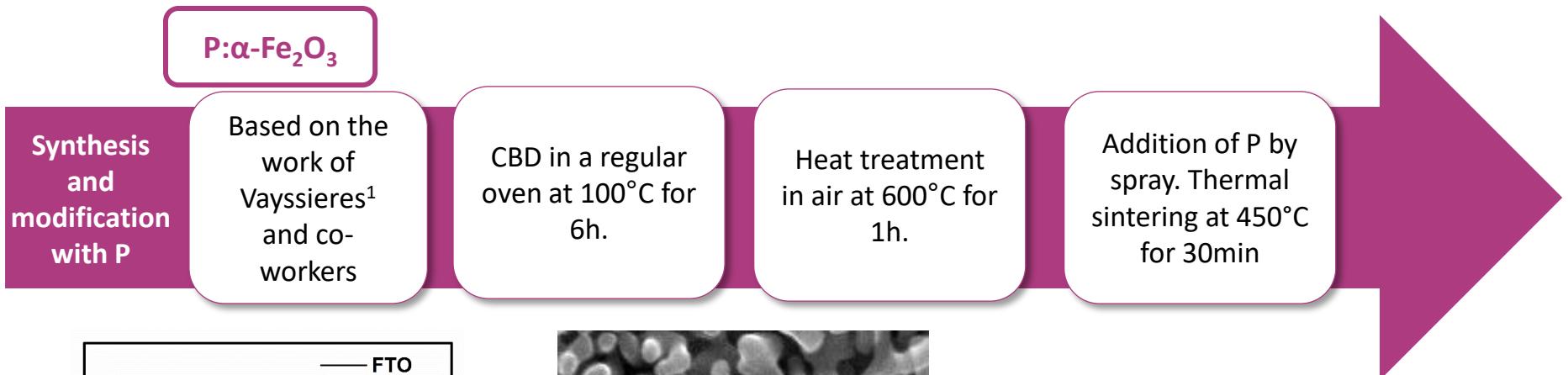
## PEM TANDEM CELL





A. Cots, P. Bonete, R.Gómez, ACS Appl. Mater. Inter., 2018

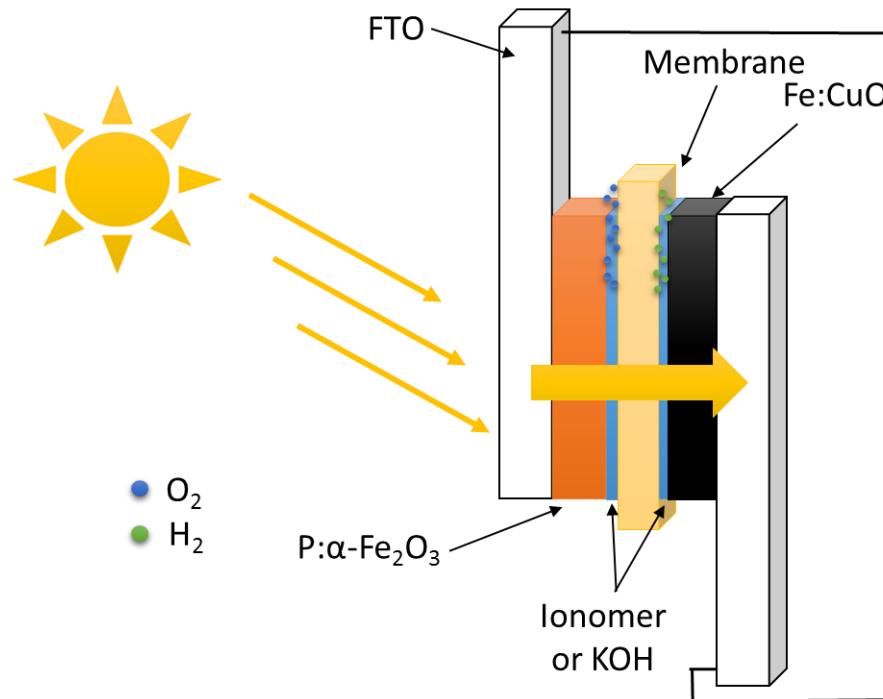
# PEM TANDEM CELL



<sup>1</sup> J. Electrochem. Soc. 147, 2456-2461 (2000)

# PEM TANDEM CELL

## ➤ Polymer Electrolyte Membranes for Water Splitting, why?



- Gas separator
- Decreases the corrosion of the electrodes



**Increase the stability of the device**

- Ionomer dispersions extend the interface with the electrolyte

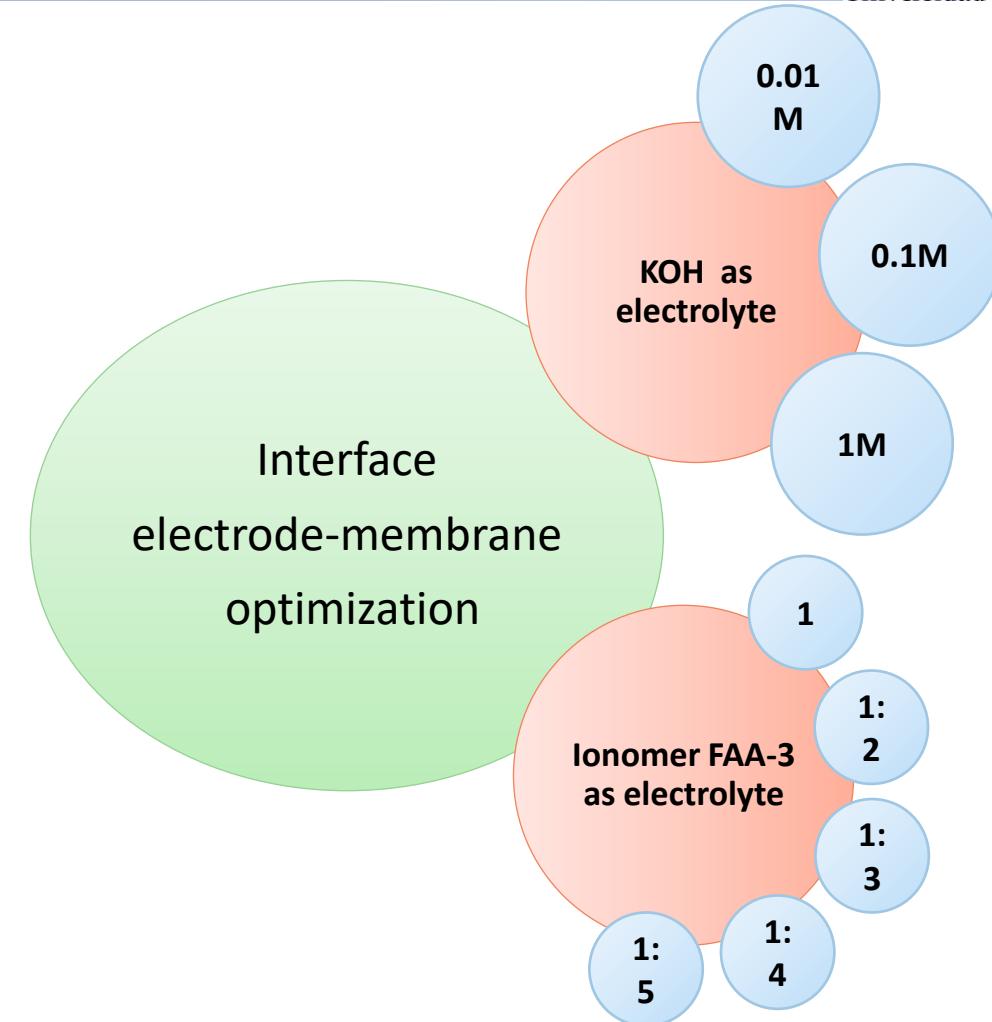
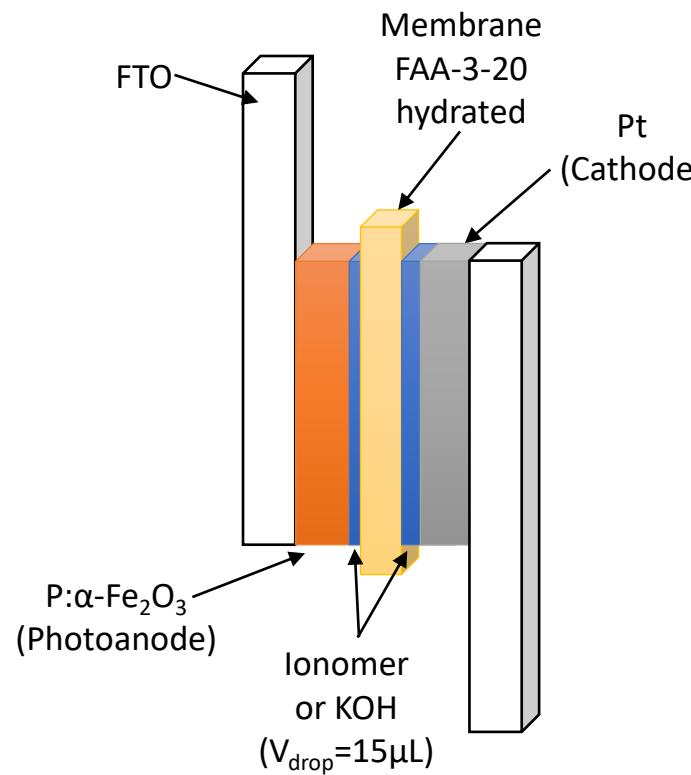


- Lower ionic conductivity
- Cross Over
- Potential problems of transparency

# PEM TANDEM CELL

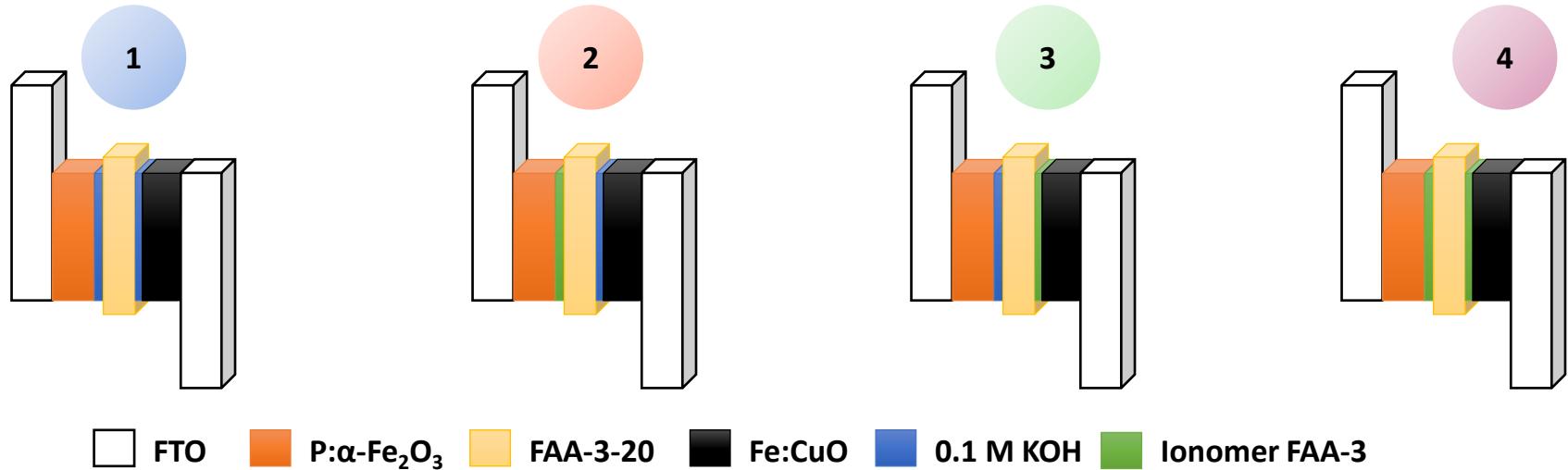
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## ➤ Experimental device



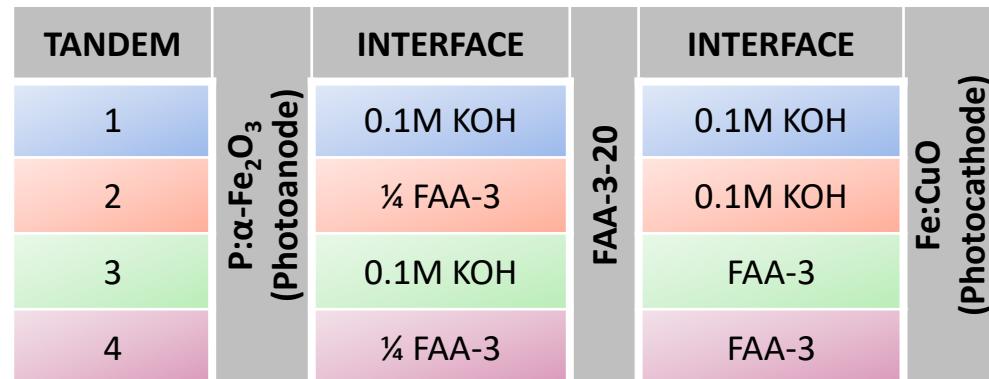
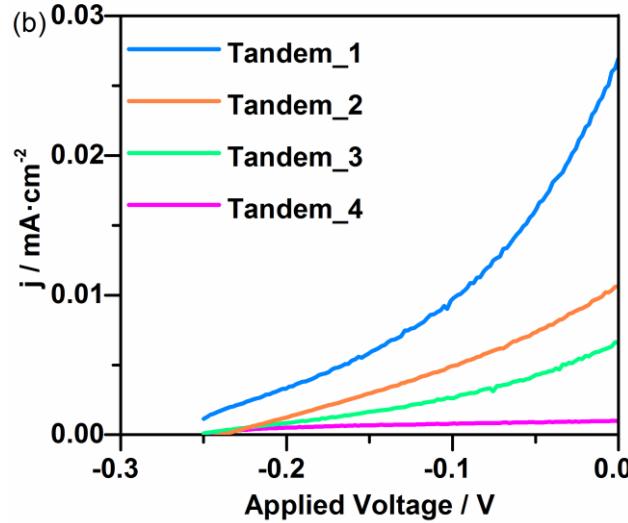
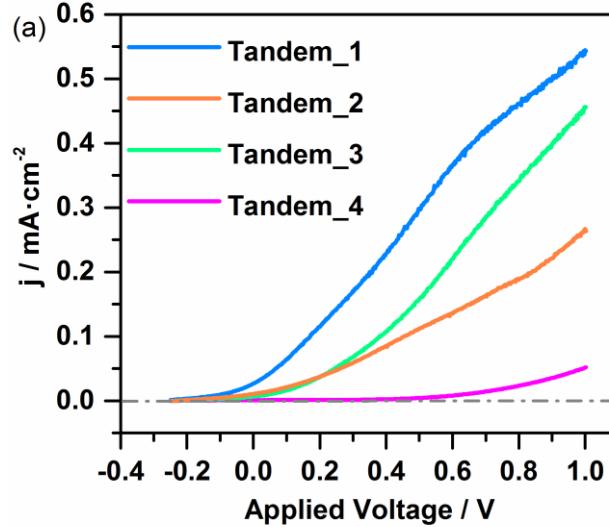
# PEM TANDEM CELL

## ➤ Experimental devices

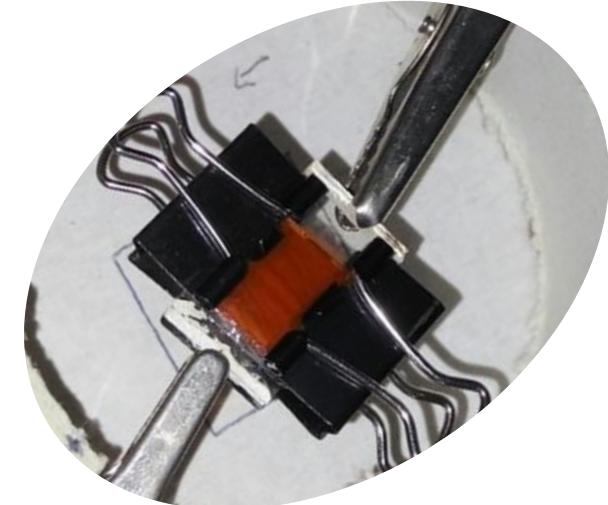


TANDEM	P: $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> (Photoanode)	INTERFACE	MEMBRANE	INTERFACE	Fe:CuO (Photocathode)
1		0.1M KOH		0.1M KOH	
2		$\frac{1}{4}$ FAA-3		0.1M KOH	
3		0.1M KOH		FAA-3	
4		$\frac{1}{4}$ FAA-3		FAA-3	

# PEM TANDEM CELL

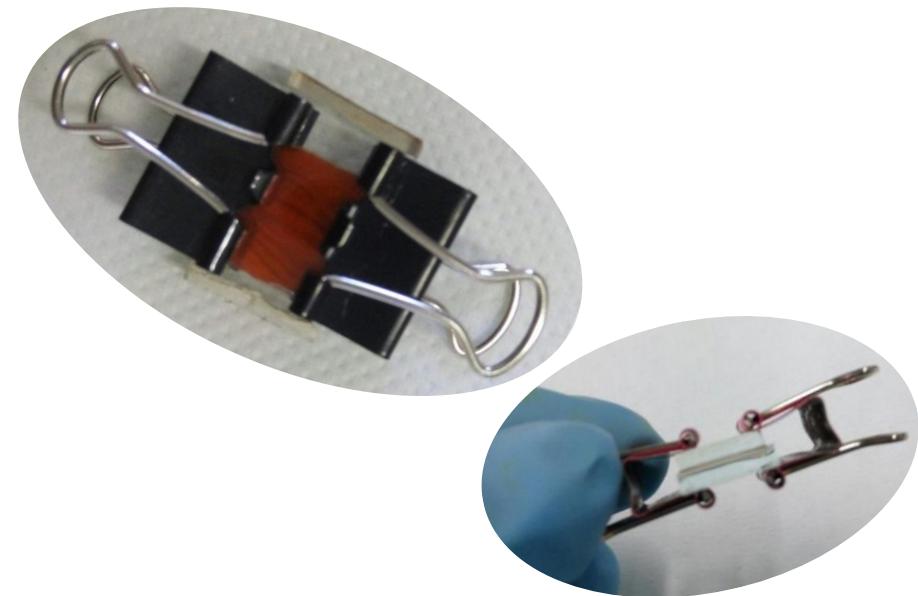
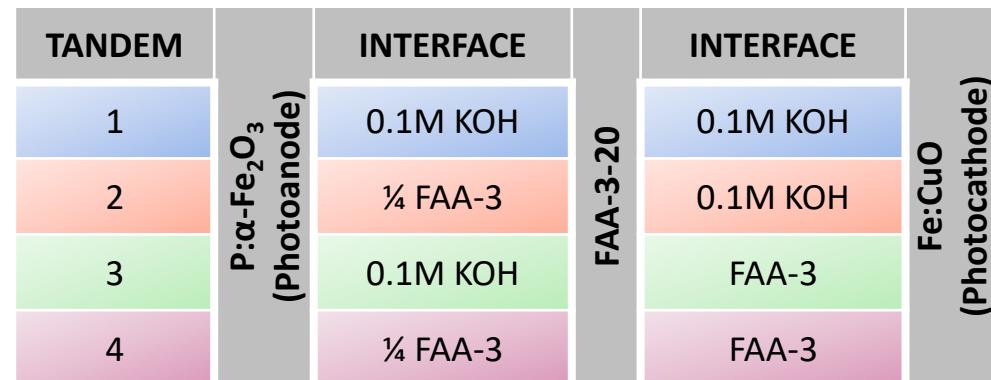
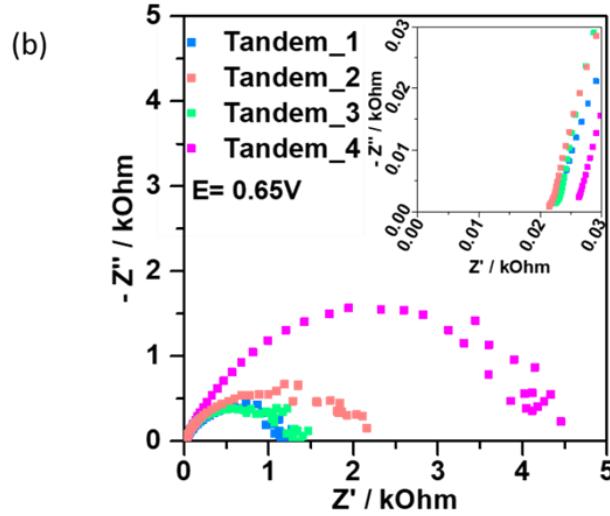
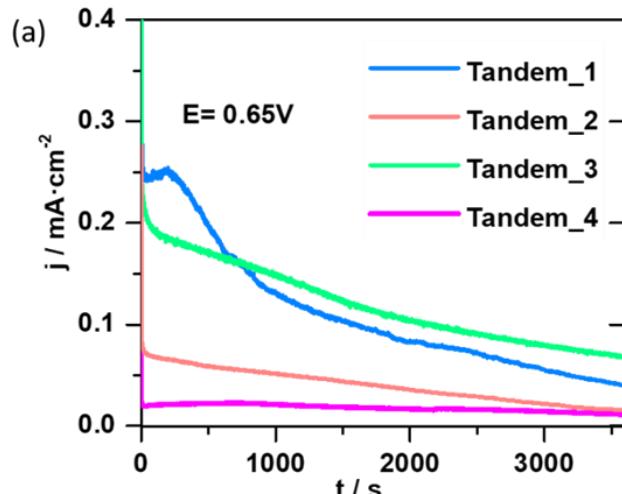


*BIAS-FREE  
CONCEPT  
DEMONSTRATED*



# PEM TANDEM CELL

## ➤ Stability test and EIS



A. Cots et al, ACS Appl. Mater. Inter., 2018

- Ternary oxides offer new opportunities in the development of efficient photoelectrodes.
- Several strategies of modification will be needed for attaining relevant results.
- The photoelectrochemical (PEC) performance of a tandem cell based on a P: $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> photoanode and a Fe:CuO photocatode for water photosplitting, with employment of a polymeric electrolyte membrane (FAA-3-20) is demonstrated with and without applied bias.
- The employment of a polymer membrane instead of the typical acidic or basic aqueous electrolytes diminishes the corrosion of the photoelectrodes and thus increases the stability of the device.
- The interface photoelectrode/PEM needs to be designed for minimizing charge transfer resistance.
- Problems with dehydration need to be addressed.

# FOTCH<sub>2</sub>



This project has received funding from the European Union's Horizon2020 Framework Programme under grant agreement no 760930



A word cloud composed of the words "thank you" in numerous languages, including English, German, Spanish, French, and many others from around the world.