

PHOTOELECTROCHEMICAL DEVICES FOR SOLAR HYDROGEN PRODUCTION

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by

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PREFACE

The present PhD work was developed at the Laboratory for Process Engineering, Environment, Biotechnology and Energy (LEPABE) facilities, in the Chemical Engineering Department of the Faculty of Engineering - University of Porto (FEUP), between 2017 and 2020 under the FCT (Foundation for Science and Technology) grant SFRH/BD/121039/2016. This work was supervised by Professor Adélio Mendes and Doctor Tânia Lopes.

The scientific contributions and main achievements of this work are published in three peer-reviewed scientific articles and are also part of two articles (one peer-reviewed scientific article and one review article), under submission by the time this thesis was delivered.

This document is divided into six chapters, starting with a broad introduction on the topic, followed by four chapters describing the experimental work and results, and finishing with the general conclusions and recommendations for future work.

Chapters 3, 4 and 5 are reprinted versions, briefly modified, of published articles.

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ABSTRACT

Sustainable energy development is a critical emerging paradigm. Fossil fuels remain the primary energy source for mankind and emissions of greenhouse gases have risen proportionately to the exponential increase of the world population, leading to an accelerated global warming with severe consequences to the climate of planet Earth. Therefore, this work embraces the vision that developing and optimizing scalable and low-cost technologies with low environmental impact, capable of supplying the increasing energy demand, is the pathway for turning the energy market sustainable.

Hydrogen produced from renewable energy sources is expected to have a critical role in the energy market for upcoming decades. At present, photovoltaic and wind-powered electrolysis are the most efficient ways to produce renewable- H_2 . However, techno-economic and life-cycle assessment studies show that photoelectrochemical (PEC) water splitting systems, with a 20-year lifespan, comprising photoelectrodes (PEs) with $\geq 1\text{ m}^2$ capable of generating $10\text{ mA}\cdot\text{cm}^{-2}$ at 1.23 V for at least 2920 h (8 working hours over 365 days), can become the most competitive green- H_2 production technology.

Over the last two decades, there has been an intensive research effort to develop highly-efficient nanomaterials for PEC water splitting. Among them, hematite ($\alpha\text{-Fe}_2\text{O}_3$) emerged as one of the most appealing candidates due to its narrow bandgap, a theoretical maximum current density of $12.6\text{ mA}\cdot\text{cm}^{-2}$ at 1.23 V, full chemical stability, nontoxicity, abundance, and low cost. The optimization of $\alpha\text{-Fe}_2\text{O}_3$ PEs usually addresses: i) current density, ii) stability and iii) upscaling; sadly, most studies focus on improving only one of these parameters, leaving the others unaddressed. In the present work, a holistic approach was implemented to optimize a hydrothermal solution-based method for fabricating reproducible, stable, and efficient sponge-like $\alpha\text{-Fe}_2\text{O}_3$ PEs, a morphology never reported before. The optimized PE continuously generated

ca. $2.0 \text{ mA}\cdot\text{cm}^{-2}$ at $1.23 \text{ V}_{\text{RHE}}$ over 84 days (2014 h) under standard PEC operating conditions, which is a record-breaking achievement.

Tandem cell arrangements, combining wider-bandgap PEs with smaller-bandgap PV cells, are considered the most feasible approach for producing unbiased solar- H_2 . Also, the integration of solar concentrating technologies is a simple and effective way for decreasing the cost of PEC- H_2 . Despite being recognized that the design of a PEC device plays an equally important role as the PE in the overall efficiency, few studies have addressed large-area devices or scalable architectures. Aiming at meeting this scalability target, an innovative 50 cm^2 PEC device – the CoolPEC cell – was developed comprising i) an open path for the sunlight through the cell, ii) a PE that is simultaneously one window of the device, and iii) a CFD-optimized electrolyte feeding that assures proper heat dissipation and collection of evolved gases. Field tests showed that H_2 is collected separately from O_2 and operation under concentrated sunlight is safe. The stability criterion was met with an 84-day test under uninterrupted illumination and without electrolyte recirculation.

Transparent conductive oxide (TCO)-glasses, the most widely used substrate for preparing PEs, impose high ohmic losses in devices with active areas $\geq 50 \text{ cm}^2$. Also, state-of-the-art lab equipment is not optimized for assuring reproducibility with such large-area substrates. Therefore, the upscaling of highly efficient PEs remains a massive challenge. In the present work, a 50 cm^2 segmented support was developed for holding multiple PEs connected in parallel, aiming at answering the upscaling task. Small-size and efficient PEs, prepared using state-of-the-art lab equipment, can then be connected in parallel, fulfilling large-area requirements. This concept was experimentally validated by connecting eight small $\alpha\text{-Fe}_2\text{O}_3$ PEs in parallel and recording a higher photocurrent density and a higher photovoltage than with a single 50 cm^2 $\alpha\text{-Fe}_2\text{O}_3$ PE.

Finally, the previous achievements were gathered to develop the first large PEC modular device with multi-PE windows capable of being operated under concentrated sunlight with electrolyte recirculation. The 200 cm² module, comprising 32 nanostructured α -Fe₂O₃ PEs, continuously generated 2.0 mA·cm⁻² at 1.45 V during an unprecedented field-testing campaign conducted outdoor under 12.8 kW·m⁻² of natural concentrated sunlight. None of the components of the module (PEs, PV cells and embodiment) experienced any damage, despite the harsh operating conditions.

This thesis is a solid contribution to the field of PEC water splitting since pioneering technical solutions were successfully integrated into upscaled PEC devices, tackling all the three-pillar – efficiency, stability, and scalability – criteria required to turn this technology competitive in the energy market.

RESUMO

A transição energética baseada no desenvolvimento sustentável é um paradigma emergente fulcral. Os combustíveis fósseis continuam a ser a principal fonte primária de energia da sociedade atual e as emissões de gases com efeito de estufa têm aumentado proporcionalmente ao aumento exponencial da população mundial, resultando num aquecimento global acelerado com consequências severas para o clima do planeta Terra. Por isso, este trabalho assume a visão de que desenvolver e otimizar tecnologias de baixo custo, facilmente escalonáveis, com baixo impacto ambiental associado, e capazes de suprir o crescente consumo de energia, é o caminho certo para tornar o mercado energético sustentável.

O hidrogénio produzido a partir de fontes renováveis de energia deverá ter um papel essencial no mercado energético nas próximas décadas. Atualmente, a eletrólise baseada na energia fotovoltaica ou eólica é a forma mais eficiente de produzir hidrogénio renovável. Contudo, estudos técnico-económicos e de avaliação de ciclo de vida mostram que sistemas fotoeletroquímicos de eletrólise que tenham um tempo de vida útil de 20 anos, que incluam fotoelétrodos com 1 m^2 , capazes de produzir $10 \text{ mA}\cdot\text{cm}^{-2}$ a um potencial de 1.23 V durante, pelo menos, 2920 h (correspondentes a 8 horas de trabalho ao longo de 365 dias), poderão ser a tecnologia mais competitiva para a produção de hidrogénio verde.

Ao longo das duas últimas décadas, tem havido um esforço na investigação para desenvolver nanomateriais utilizados em eletrólise fotoeletroquímica altamente eficientes. Entre eles, a hematite ($\alpha\text{-Fe}_2\text{O}_3$) emergiu como um dos candidatos mais aliantes, dada a sua estreita banda de energia proibida, densidade de corrente teórica máxima de $12.6 \text{ mA}\cdot\text{cm}^{-2}$ a 1.23 V, ótima estabilidade química, não-toxicidade, abundância e baixo custo. Normalmente, a otimização de fotoelétrodos de hematite aborda: i) a densidade de corrente; ii) a estabilidade; e iii) o aumento de escala; infelizmente, a maioria dos estudos

foca-se em melhorar apenas um destes parâmetros, deixando os restantes intocados. Neste trabalho implementou-se uma abordagem holística de otimização de um método hidrotérmico para produzir fotoelétrodos de hematite reproduzíveis, estáveis e eficientes, estruturados em nanocubos esponjosos, uma morfologia nunca reportada. O fotoelétrodo resultante deste processo de otimização foi capaz de gerar cerca de $2.0 \text{ mA} \cdot \text{cm}^{-2}$ a um potencial de $1.23 V_{\text{ERH}}$ ao longo de 84 dias (2014 h), sob condições standard de operação de sistemas fotoeletroquímicos, sendo um resultado recorde.

Os sistemas *tandem*, que combinam fotoelétrodos de banda de energia intrínseca maior com células fotovoltaicas de banda de energia intrínseca mais curta, são considerados a abordagem mais exequível para produzir hidrogénio solar sem recurso a voltagem auxiliar. Além destes, a integração de concentradores solares é também uma forma simples e eficaz de reduzir o custo do hidrogénio fotoeletroquímico. Apesar de ser reconhecido que o design de um dispositivo fotoeletroquímico desempenha um papel tão importante como o próprio fotoelétrodo na eficiência global, poucos estudos têm abordado dispositivos de grandes áreas ou designs orientados para o aumento de escala. Com o objetivo de dar resposta a este desafio de escalabilidade, desenvolveu-se um dispositivo inovador com 50 cm^2 , a CoolPEC cell, que engloba: i) um corredor transparente para que a luz solar atravessasse a célula; ii) um fotoelétrodo que é, simultaneamente, uma das janelas do dispositivo; e iii) um sistema de alimentação de eletrólito com escoamento otimizado para assegurar a dissipação adequada de calor e a recolha eficiente dos gases produzidos. Testes feitos no exterior mostraram que o hidrogénio pode ser recolhido separadamente do oxigénio e que o dispositivo pode ser operado com segurança sob luz solar concentrada. A meta de estabilidade foi atingida com um ensaio de 84 dias, realizado sob luz solar contínua, mas sem recirculação de eletrólito.

Os vidros com óxidos condutores transparentes, que são os substratos mais utilizados para a preparação de fotoelétrodos, originam perdas óhmicas

elevadas em dispositivos fotoeletroquímicos com áreas ativas iguais ou superiores a 50 cm². Além disso, o equipamento de laboratório mais sofisticado não está preparado para garantir resultados reprodutíveis com substratos tão grandes. Por conseguinte, o aumento de escala bem-sucedido de fotoelétrodo altamente eficientes continua a ser um desafio enorme. Para responder a este problema, desenvolveu-se uma janela segmentada de 50 cm² capaz de albergar vários fotoelétrodo ligados em paralelo. Deste modo, fotoelétrodo mais pequenos e eficientes, preparados com o equipamento de laboratório mais avançado, podem ser ligados em paralelo de forma a cumprir as metas de escalabilidade. Este conceito foi validado experimentalmente após oito fotoelétrodo de hematite ligados em paralelo terem conseguido gerar uma densidade de corrente e um fotopotencial mais elevados do que os produzidos por um único fotoelétrodo de hematite com 50 cm².

Por fim, os bons resultados obtidos ao longo deste trabalho de doutoramento foram harmonizados e combinados no desenvolvimento de um dispositivo fotoeletroquímico modular, composto por janelas segmentadas, capaz de ser operado sob luz solar concentrada e com recirculação de eletrólito. Este módulo de 200 cm², equipado com 32 fotoelétrodo de hematite nanoestruturada, gerou continuamente 2.0 mA·cm⁻² a um potencial de 1.45 V, num ensaio exterior sem precedentes, feito sob luz solar natural concentrada equivalente a 12.8 kW·m⁻². Nenhum componente do módulo (fotoelétrodo, células fotovoltaicas e corpo do dispositivo) experienciou qualquer tipo de dano provocado pelas condições operacionais severas.

Esta dissertação representa um sólido contributo para a área da produção fotoeletroquímica de hidrogénio, uma vez que várias soluções técnicas vanguardistas foram integradas com sucesso em dispositivos fotoeletroquímicos de grandes áreas, abrangendo os três critérios essenciais – eficiência, estabilidade e escalabilidade – para tornar esta tecnologia competitiva no mercado energético.

LIST OF ACRONYMS AND SYMBOLS

Symbol	Definition
A	Surface area (cm^2)
$C_{g,\text{eff}}$	Effective geometric concentration ratio on PEs
E_C	Conduction band
E_e	Solar irradiance ($\text{kW}\cdot\text{m}^{-2}$)
F	Faraday constant ($96\,485\text{ A}\cdot\text{s}\cdot\text{mol}^{-1}$)
E_F	Fermi energy level
E_V	Valence band
I	Current (mA)
I_N	Direct normal irradiance ($\text{kW}\cdot\text{m}^{-2}$)
J	Current density ($\text{mA}\cdot\text{cm}^{-2}$)
J_{OP}	Operational photocurrent density ($\text{mA}\cdot\text{cm}^{-2}$)
k	Factor of the applied potential
m	Mirrors
M	Module
n	Stoichiometric coefficient
n_m	Number of active mirrors
P_{in}	Incident irradiance ($\text{W}\cdot\text{m}^{-2}$)
P_S	Standard pressure (101 325 Pa)
Q	Hydrogen flow rate ($\text{mol}_{\text{H}_2}\cdot\text{s}^{-1}$)
R	Gas constant ($8.314\text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$)
R_m	Solar weighted hemispheric reflectance of the mirrors (0.86)
R_w	Solar weighted transmittance of the front quartz window (0.962)

t	Time (s)
T	Temperature (°C)
T_s	Standard temperature (273.15 K)
V	Potential (V)
V_{fb}	Flatband potential (V)
V_{S,N_2}	Volumetric standard flow of nitrogen (m ³ ·s ⁻¹)
W	Window
X	Molar fraction

Acronym	Definition
AE	Auxiliary electrode
AEC	Alkaline electrolysis
AEM	Anion exchange membrane
ALD	Atomic layer deposition
AP	Acidification potential
AZO	Aluminium-doped Zinc Oxide
BPM	Bipolar membrane
CE	Counter-electrode
CEM	Cation exchange membrane
CFD	Computational Fluid Dynamics
CL	Convex lenses
CPC	Compound parabolic concentrator
CPEC	Concentrator integrated photoelectrochemical
CPV	Concentrator photovoltaics
CPVE	Concentrated photovoltaic electrolysis
DLR	German Aerospace Centre (Deutsches Zentrum für Luft- und Raumfahrt)

EC	Electrolysis / electrolyzer
EDS	Energy-dispersive X-ray spectroscopy
EPBT	Energy payback time
ERoEI	Energy return on energy invested
EU	European Union
FL	Fresnel lenses
FTO	Fluorine-doped tin oxide
GC	Gas chromatograph
GHG	Greenhouse gases
GLAD	Glancing angle deposition
GWP	Global warming potential
HER	Hydrogen evolution reaction
HIT	Heterojunction with intrinsic thin layer
HTE	High-temperature electrolysis
ITO	Indium tin oxide
LCA	Life cycle assessment
LFR	Linear Fresnel reflector
LSC	Luminescent solar concentrator
NHE	Normal hydrogen electrode
OER	Oxygen evolution reaction
PCE	Power conversion efficiency
PDC	Parabolic dish concentrator
PE	Photoelectrode
PEC	Photoelectrochemical
PED	Photoelectrodeposition
PEEK	Polyether ether ketone

PEM	Polymer electrolyte membrane
PET	Polyethylene
PS	Polystyrene
PTC	Parabolic trough collector
PV	Photovoltaic
QD	Quantum dot
RHE	Reversible hydrogen electrode
SEM	Scanning electron microscope
SMR	Steam methane reforming
SOEC	Solid oxide electrolyzer cell
SP	Spray pyrolysis
SPHA	Combined spray pyrolysis and hydrothermal synthesis with acid treatment
STH	Solar-to-hydrogen
TCO	Transparent conductive oxide
TEOS	Tetraethyl orthosilicate
UPORTO	University of Porto
US	United States
UV	Ultra-violet
WE	Working electrode
ZFO	Zinc ferrite

Greek symbols	Definition
ΔG	Gibbs free energy
η	Hydrogen recovery factor (0.95)

CHAPTER 1

LARGE-AREA PHOTOELECTROCHEMICAL WATER SPLITTING: CURRENT STATUS, DEMONSTRATED DEVICES AND KEY CHALLENGES FOR THE UPCOMING YEARS

"If we don't change our way of life, we may not have life left to change."

António Guterres

UN Climate Change Conference, Madrid, Spain 2019

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1 LARGE-AREA PHOTOELECTROCHEMICAL WATER SPLITTING: CURRENT STATUS, DEMONSTRATED DEVICES AND KEY CHALLENGES FOR THE UPCOMING YEARS

Green-H₂ is considered a “key player” in the energy market for the upcoming decades, given its advantages as energy carrier and as industrial feedstock. Still, to be considered a fully green alternative to the currently available technologies, H₂ must be produced from renewable sources in a cost-competitive, emission-free, and efficient way. Based on the broad comparative analysis performed in this chapter on LCA and techno-economic studies addressing H₂ production technologies, it was concluded that PEC water splitting is the production method with the lowest environmental impact. Still, alkaline electrolysis and steam-methane reforming remain the more financially appealing options to investors and H₂ consumers, due to their maturity within the energy market. As so, the differentiating competitive factor of PEC water splitting must rely on its environmental and functional advantages, which are strongly linked to the design of the operating device, to the intrinsic properties of the photoactive materials and to their successful upscaling.

This chapter reviews the most relevant demonstrated large-area PEC devices and their combination with solar concentrators, also addressing the most promising semiconductor materials suitable for upscaling towards the dimensions of commercial panels. So far, α -Fe₂O₃ is the semiconductor material that shows the best compromise between the three-pillar criteria – efficiency, stability, and scalability – needed for commercialization, although there is still no

α -Fe₂O₃ PE capable of fully addressing more than one key target. According to the configuration of electrodes and strategies adopted for gas separation, it was possible to categorize large-area PEC devices into four main types: wired back-to-back (Type I), wireless back-to-back (Type II), wired side-by-side (Type III) and wired, separate electrode membrane-free (Type IV). Independently from the device architecture, it was concluded that using concentrated sunlight is a key strategy for achieving the efficiency targets. On the other hand, due to the voltage needed to drive water splitting (typically > 1.5 V), a dual-absorber tandem configuration, in which the bottom and top photoactive materials absorb complementary parts of the solar spectrum, was considered the most feasible.

1.1 INTRODUCTION

Renewable energy sources have been widely used by mankind for several millennia. In fact, until 250 years ago hydro, wind, solar and biomass were the only known and available energy sources.¹ After the Industrial Revolution in the 18th century, human society has witnessed an unprecedented technological development, with fossil fuels in the spotlight of energy sources.² The energy demand never stopped growing as the world population started to increase exponentially, benefiting from improved living conditions.^{3, 4} In consequence, the energy market strongly influenced global policies and economics, with a negative impact for the environment.^{5, 6} Emissions of greenhouse gases (GHG) have continuously increased due to the consumption of fossil fuels, leading to an accelerated global warming phenomenon⁷ with severe consequences to the climate stability of planet Earth, resulting in extreme and unpredictable weather events.^{8, 9} At present, there is a global consensus to implement drastic changes in the way energy is provided, stored and consumed, forcing an extensive reduction of GHG emissions from human activities aiming at keeping global warming below 2 °C relatively to the pre-industrial times.¹⁰ As mankind enters into the 4th industrial revolution, such goal represents a great challenge to the scientific community, to the industry and to the governments.^{11, 12}

Solar-powered technologies for producing electrochemical fuels are a clean and cost-competitive alternative to the traditional fossil-fuel based technologies. Electrochemical solar hydrogen (H_2) technologies have particular interest since they allow efficiently harvesting and converting the abundant solar energy into a storable and transportable environmentally friendly fuel. Green- H_2 can be converted downstream into electricity for stationary or mobile applications, can be used directly in fuel cells and can be used as feedstock for the chemical industry, especially for producing ammonia and for processes that reduce CO_2 into liquid synthetic fuels.^{13, 14} This application complements currently available clean technologies that capture solar energy and generate electricity (e.g. photovoltaics) or heat (e.g. solar-thermal systems).¹⁵ At present, the most relevant methods for generating solar- H_2 are: i) photovoltaic-electrolysis (PV-EC); ii) photoelectrochemical (PEC) water splitting, iii) photocatalysis and iv) biological processes. Decoupled PV-EC is the available technology with the highest technological readiness level (TRL), due to the maturity of both photovoltaic (PV) and electrolyzer (EC) technologies, which have been optimized for many decades.¹⁵ However, PEC systems integrate light absorption and electrocatalysis in a single device and offer the opportunity to use thermal management for improving their efficiency.^{16, 17}

The successful implementation of PEC water splitting systems in the renewable energy market relies on their efficiency, durability, scalability, and cost-effectiveness. This route requires the optimization of device architectures for developing fully integrated PEC systems, comprising technical solutions already developed for high-performing PEC cells, namely through the use of abundant materials.^{16, 18} Since the pioneering work of Fujishima and Honda in 1972 reporting the use of a PEC cell for water splitting equipped with a titanium dioxide (TiO_2) photoelectrode (PE) illuminated with UV light ¹⁹, different PEC devices and configurations have been studied. Despite the extensive overviews on PEC cell designs and performance, research work is still mostly focused on lab-scale experiments.²⁰⁻²³ Nevertheless, to become a commercial alternative in the energy supply sector it is required that lab-scale devices are engineered into a

competitive large-scale technology. Device architectures with an illuminated area of at least 50 cm² are considered a viable first approach to large-scale applications; higher scalability can be achieved by coupling module units. In fact, an ongoing change in paradigm is perceptible in the literature, with increasing relevance being given to the design and construction of large-area, or at least scalable, devices - Figure 1.1. In the last 5 years the number of publications demonstrating large-area PEC devices almost doubled the total of the previous five years (2010 - 2015).

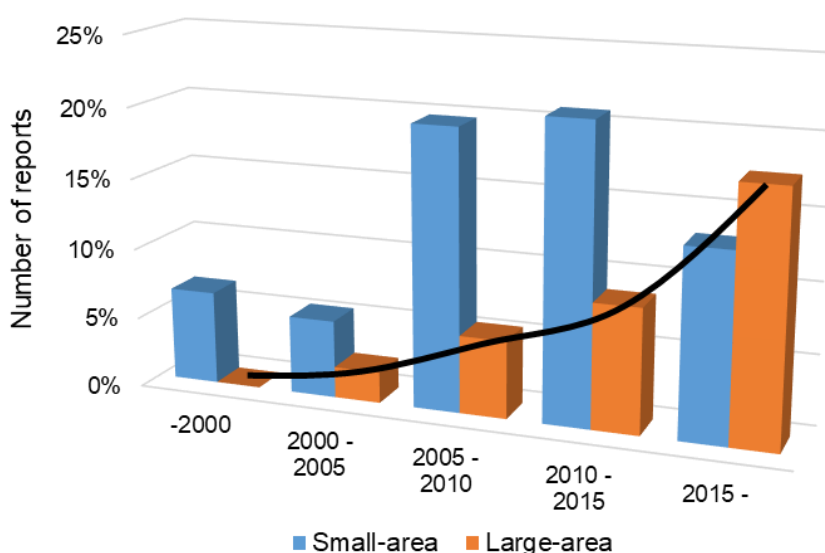


Figure 1.1. Histogram of the reported PEC reactors over the last 20 years concerning: small-area devices (blue) and large-area devices with an illuminated area higher than 50 cm² (orange) - (searched keywords: “photoelectrochemical” + “water splitting” + “small area” + “large area” + “device”; database: Google Scholar and Scopus).

The solar-to-hydrogen conversion efficiency (η_{STH}) is a critical parameter for improving the competitiveness of PEC systems.²⁴ The United States Department of Energy set a STH efficiency target of 20 % to attain market competitiveness of PEC water splitting systems.²⁵ The highest STH efficiency of commercial multijunction monolithic PEC cells with III-V semiconductors has reached 19.3 %, but the technology is still far from commercialization owing to its high cost

and complexity.²⁶ Up to date, no single, earth-abundant and low-cost semiconductor material was identified to promote unbiased solar water splitting, delivering a high efficiency while operating stably on a timescale of years. Due to the high voltage needed to drive the overall water splitting reaction (typically > 1.5 V), a dual-absorber tandem configuration, in which the bottom and top materials absorb complementary parts of the solar spectrum, has been increasingly investigated to enhance the generated photovoltage.²⁷ A PEC-PV device is envisaged as the most feasible tandem approach, surpassing the efficiency of PV-electrolysis systems when using the same PV in both cases.²⁸ Very recently, an unprecedented 17.6 % STH efficiency was reported for a low-cost PEC-PV tandem cell comprising perovskite-silicon photocathode absorbers.²⁹ These results show that there are ample opportunities for further improving the efficiency and reducing the costs of PEC systems, namely through the optimization of each component individually. Along with performance indicators, the cost of produced H₂ is a decisive metric for assessing the viability and future commercialization of the PEC-PV water-splitting technology – Figure 1.2. Pinaud *et al.*³⁰ estimated a H₂ cost of 8.76 €·kg⁻¹ (assuming 1 USD = 0.84 €) as a target for commercialization, considering a STH efficiency of 10 %, a lifetime of 10 years and a panel cost of 128.82 €·m⁻². Considering the same STH efficiency, Shaner *et al.*³¹ concluded that an electrolyzer stack and a PV module would have a total cost of 135.56 €·m⁻².

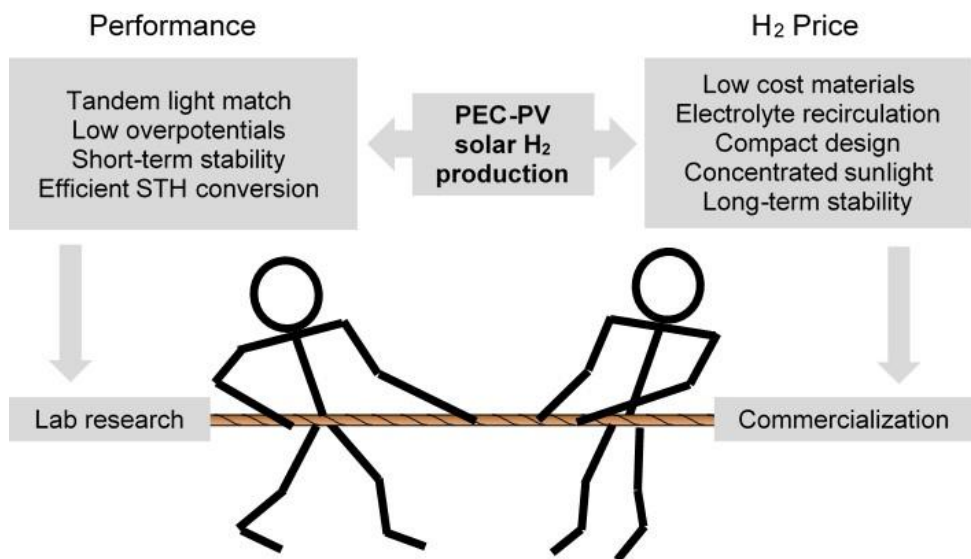


Figure 1.2. Schematic representation of the current balance between performance indicators and cost-effectiveness of produced H₂ to turn PEC-PV tandem systems economically viable.

As sketched in Figure 1.2, a set of key requirements should be taken into account in fully integrated PEC-PV systems. Apart from the performance of the photo-absorber materials and electrocatalysts, when commercialization is brought in sight, the PEC reactor integrating all the assembling components plays a crucial role in balancing the cost-effectiveness of such systems. It is established that an optimized PEC reactor must address the following requirements^{32, 33}: i) maximized absorption of solar photons by the PEs and/or PV components (also under concentrated sunlight); ii) electrolyte recirculation with an optimized internal flow pattern, assuring efficient heat dissipation and gas bubbles removal; iii) optimal arrangement of electrodes to minimize overpotential losses (ionic and electronic); iv) efficient separation of evolved gases; v) good resistance to corrosive electrolytes; vi) use of inexpensive materials and low-cost maintenance; and vii) scalability and easy integration in a H₂ production plant. A well-engineered PEC reactor suitable for large-scale PEC-PV systems must combine all these requirements³⁴. This chapter explores the current status of large-area PEC-H₂ systems, with a comprehensive

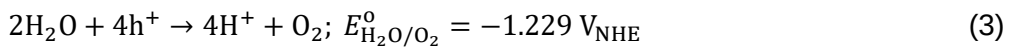
overview of the most promising semiconductors, device architectures and technical solutions for integrating solar concentrators with upscaled PEC devices. This chapter also includes a critical and reflective analysis of life cycle and economic assessment studies on the H₂ production technologies, aiming at identifying the key challenges and opportunities to achieve cost-efficient PEC-H₂ production.

1.2 BASIC WORKING PRINCIPLE OF A PEC DEVICE

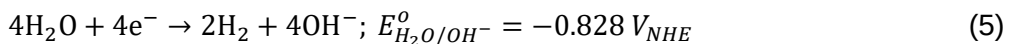
The fundamental basis of solar water splitting systems rely on working principles of the photoactive electrode since it has the ability to convert incident photons to electron-hole pairs when exposed to sunlight³⁵. Photons with energy $h \cdot \nu$ higher than the semiconductor's bandgap generate electron-hole pairs ($e_{CB}^- + h_{VB}^+$) in the conduction and valence bands, respectively:

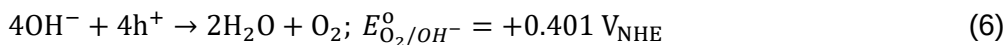


The governing thermodynamic equations of PEC systems that comprise a photoactive semiconductor concern the H₂ and O₂ half-reactions of water splitting reaction, as follows:¹⁶



where NHE is the normal hydrogen electrode; this system considers the use of an acidic electrolyte. For an alkaline medium, hydroxyl anions are formed from the dissociation reaction of water; the reduction and oxidation reactions can be written as:





The number of absorbed photons is equal to the number of produced electron-hole pairs, which is twice that of produced H_2 molecules and four times the produced O_2 molecules. The minimum thermodynamic potential needed for driving the water electrolysis is the electric reversible potential of $\Delta E^0 = -1.23 \text{ V}$, based on a Gibbs free energy change of $\Delta G^0 = 237.2 \text{ kJ}\cdot\text{mol}^{-1}$. However, the excess potential is converted to heat, which is the usual source of the heat that also ends up stored in the H_2 . The higher heating value (HHV) of H_2 is $285.8 \text{ kJ}\cdot\text{mol}^{-1}$, which translates to 1.48 V , *i.e.* the potential at which no excess heat is generated. Therefore, the process cannot proceed below $285.8 \text{ kJ}\cdot\text{mol}^{-1}$ if no external heat/energy is provided.

The ability of a semiconductor to absorb light is determined by the bandgap (E_g); only solar photons with wavelengths shorter than corresponding to the bandgap are absorbed, promoting charge separation.³⁶ The valence band is filled with electrons (at 0 K) and the conduction band corresponds to the first excited level above the gap (empty at 0 K). The difference between the bottom of the conduction band (E_C) and the top of the valence band (E_V) defines the bandgap. The Fermi energy level position (E_F) distinguishes different class of materials. The product of the electron density and the hole density does not depend on the position of the Fermi energy and, therefore, neither does it depend on the individual densities of electrons or holes. In a pure, so-called intrinsic semiconductor, the electrons in the conduction band originate from the valence band. The density of the electrons is then equal to the density of holes and both are known as the intrinsic density. In a band structure picture, the Fermi energy level can be understood as the probability that (at thermodynamic equilibrium) a state having energy E is occupied by an electron.^{35, 37, 38} For an intrinsic semiconductor, the position of the Fermi energy is not exactly in the middle of the energy gap because of different effective densities of states in the conduction and the valence band; it rather follows from the condition that the density of electrons equals the density of holes.

When the semiconductor is in contact with an electrolyte with redox energy (E_{Redox}) different from E_F , the equilibrium of the electrochemical potential in the two components is achieved by electron exchange at the interface. Electrons are transferred to the electrolyte leaving in the semiconductor a depleted layer (space charge layer), but also from the electrolyte to the semiconductor (accumulation layer)³⁵; the Fermi energy level is then adjusted due to the formation of an electric double layer between the electrode and the electrolyte.³⁹ The depletion of electrons at the surface of the PE induces an electric field between the bulk of the semiconductor and its surface, corresponding to the band bending.^{35,37} For a given semiconductor/electrolyte pair there is a unique potential for which the potential drop between the surface and the bulk is zero and there is no space charge layer – the flatband potential (V_{fb}). For a certain redox couple, V_{fb} corresponds to a particular redox potential of the electrolyte when there is no excess charge in the semiconductor and consequently no band bending.⁴⁰ When potential is applied ($V_{applied}$) between the semiconductor and a reference electrode, the band bending of the semiconductor is modified.³⁷ Incidence of light can modify the band bending of a semiconductor in equilibrium with an electrolyte as the electron and hole densities are increased due to light absorption.^{35, 37}

The band edge potentials of many semiconductors are not suitable for oxygen and hydrogen evolution and the water splitting reaction cannot take place. Consequently, an additional bias voltage is required to promote the reduction reaction.⁴¹ Thus, one of the key aspects concerning the choice of a semiconductor is related to its band edge positions, which determine the maximum reduction and oxidation potentials of the photogenerated electrons and holes.³⁵ The energy difference between the oxidizing hole and the reducing electron should be higher than the water dissociation electrochemical potential (1.23 eV).^{37, 38} Consequently a bandgap of 1.6 – 2.0 eV is considered to be the best compromise for the water splitting reaction. The position of the energy bands must also be taken into account, as the valence band shall be below the redox potential of O_2 formation and the conduction band shall be above the redox

potential of H₂ formation.³⁷ Band positions of most metal oxides show the same pH dependence as the water reduction and oxidation potentials, so relative positions remain the same at other pH values.³⁵ The main processes involved in the photo-oxidation of water, *i.e.* in a PEC system comprising a *n*-type PE, are schematized in Figure 1.3.

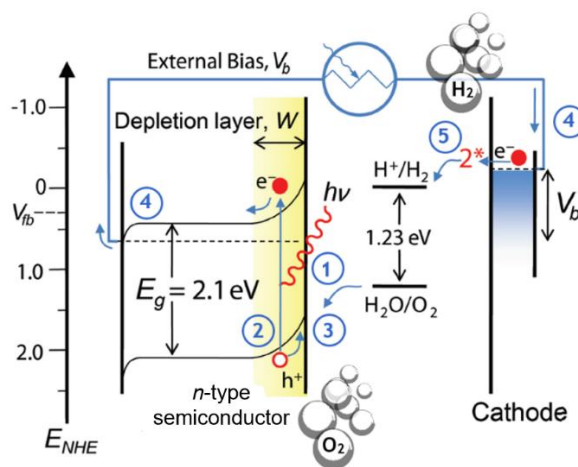


Figure 1.3. Schematic representation of the relevant processes involved in the photo-oxidation of water using a *n*-type photoanode; 1 - absorption of a photon, generating an electron-hole pair in the semiconductor; 2 - diffusion of holes towards the semiconductor-liquid interface; 3 - water oxidation at the surface of the PE; 4 – electron transport through the semiconductor and the external circuit; 5 - water reduction at the metal CE. Adapted from ³⁷.

In practice, PEC systems require an extra potential, *i.e.* hundreds of mV, to drive the water splitting reaction, mainly due to overpotentials associated with the water oxidation, but also associated with the counter-electrode (CE) intrinsic overpotential, the charge transport in the electrolyte and across the substrate, the distance between the electrodes and the device geometry.⁴² When this bias potential is applied with respect to a reference electrode (3-electrode configuration), the potential difference will be distributed over the space charge layer and the Helmholtz layer (as an example, for a *n*-type semiconductor, it consists of a continuous layer of anions that is formed in the electrolyte to

balance the positive surface of the semiconductor). Thus, one of the key aspects concerning the choice of a semiconductor material is related to its band edge positions, which determine the maximum reduction and oxidation potentials of the photogenerated electrons and holes in it. The quantification of the STH efficiency conventionally uses the thermodynamic voltage of 1.23 V, when calculating the amount of energy stored in H₂ from PEC water splitting is intended:

$$\eta_{\text{STH}}(\%) = \frac{1.23 \text{ V} \times J_{\text{op}}}{P_{\text{in}}} \times \eta_{\text{eff}} \quad (7)$$

where J_{op} is the operational photocurrent density (mA·cm⁻²), P_{in} is the incident irradiance (1000 W·m⁻², AM 1.5 G, considering standard PEC operating conditions) and η_{eff} is the faradaic efficiency for H₂ evolution. From equation (7), the photocurrent relates proportionally to the STH efficiency, being therefore a crucial parameter for improving the overall efficiency of a PEC device. However, maximizing the photocurrent of a PEC system, implies a complementary improvement of the photovoltage and the fill factor of the PEs.

In PEC-PV tandem systems, the PV cell is electrically connected in series between the PE and CE, *i.e.* it only provides the extra bias needed for unassisted water splitting, given that only the PE and CE are in direct contact with the electrolyte. Under operation, the values of current travelling through each electrode are equal, and the potentials spontaneously adjust to reach this equilibrium. Under illumination, the injected electrons raise the Fermi level, decreasing the band bending and splitting into a quasi-Fermi level for electrons and for holes close to the interface. The excited electrons flow from the back contact of the semiconductor, via the external circuit, to the CE, where they reduce water to H₂ – equation 1 or equation 4, depending on the electrolyte medium. Either water reacts with the semiconductor surface holes, or OH⁻ ions diffuse back to react with holes at the surface of the PE, producing O₂ – respectively equations 3 or 6. In the case of using a *p*-type semiconductor

(photocathode), it reduces protons or water to H_2 at the interface – equations 2 or 5, depending on pH medium – while O_2 is evolved at the metal anode.

Having defined the working principles of PEC water splitting systems, the following sections will address the progress on nanomaterials for PEs, considering their upscaling as a key metric, but also including the efficiency, stability, and cost, as essential criteria for achieving feasible PEC- H_2 production.

1.3 MATERIALS ENGINEERING FOR UPSCALED

PHOTOELECTROCHEMICAL HYDROGEN PRODUCTION

The basic concept underneath PEC- H_2 production is the natural process of photosynthesis since PEC devices aim at directly converting incident photons into a fuel. This STH conversion process involves an anode and a cathode, in contact with an electrolyte, to drive the oxygen evolution reaction (OER) and the hydrogen evolution reaction (HER), respectively.⁴³ Catalysts can be applied on both electrodes to improve reaction kinetics and enhance the overall efficiency. For practical applications, both electrodes and the electrolyte need to be supported and encapsulated in a reactor, comprising transparent windows that allow sunlight to reach the surface of the photoactive materials.⁴⁴ Typically, both electrodes are located in separate compartments, divided by an ionic exchange membrane, which facilitates species transport while avoiding gas mixing inside the reactor. Still, when someone addresses the topic of materials engineering within the field of PEC- H_2 production, the component that instantly comes to mind is the photoabsorber material, *i.e.* the semiconductor or PE, since it materializes the photon-to- H_2 conversion, having a major influence in the efficiency of the PEC device. At the semiconductor-liquid junction, the chemical equilibrium potential of the electrons in the semiconductor (*i.e.* the Fermi level) and the oxidation–reduction potential in the electrolyte induces the transfer of electrons; the photopotential generated by the separation of charges can directly drive the solar- H_2 production reaction.⁴⁵ This characteristic makes PEC cells advantageous over coupled PV-EC systems as they combine light absorption,

charge generation and separation, hole, electron, ionic and molecular transport in a single device. Additionally, PEC devices can be operated at a lower current density, exhibiting lower overpotentials, and ultimately incorporating earth-abundant and cheap materials instead of the expensive and scarce materials typically used in commercial electrolyzers.^{46, 47}

In the field of PEC-H₂ production, materials engineering is a critical topic for addressing most of the key challenges needed to accomplish commercialization: i) the PE, the CE and the membrane need to be chemically stable under harsh working conditions, *i.e.* continuous operation in strong acid or alkaline environment, continuous electrolyte recirculation, exposure to normal or concentrated sunlight; ii) the embodiment must be robust, enabling operation under severe weather conditions; and iii) each component of the device must incorporate earth-abundant and low-cost materials prepared by simple and scalable techniques for assuring sustainability targets.^{27, 48} As so, choosing the adequate materials for each component of a PEC device is essential for assuring efficient and stable H₂ production in a compact and low-cost device on a large scale. This chapter makes an overview on the most promising semiconductor materials for upscaled PEC-H₂ production, addressing relevant strategies that have been used for improving their performance and cost-saving fabrication techniques. Catalysts, counter-electrodes, and membranes are also covered in this chapter given their substantial contribution to the overall efficiency and cost of a PEC device.

1.3.1 MOST STUDIED PHOTOELECTRODES FOR LARGE-AREA PEC WATER SPLITTING

Choosing the ideal semiconductor for a PEC device should meet some key criteria, as follows: i) good visible light absorption and narrow bandgap energies between 1.8 eV and 2.4 eV (1.8 eV corresponds to the theoretical minimum band-gap for water splitting of 1.23 eV plus the thermodynamic losses (0.3–0.4 eV) and overpotentials (0.4–0.6 eV); 2.4 eV is the maximum bandgap value to

achieve the target of 10 % STH efficiency); ii) suitable valence and conduction band edge positions, as the valence band should be below the redox potential of O₂ evolution and the conduction band should be above the redox potential of H₂ evolution; iii) efficient charge carrier separation and transportation, which depend both on the intrinsic properties (hole and electron mobility) and on the extrinsic properties (surface area, crystallinity, grain boundaries) of the semiconductor; iv) strong catalytic activity, essential for avoiding surface charge accumulation, which leads to electron–hole recombination; v) chemical stability, without photocorrosion, which depends on the relative positions of the band edges and on the respective decomposition potentials; and vi) non-toxicity, earth-abundance and low-cost fabrication processes.^{32, 49} So far, there is no semiconductor PE reported in the literature that meets all these requirements.

Review articles addressing the so-called “classic” and emerging materials for PEC water splitting can easily be found in the literature, providing detailed information on the intrinsic properties, current progresses, and make accurate analysis on the main advantageous and critical aspects of each material.^{43, 50, 51} This work addresses only the “classic” semiconductors since they have already been deeply studied, demonstrated and are currently being subject of upscaling strategies for large-scale applications. Therefore, a wide literature review was performed on the following materials: hematite (α -Fe₂O₃), tungsten trioxide (WO₃), bismuth vanadate (BiVO₄), cuprous oxide (Cu₂O), zinc ferrite (ZnFe₂O₄) and tantalum nitride (Ta₃N₅). Figure 1.3-a plots the number of publications of each semiconductor over the past decades.

This study shows that α -Fe₂O₃ has been the most studied material, but publications on BiVO₄ have risen exponentially, followed by WO₃ and Cu₂O; these materials have already been demonstrated in large-area devices. Figure 1.3-b summarizes the state-of-the-art of these four PEs based on the three-pillar criteria for commercialization: scalability, stability and efficiency. It becomes clear that efficiency has received more attention among research work, as scalability and stability targets have been barely addressed. So far, α -Fe₂O₃ is

the semiconductor material that shows the best compromise between the three key criteria, although there is still no α -Fe₂O₃ PE capable of fully addressing more than one key target. Overall, these results highlight the complexity of preparing PEs that are simultaneously large, efficient, and stable.

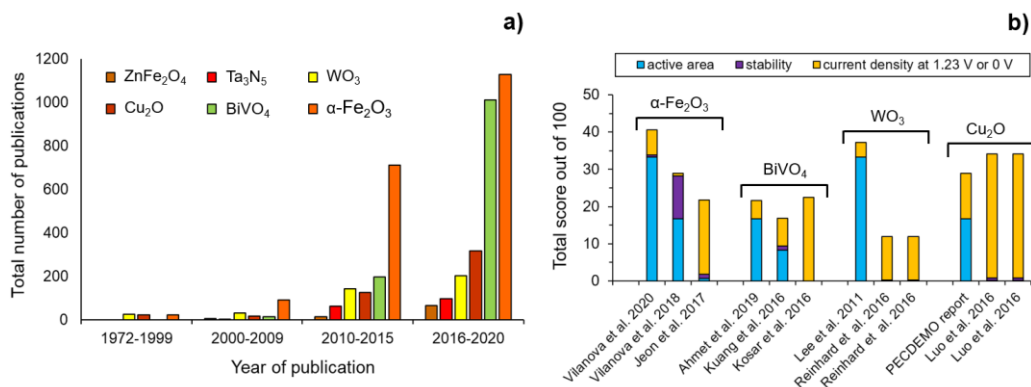


Figure 1.4. Overview on the most studied semiconductors for PEC water splitting devices: a) number of publications that include one of the keywords “water splitting”, “photoanode”, “photoanodes”, “photoelectrochemical”, “PEC”, and “solar hydrogen”, together with the semiconductor material, written using the chemical formula or the full name; e.g. “Fe₂O₃ water splitting”, “hematite water splitting”, etc.; plotted results were obtained from the Google scholar database; b) performance ranking of α -Fe₂O₃, BiVO₄, WO₃ and Cu₂O PEs based on the active area, stability and current density generated at a reference potential (1.23 V for α -Fe₂O₃, BiVO₄ and WO₃; 0 V for Cu₂O); each column of the chart corresponds to a PE that established the state-of-the-art for one commercialization criterion; normalization considered equal relevance for each criterion, delivering a total score out of 100, *i.e.* equal 33.3(3) % contribution for the active area, stability and current density; targets for each criterion were defined as follows: i) an active area of 1 m²; ii) 2920 h of stable performance (8 hours over 365 days); iii) and a current density of 10 mA·cm⁻². Appendix 1-a and Appendix 1-b provide the data used to plot the obtained results.

“Classic” photoanodes and photocathodes for PEC water splitting

From the family of *n*-type semiconductors, TiO₂ was the first used to demonstrate water splitting under simulated UV light.¹⁹ This study encouraged research work on PEC-H₂ production and several studies were made with TiO₂ in the following years, taking advantage of its favourable characteristics for a viable PE, mainly its low-cost, non-toxicity, abundance, and stability in strong acidic or basic solutions. Additionally, due to its wide range of applications, multiple techniques were optimized for preparing nanostructured TiO₂ on different substrates, which greatly assists the upscaling process. Still, its wide bandgap (3.2 eV for anatase and 3.0 eV for rutile) strongly restricts the maximum theoretical STH efficiency (1.3 % for anatase and 2.2 % for rutile), since only 5 % of the solar spectrum (predominantly UV light) can be absorbed. These drawbacks have shortened the interest on developing efficient TiO₂-based PEs for solar water splitting.⁵² Nevertheless, during the last few years, different approaches have been pursued to extend the working scope of TiO₂-PEs into the visible region, targeting an improved overall absorption while keeping its remarkable stability and low-cost.⁵³ The valence band can be modified with the incorporation of non-metal species, such as carbon or nitrogen, whereas the conduction band can be changed via doping with 3d transition metal ions.^{54, 55} Surface engineering techniques and innovative preparation techniques can be applied for further enhancing visible light absorption. Even so, no substantial change in the bandgap was reported so far and, consequently, no substantial enhancement was observed in the STH efficiency for TiO₂-based nanomaterials. For this reason, TiO₂ is no longer used as base-material for PEs, being used instead as doping agent or protective coating material of other semiconductors that have been emerging in the field.⁵⁶

Hematite (α -Fe₂O₃) is one of the most promising photoanodes for solar water splitting, being widely studied since the late 1990s. This metal oxide has remarkable chemical stability, low toxicity, and low-cost, mainly due to its high natural abundance. Also, it has a bandgap between 1.9 and 2.3 eV, nearly ideal

for visible light harvesting, which translates to a maximum theoretical STH efficiency of ca. 16% (corresponding to $12.6 \text{ mA}\cdot\text{cm}^{-2}$ at $1.23 \text{ V}_{\text{RHE}}$).⁵² However, its use as a semiconductor for PEC- H_2 generation entails some drawbacks, including: i) slow mobility of holes (ca. $0.2 \text{ cm}^2\cdot\text{V}^{-1} \text{ s}^{-1}$), resulting in a very short diffusion length of 2–4 nm; ii) poor surface water oxidation kinetics, leading to high surface recombination due to the accumulation of holes; iii) short carrier lifetime, on the order of picoseconds, due to the fast charge carrier recombination in the bulk; iv) low absorption coefficient (on the order of 10^3 cm^{-1}), requiring film thicknesses of at least a 400–500 nm for optimal light absorption; and v) relatively low conduction band position (ca. $0.4 \text{ V}_{\text{RHE}}$, at $\text{pH} = 0$) with respect to the water reduction potential, requiring an external bias to efficiently carry out the water splitting reaction.^{57, 58}

There is a vast range of published techniques used to prepare $\alpha\text{-Fe}_2\text{O}_3$ PEs, but solution-based methods have been the chosen technique in more recent publications, possibly because they are easy to implement in any lab facility, they are a low-cost technique and require the use of simple equipment. The resulting PEs present a porous morphology, like nanorods, nanowires or worm-like protuberances, which have a high surface area. The state-of-the-art $\alpha\text{-Fe}_2\text{O}_3$ PE is shaped in nanowire arrays, prepared with a hydrothermal method, and capable of delivering a record photocurrent density of $6 \text{ mA}\cdot\text{cm}^{-2}$ at $1.23 \text{ V}_{\text{RHE}}$ (ca. 7% STH efficiency);⁵⁹ despite being already a remarkable achievement, this result corresponds to 50% of the theoretical limit for this semiconductor, thus offering large room for improvement, considerably more than other semiconductors, like BiVO_4 .

The main drawback of nanostructured $\alpha\text{-Fe}_2\text{O}_3$ is its lower stability compared with other morphologies, namely ultrathin films. These compact structures present remarkable stability, reproducibility and transparency, being typically prepared by atomic layer deposition (ALD) or spray pyrolysis (SP). The most stable $\alpha\text{-Fe}_2\text{O}_3$ PE reported to date is a 19 nm film prepared by SP, capable of generating $1.05 \text{ mA}\cdot\text{cm}^{-2}$ at $1.45 \text{ V}_{\text{RHE}}$ over 1000 h, under continuous simulated

sunlight conditions, in 1 M KOH.⁶⁰ This preparation technique was successfully upscaled, allowing to demonstrate a 50 cm² ultrathin α -Fe₂O₃ PE that was able to maintain its notable stability; this PE generated ca. 0.45 mA·cm⁻² at a bias potential of 1.6 V, provided by two silicon heterojunction (SHJ) solar cells, over 1008 h, under continuous illumination (1000 W·cm⁻²), and with electrolyte recirculation at 45 °C. The achievements obtained with nanostructured and compact α -Fe₂O₃ reinforce the need to optimize a technique that allows preparing large α -Fe₂O₃ PEs that combine the best of both worlds, *i.e.* high surface area and stable performance. Nevertheless, the morphologies obtained with both techniques (SP and solution based-methods) show high reproducibility and scalability, ideal for tackling the upscaling challenge.

Tungsten trioxide (WO₃) is also a *n*-type semiconductor that has been studied for photoelectrolysis applications since the mid-1970s, presenting a good electron mobility (6 cm²·V⁻¹ s⁻¹) and a long charge carrier diffusion length (ca. 150 nm). Although this material has a bandgap of 2.7-2.8 eV, wider than α -Fe₂O₃, it is still capable of absorbing a reasonable part of the solar spectrum, but with limited maximum theoretical STH efficiency (4.8 %).⁶¹ Contrarily to α -Fe₂O₃, it is stable only in acidic solutions (pH < 4), such as aqueous H₂SO₄ or H₃PO₄.

There are several reported techniques for preparing nanostructured WO₃ PEs, namely sputtering, electrochemical anodization and electrodeposition, sol-gel, hydrothermal, solvothermal, chemical vapor deposition, and spray-pyrolysis.⁶² ⁶³ Sputtering allows obtaining photoanodes with good crystallinity, low intergrain and lattice defects; however, this technique is quite expensive and not easily scalable. Nanoporous or worm-like structures can be obtained by electrochemical anodization of metallic tungsten foils, which is a more simple, low-cost and scalable process; however, the as-prepared PEs are opaque (since WO₃ grows on a metallic foil) and the roughness of the foil affects the shape and direction of growth of WO₃ nanostructures.⁶⁴ Electrodeposition is another low-cost and scalable technique for preparing nanostructured WO₃ on glass

substrates; still, WO₃ PEs prepared this way usually present low current densities (ca. 0.35 mA·cm⁻² at 1.23 V_{RHE}).⁶⁵ Solvothermal (including hydrothermal) methods are a simple fabrication technique that allows obtaining different types of nanostructures, grown directly upon the glass substrates, *e.g.* WO₃ flake-walls capable of generating 1.8 mA·cm⁻² at 1.4 V_{RHE},⁶⁶ nanorods prepared via hydrothermal methods can present higher photocurrent densities, up to 2.7 mA·cm⁻² at 1.4 V_{RHE}.⁶⁷ Even so, sol-gel is the most common process used to prepare WO₃ PEs via chemical route. This low-cost and scalable method basically consists of consecutive depositions of a colloidal precursor solution by doctor-blading onto the FTO substrate, followed by thermal annealing, resulting in thick and highly porous films. Niederberger *et al.* reported bare WO₃ PEs, prepared via this method, that present 3.5 mA·cm⁻² at 1.23 V_{RHE}, which remains a state-of-the-art achievement.⁶⁸

Bismuth vanadate (BiVO₄) is the most successfully demonstrated ternary metal oxide photoanode, being also a promising candidate for large-area PEC-H₂ production. This material is composed of relatively earth-abundant elements and has a bandgap of 2.4 eV, which makes it capable of absorbing visible light and able to deliver a theoretical maximum photocurrent density of 7.4 mA·cm⁻² at 1.23 V_{RHE}, corresponding to a STH efficiency of 9.1%. Similar to hematite, the performance of BiVO₄ photoanodes is mainly limited by fast charge carrier recombination, due to its short hole diffusion length, estimated as 70–100 nm, which restricts the light penetration depth; it is also limited by low water oxidation kinetics.^{69, 70} To overcome these limitations, BiVO₄ is often doped with Mo and W, which enhances the charge carrier-separation efficiency.⁷¹ SP is a common technique used to fabricate BiVO₄ photoanodes, being a low-cost and scalable process.⁷⁰ Ahmet *et al.* reported BiVO₄ photoanodes prepared by SP that reached a photocurrent density of ca. 3.3 mA·cm⁻² at 1.23 V_{RHE}, with an onset potential of 0.4 V_{RHE}.⁷²

BiVO₄ photoanodes are often used in hetero-junctions, usually with WO₃, allowing to achieve photocurrent densities > 6 mA·cm⁻² at 1.23 V_{RHE}, where

nanostructured WO_3 is used as scaffolds for the BiVO_4 top layer.⁶⁹ There are several reported techniques for fabricating these heterostructures. Porous WO_3 structures (the scaffold) can be fabricated using colloidal templates, like polystyrene spheres; the BiVO_4 precursor solution is later impregnated on the template followed by a heat treatment, which allows removing the polystyrene and crystallizing the doped BiVO_4 .^{73, 74} Another interesting approach consists of combining glancing angle deposition (GLAD) to fabricate WO_3 nanorods with electrochemical deposition to grow BiVO_4 , allowing to achieve a photocurrent density of $6.72 \text{ mA}\cdot\text{cm}^{-2}$ at $1.23 \text{ V}_{\text{RHE}}$ ($> 90 \%$ of its theoretical limit).⁷⁵

The most stable BiVO_4 PE was demonstrated by Kuang *et al.*⁷⁶ The authors reported particulate $\text{Mo:BiVO}_4/\text{Ni}/\text{Sn}$ electrode that generated ca. $2.6 \text{ mA}\cdot\text{cm}^{-2}$ at $0.6 \text{ V}_{\text{RHE}}$ over 1100 h; stability measurements comprised eleven 100-h runs, with electrolyte replacement between any two runs and *in situ* self-regeneration of the catalyst. The photocorrosion inhibition was attributed to the specific high-temperature treatment; *in situ* self-generation of catalyst was assured by the thin Ni layer, which acted simultaneously as ion source and electrical back contact.

In more recent years, other photoanodes have aroused interest in the field, due to remarkable advancements made in nanomaterials research; among them, ZnFe_2O_4 and Ta_3N_5 appeared as quite promising candidates. Spinel ferrites (MFe_2O_4 , $M = \text{Zn, Mg, Cu, Ca, etc.}$) appeared as attractive ternary metal oxides, mainly due to their bandgap energy of 1.4–2.1 eV, suitable for light-harvesting in the visible range, and due to the demonstrated long-term photostability and abundance.

Zinc ferrite (ZnFe_2O_4 , known as ZFO) has a bandgap of 1.9–2.1 eV, enabling a broad absorption of visible light, while presenting favourable chemical and physical stability.⁷⁷ This material first emerged as a substitute for typical less efficient PEs. More specifically, *n*-type ZFO is normally used as a secondary overlayer on composite PEs, such as TiO_2/ZFO or $\alpha\text{-Fe}_2\text{O}_3/\text{ZFO}$, boosting the charge extraction in the primary oxide.⁷⁸ However, as main active photoanode

material, the performance of ZFO has remained modest; among the best results, Xu *et al.* reported a ZFO decorated AZO nanowires that generated $1.72 \text{ mA}\cdot\text{cm}^{-2}$ at $1.23 V_{\text{RHE}}$ in neutral electrolyte ($0.1 \text{ M Na}_2\text{SO}_4$).⁷⁷

On the other hand, from the family of oxynitrides, tantalum nitride (Ta_3N_5) has received special attention in recent years, due to its desirable band alignment for water splitting and high theoretical STH efficiency of 15.9 %. In fact, Ta_3N_5 PEs already reached 94 % of their theoretical performance limit, *i.e.* a photocurrent of *ca.* $12.1 \text{ mA}\cdot\text{cm}^{-2}$ (measured at $1.23 V_{\text{RHE}}$), which is an unparalleled achievement within the PEC- H_2 field.⁷⁹ In short, Liu *et al.* reported a multi-step strategy for improving the performance of this semiconductor, including the application of $(\text{Ni}(\text{OH})_x/\text{ferrhydrite})$ to mediate the interfacial charge transfer with Co and Ir catalysts, and a TiO_x blocking layer that allowed reducing the electron-hole recombination. However, this material is not stable in highly oxidative environments. Aiming at solving this issue, Liu *et al.* employed a ferrihydrite layer for protecting Ta_3N_5 against photocorrosion; the $\text{Co}_3\text{O}_4/\text{Fh}/\text{Ta}_3\text{N}_5$ PE yielded $5.2 \text{ mA}\cdot\text{cm}^{-2}$ at $1.23 V_{\text{RHE}}$ and kept 94 % of the initial activity after 6 h of irradiation.⁸⁰ Another strategy of particular interest for improving the stability is the addition of ferrocyanide hole scavenger; still, the reported 30 h of stable performance remains far from real application ambitions.⁸¹ Despite the recent success with Ta_3N_5 , these materials are prepared in opaque Ta foils, which avoids its application in tandem approaches. Semi-transparent materials have been reported, however, with lower photocurrents ($< 4 \text{ mA}\cdot\text{cm}^{-2}$).⁸²

Cuprous oxide (Cu_2O) is the most studied photocathode for solar water splitting. This metal oxide is non-toxic, abundant, low-cost and has a bandgap of 2.0 eV, suitable for absorbing a significant part of the solar spectrum.⁸³ Despite having a maximum theoretical STH efficiency of 18 %, Cu_2O has two main drawbacks that have delayed its application in commercial PEC devices. First, this material is quite unstable under water-based solutions, as the reduction and oxidation potentials of monovalent copper oxide are located within the water splitting

potentials, favouring photocorrosion.⁸⁴ Luckily, the stability can be significantly improved by applying protective overlayers, such as TiO₂ deposited by ALD; 50 h of stable performance were reported by Tilley *et al.*⁸⁵. Also, the combination with an *n*-type semiconductor with a more positive conduction band, which forms a *p*–*n* junction that promotes a faster transfer of electrons from Cu₂O to the *n*-type semiconductor, improving both the stability and efficiency. The second drawback of Cu₂O is related to its charge carrier diffusion length. Cu₂O films typically are > 1 μm thick to efficiently absorb sunlight; however, the electron diffusion length is limited to about 200 nm, which hinders the collection of photogenerated carriers. Morphology control through preparation techniques that allow obtaining nanostructured PEs becomes, once again, the most attractive approach to solve this problem. A good example of this strategy was implemented by Luo *et al.*⁸⁶, which established the state-of-the-art for Cu₂O photocathodes, prepared with a scalable multi-step approach, delivering an unprecedented photocurrent density of 10 mA·cm⁻² over 50 h of continuous operation.

Silicon-based PEs, the most common semiconductors in the PV industry, have also been widely used for PEC water splitting; the bandgap of 1.1 eV matches well with the solar spectrum, presenting a theoretical maximum photocurrent of 44 mA·cm⁻² under 1-sun. Indeed, Si photocathodes have been deeply explored for PEC water splitting since they have demonstrated promising results for the HER. However, bare Si PEs undergo fast oxidation in direct contact with aqueous electrolytes. This issue can be overcome with protective layers to passivate the surface states of Si, thus improving stability. As example, the alignment of TiO₂ and Si conduction bands with the HER enables its use as protective overlayer; additionally, TiO₂ facilitates the electron transfer from Si with negligible resistance.⁸⁷ Inspired by the low cost and high open-circuit voltage presented by amorphous Si (a-Si) solar cells, Lin *et al.* reported a Si photocathode coated with a TiO₂ protection layer, and with Pt or Ni–Mo co-catalysts for efficient water reduction.⁸⁸ The a-Si photocathode exhibited an impressive photocurrent density of 10 mA·cm⁻² at 0.6 V_{RHE} in a 0.5 M aqueous

potassium hydrogen phthalate for 12 h of continuous operation. Very recently, a bifacial Si photocathode coated with a semi-transparent Pt layer of 5 nm showed an unprecedented photocurrent density of $61.20 \text{ mA} \cdot \text{cm}^{-2}$ at 0 V_{RHE} under bifacial 2-sun illumination; this system enables collecting sunlight not only on the front side of the device, but also at the back, yielding ca. 57 % of excess H_2 when compared to monofacial PEC systems.⁸⁹ The later system was stable over 370 h in 1 M H_2SO_4 electrolyte.

Regardless of the choice for the semiconductor material that is used as main photoabsorber, tandem PEs are considered the most practical way to reach the efficiency targets for PEC water splitting; this approach allows providing the PEC system with the required extra bias potential for accomplishing unassisted water splitting.^{28, 90} Bolton *et al.* suggested that a STH efficiency of more than 20 % can be achieved by pairing two photoabsorbers with ideal bandgaps of ca. 1.7 eV and 1.2 eV.⁹¹ Among the several studied tandem configurations, special attention has been given to PEC-PV devices that comprise Earth-abundant materials, *i.e.* PEC-PV tandem devices coupling a semiconductor PE in series with low-cost PV cells, including silicon (Si), perovskite solar cells (PSC) and dye-sensitized solar cells (DSSCs). As an example, tandem systems using BiVO_4 photoanodes already generated photocurrent densities close to the theoretical maximum⁹²⁻⁹⁴; indeed, due to the BiVO_4 bandgap of 2.4 eV, such devices are limited to a STH efficiency of 9 %. On the other hand, the 1.1 eV bandgap of Si makes it an ideal bottom photoabsorber; in fact, the highest STH efficiency reported for a PEC-PV tandem PE was reported for a buried *p-n* junction silicon photocathode with a semitransparent PSC.²⁹

Main strategies to improve the performance of semiconductors

In the most varied studies on the preparation of nanomaterials for PEs used in PEC- H_2 production, there has been a common approach for improving the performance of semiconductors based on three main pillars: i) morphology control, ii) addition of dopants, and iii) surface control.^{58, 95}

Morphology control of the PEs by nanostructuring has been widely used for increasing the photocurrent density generated at lower potentials; it overcomes the trade-off between enhancing the optical absorption and shortening the diffusion lengths of minority carriers, as well as improves the catalytic activity through surface area increase.⁹⁶ The field of solar-H₂ production is currently experiencing an unprecedented research effort applied to nanomaterials, and countless preparation techniques have been described for obtaining semiconductors with specific morphologies.^{42, 97, 98}

Morphologies like nanoparticles, dendrites, and mesoporous structures also suffer from recombination and poor transport across the semiconductor, but in this case due to grain boundaries between particles. One dimensional (1-D) nanostructures such as worm-like protrusions, nanowires, nanotubes and nanorods, which have a high aspect ratio and large surface area, enhance charge carrier collection by minimizing recombination at grain boundaries; as an example, in 1-D nanostructures with small diameters, the distance needed for the holes to diffuse to the semiconductor-electrolyte interface is shortened, thus increasing charge mobility.⁵⁸

Typically, thick and porous morphologies have a higher surface area in contact with the electrolyte and can generate high photocurrent densities; however, they usually present low stability and the resulting photoanodes are opaque (which is a drawback when multi-layer approaches or tandem arrangements are envisioned). Also, thick semiconductors have serious recombination problems since most of the carriers are generated far from the current collector.⁴² On the other side, compact planar films, usually relatively thin (< 40 nm), present high transmittance and assure the full coverage of the underneath conductive substrate, being therefore remarkably stable.⁹⁹ However, due to poor porosity and tortuosity, these morphologies present a lower performance, usually photocurrent densities < 1.5 mA·cm⁻² measured at 1.23 V_{RHE}.^{60, 100}

The incorporation of doping agents in the main morphological structures of the semiconductor introduces additional majority carriers and creates steeper voltage gradients (thinner space-charge layers), therefore improving the charge separation.¹⁰¹ On one side, doping agents can act as an electron donor due to its incorporation in the semiconductor lattice, thus improving charge mobility. However, on the other side, doping can decrease the particle size and crystallinity, inducing the formation of a grainy structure, forcing the electrons to travel longer distances to reach the current collector. This effect can be explained by the perturbation of the lattice growth when dopants have smaller ionic radius than the semiconductor, which results in the reduction of the grain size to a level that is proportionate with the hole diffusion length of only a few nanometres.¹⁰²

There are different reported strategies for successfully incorporating a doping agent in the semiconductor.^{103, 104} Intrinsic doping is the simplest approach, since it regards fabrication procedures that include annealing at high temperatures (normally over 650 °C); this doping phenomenon is possible when fluorine-doped tin oxide (FTO) glass substrates are used, enabling the migration of Sn from the FTO layer to the main lattice of the semiconductor.^{105, 106} Other strategies usually comprise the addition of the doping agent to the deposition precursor. However, there is no standardized procedure for choosing the “best” doping agent, or the optimal doping level, since the beneficial effect of each doping agent is highly dependent both on the intrinsic properties of the semiconductor and on its morphology. As an example, the addition of Ti dopant to α -Fe₂O₃ precursors must be carried with utmost precision since slight changes in the concentration may lead to the complete vanishing of the photoactivity. For the specific case of α -Fe₂O₃, several doping agents can be used to enhance its performance, namely Si, Ti, Sn, Nb, Zr, Pt, Mn, Zn and Ni; from these dopants, Sn is more effective for thin planar films, whereas Ti plays a more significant role on porous nanostructures.¹⁰⁷ For highly doped semiconductors, one possibility is to introduce a gradient in the dopant concentration across the film; e.g. doping the BiVO₄ semiconductor with a gradient of W agent allows creating a distributed

n^+-n homojunction with a corresponding electric field that enhances charge separation within the film.⁷¹

The surface of the semiconductor, in contact with the electrolyte, requires special attention for improving the photocurrent density generated at lower potentials. In a semiconductor-liquid junction system, the rate of charge transfer at the interface relates with the rate of carrier generation and separation in the semiconductor, which makes surface states critical to form the depletion region that influences the charge transport. Therefore, surface states located on truncated sites may act as charge trapping spots, recombination centres and Fermi level pinning states, which is detrimental for the performance of the device.

Surface corrosion is a simple and effective technique for improving the OER, also promoting the interfacial charge transfer, and inhibiting surface recombination, by changing the chemical state of the semiconductor surface. A good example of this strategy was reported by Cao *et al.*¹⁰⁸ on $\alpha\text{-Fe}_2\text{O}_3$ PEs; a synergetic cathodic shift of 100 mV in the photocurrent onset potential and an increase of the photocurrent density from $1.2\text{ mA}\cdot\text{cm}^{-2}$ to $1.6\text{ mA}\cdot\text{cm}^{-2}$ measured at $1.23\text{ V}_{\text{RHE}}$ were demonstrated and attributed to surface corrosion promoted by an acid treatment over 90 min (with an aqueous solution of HCl). Although no obvious change was observed on the surface morphology, electrochemical impedance spectroscopy (EIS) analyses showed that the interface charge transfer rate increased after surface corrosion, indicating that backreaction losses were suppressed.

The use of co-catalysts is another surface treatment that allows reducing the surface states, enhancing the performance of a PE, mainly at more cathodic potentials. Co-catalyst materials can play different roles at the semiconductor-liquid interface as they can: i) facilitate the bond-making and bond-breaking reactions; ii) passivate recombination sites; iii) tune the band structure energetics; and iv) act as protective layer against corrosion.¹⁰⁹ Catalysts can be

applied as an impermeable layer, turning the semiconductor-liquid junction into a semiconductor–catalyst junction. Therefore, the band bending is no longer governed by the electrolyte redox potential but becomes dependent on the work function difference at the semiconductor–catalyst interface. The band edge positions can be moved up or down on the energy scale depending on an appropriate selection of catalysts, which allows overcoming the problem of unfavourable band edge positions.

Depending on the type of application and cost, photocatalysts are usually divided into three main categories: i) noble metals, including platinum, gold, palladium, rhodium, ruthenium, and silver; ii) transition metals, mainly including titanium, iron, cobalt, nickel, copper, zinc, molybdenum, cadmium, and tungsten; and iii) non-metals & metalloids, which include mainly boron, carbon, silicon, phosphorus, sulphur, gallium, germanium, selenium, indium, tin, antimony, lead, and bismuth. Among all, and specifically for PEC applications, noble metals, such as Ir- or Ru-based, and Pt are among the highest performing OER and HER catalysts, respectively; however, its high cost and reduced availability in nature remain an obstacle for implementation at industrial level.^{49, 110, 111} Some of these drawbacks can be overcome by increasing the surface-to-bulk atomic ratio, which reduces the metal loading without compromising efficiency. As example, a dual IrO₂/RuO₂ co-catalyst was deposited on α -Fe₂O₃ thin films to reduce overpotentials and improve the photovoltage, as reported by Dias *et al.*¹⁰⁵ The authors achieved a 140 % increase in the photocurrent density measured at 1.23 V_{RHE}, comparatively to a bare α -Fe₂O₃ PE, prepared with the same experimental procedure. These PEs also presented a low turn-on potential of 0.52 V_{RHE} and a final photovoltage of 1.20 V, the highest reported for α -Fe₂O₃-based PEs. Alternatively, transition metals and metalloids have been studied and used as co-catalysts in PEC systems. Despite presenting a slightly lower activity than noble-metal based catalysts, these elements are cheaper and more abundant, being a more reliable approach for large-area ambitions. Over the past decade, earth-abundant catalysts, such as cobalt phosphate (Co-Pi) and Fe- or Ni-oxides have been widely studied for passivation of surface states on

different semiconductors; ¹¹² as example, Co-based catalysts assist photogenerated holes to move away from recombination sites located at the surface.¹¹³ Nickel oxide (NiO_x) has received particular attention due to its remarkable stability and functionality.¹¹⁴ For example, the use of NiO_x overlayers on BiVO₄ photoanodes promotes efficient charge transfer on the surface, thus reducing charge recombination and improving the OER kinetics. In a recent study made by Zhang *et al.* NiO_x-modified/Mo:BiVO₄ photoanodes generated a photocurrent density of 2.44 mA·cm⁻² at 1.23 V_{RHE}, which represents a 2-fold increase comparatively to uncatalyzed samples.¹¹⁴

Some catalysts can also act as a protective overlayer against photocorrosion, which is critical for top-performing PEs.¹¹⁵ When the catalysts are applied as a thin uniform overlayer, they act as a physical barrier against severe reaction conditions, protecting the semiconductor and providing the chemical stability.¹¹⁶ Nevertheless, the protective effect can only be accomplished if the catalyst layer is highly stable itself, and transparent, to not compromise the light-harvesting.⁸⁷ When catalyst films are not applied uniformly, the STH efficiency can be hindered by the parasitic deposition/loading, since most catalysts are either intrinsically opaque or electrochromic under electrolysis;¹¹⁷ as so, the optimal thickness of a uniform catalyst overlayer should be < 1 nm. Alternatively, catalysts can be applied as a random or regular arrays with low geometric filling fractions, which reduces the negative effect of opacity; transparent and active catalyst films, such as porous Pt films or transparent NiO_x with suppressed electrochromism are examples of the progress made within the topic. Also, the addition of protective layers, such as thick TiO₂ (up to 100 nm) can extend the PE lifetime by reducing the likelihood of pinholes in the protective film; these findings were reported for CuO₂ and Si-based PEs.⁸⁵

1.3.2 COUNTER-ELECTRODES

The classic configuration of a PEC device, where only one of the electrodes is photoactive, comprises a semiconductor operated as working-electrode and a

metallic CE, where the complementary HER or OER takes place.¹¹⁸ As so, the CE plays an equally relevant role in the overall STH efficiency, and an inappropriate selection of materials or design criteria can significantly hinder the performance of a PEC device, as it must address some key features: i) high surface area to promote fast reaction kinetics, at least the double than that of PE; ii) good stability on strong acidic or alkaline media; iii) ductility for assuring a symmetrical assembly relatively to the PE, avoiding inhomogeneous pathways of charge carriers in the semiconductor and parasitic ionic paths in the electrolyte; and finally iv) non-toxicity and low-cost. Unfortunately, there are few available materials meeting all the aforementioned requirements, which makes some noble metals the obvious choice for lab-scale PEC water splitting experiments. As result, platinum has been used as CE in small PEC devices for decades, mainly due to its low overpotential (ca. 0.1 V) and high chemical stability over a wide range of electrolytes and pH. Almost like a standardized procedure, using a spiral-shaped Pt wire as CE placed next to the PE became the most reported configuration among PEC characterization setups. Despite being commercially available in multiple configurations for this type of applications, platinum is an expensive and scarce material, making it non-viable for large-area applications.¹¹⁹

Platinized meshes can be an interesting alternative for larger devices, usually consisting of Pt-coated titanium or niobium meshes that have a high surface area due to the roughness of the applied coating, while preserving the stability and low overpotential features.²⁷ Even so, these electrodes incorporate a high amount of Pt and other scarce resources, making them suitable only for pilot-scale demonstration devices, but non-viable for industrial applications.

Research efforts have been made to develop highly efficient and stable non-noble transition-metal-based and metal-free electrodes for water splitting applications. Liu *et al.* proposed an efficient flexible binder-free electrode for the HER, showing a low overpotential comparatively to Pt, and notable performance as an electrocatalyst.¹²⁰ They successfully demonstrated uniform

electrophoretic-deposited MoSe₂ nanosheets on carbon cloth, which is a low-cost textile with high conductivity and excellent flexibility and strength, facilitating its integration in PEC devices. This electrode presents a large number of exposed active edges due to the nanostructured MoSe₂ sheets and 3-D network of carbon cloth, presenting remarkable catalytic activity. An ongoing work at the hosting-lab aims at exploring a similar approach for half-membrane electrode assemblies (H-MEA), where the separate evolution of O₂ and H₂ gases is assured by bonding the CE to an ion-exchange membrane. This concept considers nanoparticles of non-noble metals, such as Ni- and platinized Ni-nanoparticles, sprayed to a hydrophilic carbon-based current collector, which is bonded to an ion-exchange membrane using an ionomer glue. The shape of the electrode can be adapted to any reactor design and has the advantage of enabling to operate with a vapour phase on the HER side. Another example of a carbon-based electrode was reported by Wang *et al.*¹²¹, where 3-D carbon paper/tubes/cobalt-sulphide sheets were fabricated and tested as electrode for the HER and OER. These electrodes presented high activity and stability for both cases, which was attributed to increased exposure of active sites, improved electron transport, and good release of gaseous products, with demonstrated continuous water electrolysis over 2 h, and presenting an overpotential of only 64 mV comparatively to Pt/C electrodes.

1.3.3 MEMBRANES

Typical PEC devices require the incorporation of an internal separator, like many other chemical reactors, to prevent gas mixing, avoiding the need of further processing downstream and assuring safe operation. For the current status of PEC water splitting and considering the operation at current densities $\leq 10 \text{ mA}\cdot\text{cm}^{-2}$, the membrane can represent up to 17 % of the total cost of the device, more than that of the electrodes.³¹ Ion-exchange membranes, *i.e.* cation or anion exchange membranes (CEM, AEM), are frequently used in PEC devices; these membranes have also been widely applied in electrolyzers for

many decades and, more recently, in other electrochemical systems, such as fuel cells and redox flow batteries.¹²²⁻¹²⁴

Considering water electrolysis in acidic media, perfluorinated sulfonic acid (PFSA) polymers, such as DuPont's Nafion, are the most commonly used.¹²⁵ Despite being commercially available for large-area applications, CEMs still have a high cost per unit area (0.25-0.85 €·cm⁻²). Similar to CEMs, AEMs comprise fixed positive charges, which are compensated by mobile anions, with costs ranging from 0.16 €·cm⁻² to 2.5 €·cm⁻². Typical AEMs include reinforced PET or PEEK, which have been reported in several PEC devices. Poly(norbornene) based resin membranes are among the most expensive; they present an innovative ionomer structure that contains a poly(norbornene) backbone with quaternary ammonium functional groups, with an integrated reinforcement layer that provides enhanced mechanical properties, resulting in higher ionic conductivity without sacrificing strength.

In contrast to conventional monopolar membranes used for gas separation, bipolar membranes (BPMs) were not conceived to have ion transport across them. These polymeric membranes comprise a negatively charged cation-exchange layer, and a positively charged anion-exchange layer. BPMs promote the electro dissociation of water into protons and hydroxide ions at the bipolar junction, without any gas formation; still, their use in PEC devices is barely described.¹²⁶ Nevertheless, BPMs can be an interesting approach for PEC devices that comprise photocathodes and photoanodes, allowing to pair two different electrolytes suitable for their respective oxidation and reduction reactions. Moreover, the overall losses in a BPM-based cell are minimized when strong acidic and basic electrolytes are used on the cathode and anode sides, respectively, and the induced pH-gradient may tune the redox potentials for a better alignment of the PE band edges. In this arrangement, H⁺ ions can pass through the cation exchange layer, while OH⁻ can pass through the anion exchange layer; the amount of protons and hydroxides generated by water dissociation at the BPM equals the consumption at the electrodes, promoting a

constant pH difference over the membrane. The total bias over the cell is not increased nor decreased by the water dissociation in the bipolar membrane, since the voltage required to dissociate water over the membrane causes an equal shift in redox potentials for the HER and OER, due to the pH difference between electrodes. Vermaas *et al.* demonstrated for the first-time photo-assisted water splitting performed in a PEC device with an acidic cathodic compartment and a neutral or alkaline anodic compartment separated with a BPM.¹²⁷ The use of a BPM allowed maintaining the pH gradients; moreover, the authors demonstrated that the bias over the system was slightly smaller than that using a PEC system with a single pH compartment. PEC water splitting was promoted by a Pt cathode immersed in 1 M H₂SO₄ (pH 0), and by a BiVO₄ photoanode, immersed in 1 M KOH (pH 14), resulting in a current density of 2 mA·cm⁻² at 1.3 V. When the BiVO₄ PE was immersed in a 1 M phosphate buffer solution (pH 7), the cell generated a current density of 2.5 mA·cm⁻² at 1.3 V. The authors also reported that a minor fraction of other ions was transported through the membrane due to imperfect selectivity.

Whatever the choice for the membrane, inserting a selective porous separator in a PEC cell represents an additional resistance to species transport between electrodes due to its intrinsic properties (conductivity, permeation and exchange coefficients) and due to its influence in the design of the device, *i.e.* the location of the membrane in a large-area device directly influences the distance between electrodes. As an example, during the optimization of the CoolPEC cell design (a PEC device developed within this PhD work), it was demonstrated that increasing the distance between two Pt-Ti meshes from 1 cm to 9 cm resulted in an overpotential of 297 mV, for operation at 8.1 mA·cm⁻² (simulating 12 % STH efficiency) in 1.0 M KOH.²⁷ When the electrodes were placed 1 cm away from each other, the overpotential resulting from the intrinsic properties of the membrane was estimated to be 73 mV.

Depending on the arrangement of PEs, namely in tandem configurations, membranes for PEC water splitting may need to address other critical

requirements, such as high transmittance. Additionally, the properties of the membrane can directly influence the design of a PEC device. Berger *et al.* conclude that, among the main properties of membranes, the permeability to gases is the one that has the greater influence in the device configuration.¹²⁸ Apart from safety-related problems, gas crossover in a PEC device leads to the obvious decrease in net H₂ collection, therefore requiring the operation at higher current densities to collect the same amount of H₂. The authors concluded that reducing the permeability by one order of magnitude allowed increasing the current density by 63 %; they also concluded that the conductivity of the membrane could be lowered up to two orders of magnitude to reduce at least one order of magnitude in permeability.

Aiming at eliminating the resistance imposed by a selective internal separator, membrane-free PEC devices and integrated PEC (IPEC) systems have been proposed and demonstrated. However, membrane-free PEC approaches often result in higher ohmic losses, due to the larger electrode spacing, or in additional and unnecessary design and assembly complexity, due to the need of placing extra parts or integrating convoluted electrolyte paths to prevent gas mixing. Nevertheless, for small-scale applications, such as standardized lab measurements, membrane-free devices are widely used, like the Cappuccino PEC cell.¹²⁹ Here, given the small illuminated area (ca. 0.5 cm²), the amount of produced gases does not represent safety concerns, and internal gas mixing becomes negligible.¹¹⁸ Also, in small devices, the workload for assembling the membrane, and the added ohmic losses, simply do not justify its use. Recently, Landman *et al.* proposed an innovative decoupled PEC water splitting system.¹³⁰ The authors described a new design where H₂ and O₂ are generated in separated cells, and a solid-state redox system mediates the ion exchange between the anode and cathode, both immersed in alkaline aqueous solutions. A NiOOH/Ni(OH)₂ redox couple was selected to work as auxiliary electrodes (AE), with the possibility of being cycled multiple times; electrons are transferred between the AEs through metal wires. This approach presents some advantages over the typical approach that comprises a physical gas separator: i) H₂ is

produced in a centralized generator that can be placed at the end-user's location, far away from the solar field; ii) gas mixing inside the PEC reactor is totally eliminated; and iii) the O₂ evolution compartment doesn't need to be sealed, thus avoiding gas piping costs.

Unfortunately, for large-area applications, membrane-free systems are far from implementation and require further experimental validation. On the other hand, IPEC systems aim at using a membrane electrode assembly (MEA), which comprises a proton-exchange nanoporous solid conductor and a semipermeable membrane (e.g. Nafion), coated with catalyst particles on each side. In such configuration, the membrane has the function of conducting the protons and separating the produced gases. Very recently, Tembhurne *et al.* validated the use of a Nafion 115 membrane (the solid electrolyte) coated with expensive and rare IrRuOx–Pt catalysts, platinized titanium GDLs, and 3-D printed titanium anodic and cathodic flow plates for PEC water splitting operated up to 80 °C.¹⁷

1.3.4 ENGINEERING AND UPSCALING OF TOP-PERFORMING MATERIALS: MAIN CHALLENGES AND CURRENT STATUS

The successful upscaling of efficient PEs is the main hindrance for reaching practical PEC-H₂ generation. Although nanostructured materials have been greatly optimized for lab-scale experiments (usually $\leq 5\text{cm}^2$),^{59, 105} upscaling top-performing PEs towards the expected dimensions of commercial PEC panels ($\geq 1\text{m}^2$) without significant losses in efficiency remains a demanding task^{131, 132}.

The first drawback for successfully upscaling top-performing PEs is how to properly choose and optimize the substrate. Transparent conducting oxides (TCOs), such as fluorine-doped tin oxide (FTO), are the most common substrates of PEs used in PEC water splitting^{133, 134}. These substrates are resistant to corrosion from commonly used electrolyte solutions and allow pairing two photoabsorbers in series, which is a requisite for PEC-PV tandem systems,

often considered the most feasible arrangement for reaching the solar-to-hydrogen (STH) efficiency targets ^{22, 70}. However, comparatively to metallic substrates, glass-coated substrates have a relatively high sheet resistance (usually ranging from 7 to 15 $\Omega \cdot \square^{-1}$). Hankin *et al.* ¹³⁵ demonstrated that the performance of PEC devices is greatly affected by the geometry of the electrodes, especially for PEs with lengths > 0.1 m. Some promising strategies for overcoming this drawback have been demonstrated over the past decade – Figure 1.5.

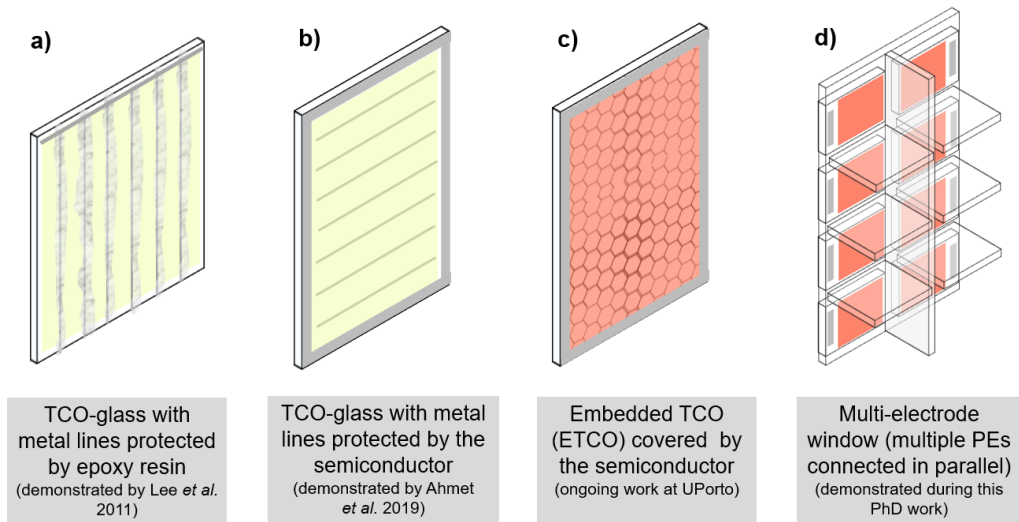


Figure 1.5. Demonstrated strategies for overcoming the ohmic losses in large FTO glass substrates: metal lines deposited on TCO glass substrates protected by epoxy resin; b) metal lines deposited on TCO glass substrates and protected by the semiconductor, applied directly over the metal lines; c) metal lines applied on ablated glass, covered by TCO, prior to the deposition of the semiconductor; d) multi-PE, comprising several small-size PEs externally connected in parallel.

The use of conductive lines across the substrate seems to be an obvious and easy approach that allows reducing the electronic path until the current collection point ¹³⁶. Lee *et al.* successfully demonstrated a 131 cm² WO₃ PE prepared on a FTO glass substrate with an embedded silver grid - Figure 1.6-a; this PE remains the largest prepared on a glass substrate containing metal lines. ¹³⁷

Silver current collector grid lines (width $\times$ height: 0.6 mm $\times$ 10 μ m) were prepared by screen printing a silver paste on the FTO substrates, followed by annealing at 180 $^{\circ}$ C. This substrate presented a resistance of ca. 1 Ω between two points 5 cm apart, considerably lower than the standard specification of the substrate, 10 $\Omega \cdot \square^{-1}$. The WO_3 layer was latter deposited by screen printing. Finally, Ag grids were encapsulated with a non-conductive and non-corrosive epoxy resin. This 131 cm^2 PE generated a current density of 1.18 $\text{mA} \cdot \text{cm}^{-2}$ at 1.23 V_{RHE} .

More recently, Ahmet *et al.* reported a 50 cm^2 BiVO_4 PE prepared on an FTO glass with electrodeposited Ni lines that allowed reaching a current density of 1.5 $\text{mA} \cdot \text{cm}^{-2}$ at 1.23 V_{RHE} - Figure 1.6-b.⁷² This work followed a different procedure to apply conductive metal lines in a large-area glass substrate; the photoactive material was deposited over the whole substrate, including exposed FTO and the Ni lines. Ni lines (7 cm long, 2 mm wide) were electrochemically deposited in a pre-treated and masked FTO glass, at a current density of -5 $\text{mA} \cdot \text{cm}^{-2}$, at 50 $^{\circ}$ C, during 15 min. Then, a 10 nm tin oxide (SnO_2) layer was deposited previously to the deposition of the 200 nm thick BiVO_4 layer.

Despite in both works the current density generated by large-area PEs was less than half of that generated by the equivalent small size PEs, the use of metal lines was demonstrated to be an effective solution to overcome the electronic resistance across the substrate. However, stability remains a massive challenge, since the metal lines need to be protected against corrosion promoted by the liquid electrolyte.^{18, 138} Even with the encapsulation with a resin or with the complete coverage of the substrate with the photoactive material, it is difficult to guarantee the full protection of the lines¹³⁷. Recently, Ivanou *et al.* developed a technical solution for overcoming this drawback; instead of applying metal lines on the top of the TCO layer, current collectors were applied beneath it, inside channels ablated in the TCO-coated glass, denominated ETCO - Figure 1.6-c.¹³⁹ This approach allowed increasing the cross-sectional area of current collectors and enabled using metals with good specific conductivity, that would be corroded if exposed to the electrolyte. The ETCO collectors were demonstrated in a 6.5 $\times$

6.5 cm² FTO glass substrate, showing full stability and a suppressive behaviour for recombination. Still, this technical solution was developed and demonstrated only for DSSCs. Ongoing work at UPORTO aims at adapting ETCO for large area PEs used in PEC water splitting and validating the concept under the standard operating conditions of PEC devices, *i.e.* with recirculation of corrosive electrolytes under uninterrupted solar illumination.

In this PhD work it was possible to disclose a disruptive approach for reducing the resistance imposed by large FTO glass substrates –Figure 1.6-d.¹⁴⁰ Instead of applying current collectors in the glass substrate, a segmented support capable of holding multiple PEs connected in parallel, used as PEC cell window, was developed. This multi-electrode support was developed and optimized for the CoolPEC cell, which is a 5 × 10 cm² PEC cell. When eight bare- α -Fe₂O₃ PEs were connected in parallel, a photocurrent density of 0.52 mA·cm⁻² was recorded at 1.23 V (under 2500 W·m⁻²).

When compared with a single 50 cm² α -Fe₂O₃ PE, eight PEs working in parallel produced a slightly higher photocurrent density, also showing also a higher photovoltage. Therefore, this solution enables using highly efficient nanostructured PEs with small dimensions while avoiding the need to apply metal lines along the substrate, thus preventing corrosion.

The second main drawback for the successful demonstration of upscaled PEs is related to the preparation of the semiconductor, *i.e.* the deposition technique. Table 1.1 summarizes some common deposition technologies suitable for preparing large-area PEs.⁴⁸

Table 1.1. Summary of preparation techniques suitable for PEC water splitting materials (adapted from ⁴⁸); ○○○ corresponds to low and ●●● corresponds to high score.

Synthesis	Techniques	Characteristics				
		Waste	Time-consuming	Quality	Cost	Comments
Physical	Spin coating (wet)	○●●	○○●	○○●	○○○	Limited for multilayers
	Evaporation	○○○	○●●	○○●	○●●	Low melting point only
	Magnetron sputtering	○○○	●●●	●●●	●●●	Expensive equipment
Chemical	ALD	○○○	●●●	●●●	●●●	Limited chemistries; expensive equipment
	CVD	●●●	○○●	○○●	○●●	High contaminants
	Plasma ALD/CVD	○○○	○●●	●●●	●●●	Expensive equipment
	Spray pyrolysis (wet)	○○○	○●●	○●●	○○○	Ideal for oxides
	Ink jet (wet)	○○●	○○○	○○●	○○●	Ideal for small, patterned areas
	Electro/Electroless plating (wet)	●●●	○○●	○○●	○○○	Ideal for metals
	Sol-gel/slurry (wet)	○○●	○○●	○○○	○○○	Low reproducibility
	Solution-based methods (hydrothermal)	○○●	○●●	○●●	○○○	Low-cost, limited quality control

According to Table 1.1, deposition techniques can be divided into chemical and physical synthesis, as well as into dry and wet methods. Dry techniques include processes such as thermal and plasma-assisted atomic layer deposition (ALD), sputtering and evaporation, whereas wet methods include the application of inks and pastes, hydrothermal procedures and chemical sprays with subsequent thermal processing; the latter is appropriate for chemically uncomplicated, amorphous or composite nanoparticle materials.¹⁴¹

Most lab equipment optimized and calibrated to prepare highly efficient PEs is not suitable for large area substrates ($\geq 50 \text{ cm}^2$), which compromises the upscaling process.^{117, 142} Record-performing PEs usually have few square

centimetres and their demonstration in large-area devices is still missing.^{32, 118} Moreover, even when preparation techniques allow using large substrates, it is difficult to ensure the uniformity of the semiconductor throughout the active area. Ahmet *et al.* assessed this problem by dividing their 50 cm² BiVO₄ PE into four equal parcels of 12.5 cm²;⁷² each part was tested individually. The authors concluded that the variation between the samples remained below 13 %. Still, even when the prepared material is uniform, the difference in performance observed between small and large samples can be related to the preparation technique itself.

Frequently, experimental procedures are developed and optimized on small substrates, being difficult to replicate the technique on larger substrates. As example, Lee *et al.* reported that the shape of the metal grid applied on the 131 cm² WO₃ PE did not allow using the 5 multi-step deposition procedure optimized for smaller samples (which do not have the metal grid).¹³⁷ Consequently, instead of presenting an optimal thickness of 25 µm, large WO₃ PEs were prepared via one-step deposition procedures, presenting a thickness of 5 µm. In this context, having a multi-PE window also appears as an interesting solution, since it allows using small PEs prepared with state-of-the-art techniques/equipment. Even so, this multi-electrode window needs to go through further optimization to be viable on an industrial scale, especially due to the increased complexity brought by electrical connections and the associated costs for producing a larger amount of PEs. Indeed, this window limits the implementation of tandem arrangements, since the electrical connections made at the back of the cell (to connect the 8 PEs in parallel) block part of the light that should be transmitted to the back. Even so, the reported multi-PE support was developed to fit the CoolPEC cell, with a limited margin for design innovation; more important, the concept was experimentally validated and there is a wide room for improving the original design and adapting it to other PEC devices.

Despite the obstacles that the upscaling of PEs represents, the most commonly used semiconductor materials for solar water splitting have been subject of

several studies, aiming at addressing the three-pilar criteria for commercialization, *i.e.* improving their stability under standard PEC operating conditions and increasing the active area without significant losses in performance. Table 1.2 includes an overview of the current status of large-area PEC water splitting.

Table 1.2. Overview of demonstrated PEs for PEC water splitting with an active area $\geq 25 \text{ cm}^2$ and ordered from lower to higher active area; adapted from ¹⁴³.

Top absorber [bottom or side absorber]	Electrolyte / pH	Area / cm^2	Current density / $\text{mA}\cdot\text{cm}^{-2}$	Stability / h	Year	Ref.
FTO / WO_3 / Mo-BiVO ₄ / Co-Pi	0.5 M Na ₂ SO ₄ + 0.1 M KH ₂ PO ₄ / pH 7	25	2.20 @ 1.23 V	1	2018	Yao <i>et al.</i> ¹⁴⁴
FTO / Fe ₂ O ₃	1.0 M KOH / pH 13.6	26	1.11 @ 1.45 V	-	2018	Vilanova <i>et al.</i> ¹⁴⁰
LaTiO ₂ N	0.1 M Na ₂ SO ₄ + 1 M NaOH / pH 13.4	40	0.56 @ 1.23 V	-	2019	Dilger <i>et al.</i> ¹⁴⁵
W / WO_3	3 M MSA acid / pH 0.14	49	0.90 @ 1.45 V	-	2014	Lopes <i>et al.</i> ³²
FTO / Fe ₂ O ₃ [2 x SHJ Si]	1.0 M KOH / pH 13.6	50	0.25 @ 1.45 V	1008	2017	Vilanova <i>et al.</i> ²⁷
FTO / Ag-Pt / W:BiVO ₄ / CoPi [2 x SHJ Si]	0.1 M KPi buffer / pH 7	50	1.50 @ 1.23 V	-	2019	Ahmet <i>et al.</i> ⁷²
FTO / Cu grids / Cu ₂ O / AZO/Ga ₂ O ₃ / RuOx	0.5 M Na ₂ SO ₄ + 0.1 M KPi / pH 5	50.4	3.7 @ 0 V	-	2016	PECDEM O ¹⁴⁶
FTO / Fe ₂ O ₃	1.0 M KOH / pH 13.6	51	0.47 @ 1.45 V	-	2014	Lopes <i>et al.</i> ³²
2 series-connected a- Si:H / $\mu\text{c-Si:H}$ tandem PV cells	1.0 M KOH / pH 13.6	64	-	40	2016	Turan <i>et al.</i> ¹⁸
FTO / WO_3 [2 x SHJ Si]	0.5 M H ₂ SO ₄ / pH 0.3	131	1.18 @ 1.23 V	-	2011	Lee <i>et al.</i> ¹³⁷
FTO / Ti-Fe ₂ O ₃	1.0 M KOH / pH 13.6	200	2.00 @ 1.45 V	48	2019	Vilanova <i>et al.</i> ¹⁴³
Mo-BiVO ₄ / CoPi [Si PV]	0.1 M KPi buffer / pH 7	16 000	-	-	2017	Tolod <i>et al.</i> ¹³¹

1.4 PEC DEVICE ARCHITECTURES FOR LARGE-SCALE APPLICATIONS

PEC-PV tandem designs that comprise a planar surface exposed to light and buried junctions to drive the photocurrent, are the more feasible approach for large scale applications. There are two main groups of planar PEC reactor architectures based on the implemented strategy for separating the evolved H_2 and O_2 : i) PEC reactors comprising an internal mechanism to separate the evolved gases; and ii) membrane-free systems comprising separated cells.⁴⁸ PEC devices can be then subcategorized in four different types, depending on the electrodes configuration as schematically represented in Figure 1.6.

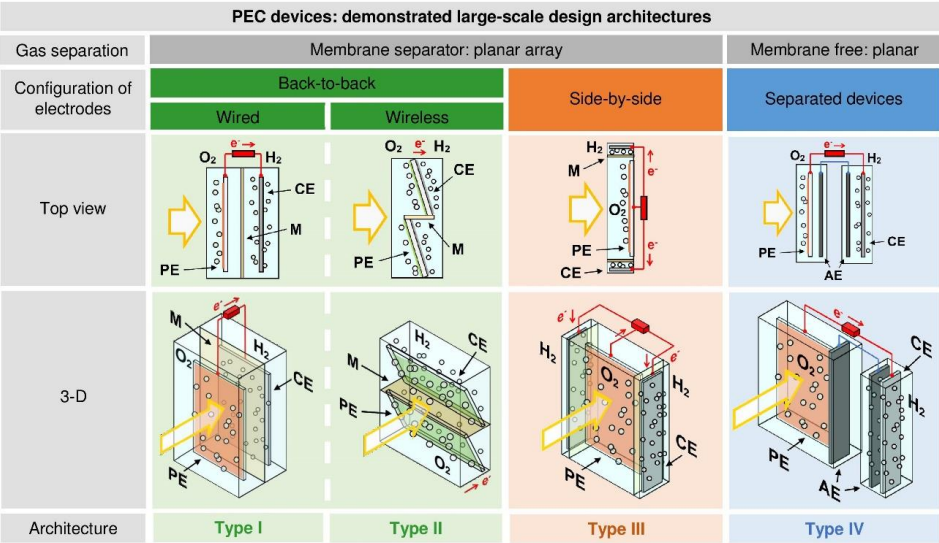


Figure 1.6. Schematic representation of the demonstrated large-scale PEC-PV tandem devices. PE - Photoelectrode; CE – Counter-electrode; M – Membrane; AE – Auxiliary Electrode.

Figure 1.6 summarizes the four types of planar PEC reactors considered herein: the back-to-back design, where the electrodes can be connected wired or wireless - Type I and Type II, respectively; the side-by-side design - Type III; and the membrane-less dual reactor device - Type IV. Types I, II and III use a

membrane separator for dividing the anode from the cathode inserted in a single container. Table 1.3 presents more detailed information regarding PEC reactors of each type, experimentally assessed and designed for large-scale solar hydrogen production. Besides the device architectures considered in Figure 1.6 and Table 1.3, other PEC designs can be found in the literature.^{21, 34, 147} However, either these designs are still in a conceptual stage, with no experimental validation, or their scalability is not possible. For instance, a particle-suspension PEC system appears to be a simple and attractive design, with no need of large electrodes, wires and compartmentalization; however, an efficient gas separation method is not available for this approach and the price of good-performing particles is prohibitively high.^{22, 148} Some other reported architectures might be promising in the near future, but the lack of experimental validation hinders a fair comparison with designs that were experimentally assessed. Holmes-Gentle *et al.* demonstrated an innovative approach of a membrane-less PEC cell using multi-physics modelling, where the evolved gases are kept separated by hydrodynamic control³⁴; this conceptual design was engineered to minimize energy losses associated with the ionic transport and to avoid the membrane cost. PEC designs considering operation with water vapour have recently arisen, but are still in an early stage of development.^{21, 149} Several patents disclosing PEC reactors have also been filled by different groups/companies over the years; however, in most cases, only the conceptual design is reported. Few patents aim at the implementation of large-area devices.¹⁵⁰⁻¹⁵²

Table 1.3. A general overview of PEC-PV tandem devices built and tested over time: detailed information concerning large scale design features; ✓ - Successfully implemented/optimized; ● - Not assessed; ● - Non-optimized or not possible to implement.

Year	Author Designation	Design Type According to Fig. 1.6	Photoactive Area / cm ²	Design Features	General Indicators	REF
2011	Stacked PEC reactor	Type I	- Demonstrated: (10 x 10) cm²	Gas separation mechanism through a Nafion membrane; ✓ PV connection was not assessed, but the PV cell can be placed outside the PEC reactor, or immersed in the electrolyte using protective materials; ● Electrolyte feeding system was simulated, but not optimized for continuous operation; ● Configuration of electrodes not suitable for tandem arrangements (photoanode // HER metal catalyst); ● Operation under concentrated sunlight conditions was not assessed.	- Si-doped α-Fe₂O₃ photoanode; - Performance - 2.5 mA·m⁻² @ 0.7 V_{HgO Hg} in 1 M NaOH under white (Xe) lamp irradiation (35 W·m⁻²); - Stability - Not assessed.	153, 154
2014-2016	PortoCell	Type I	- Demonstrated: 2014 version: (10 x 10) cm² 2016 version: (7.2 x 7.2) cm² - Prototype: 4 PEC cell modules of (7 x 7) cm²	● Gas separation mechanism through Teflon® or ion exchanges membranes; some gas crossover was observed when the device was operated in a tilted position; ✓ PV cell placed behind the electrode; ✓ Electrolyte feeding system was fully optimized in the 2nd device version (2016); ● Configuration of electrodes not ideal for tandem arrangements (photoanode // photocathode - dual side illumination using a dual mirror system; photoanode // HER metal catalyst; and photocathode // OER metal catalyst); ● Operation under concentrated sunlight was assessed in 2016 (2nd device version - the front window slightly overheated; further adjustments are necessary).	α-Fe₂O₃ photoanode; - Performance - 0.5 mA·m⁻² @ 1.45 V_{RHE} in 1 M NaOH under AM 1.5G illumination (100 W m⁻²); - STH efficiency not presented for tandem configuration; - Stability - Not assessed.	32, 155, 156
2014-2016	EMPA PEC reactor -	Type III	- Demonstrated: (10 x 10) cm²	● Gas separation mechanism was not specified; ✓ PV connection was not assessed, but the PV cell can be placed outside the PEC reactor, or immersed in the electrolyte using protective materials or tandem PES; ● Electrolyte feeding system was not investigated;	α-Fe₂O₃ photoanode; - Performance - 0.45 mA·m⁻² @ 1.45 V_{RHE} in 1 M KOH under AM	157-159

	BioPEC			✓ Configuration of electrodes suitable for tandem arrangements (photoanode $\perp$ HER metal catalyst and photocathode $\perp$ OER metal catalyst); ⦿ Operation under concentration sunlight conditions was not assessed.	1.5G illumination (100 W m⁻²); • Stability - 70 min running time;	
2015	ArtiphHyction Prototype	Type I	• Demonstrated: - 1.6 m², composed of 20 strings of 5 PEC cell modules of (58 x 12.4) cm²	✓ Gas separation mechanism through a Nafion membrane; ✓ PV cells placed outside the PEC reactor (the overall exposed illuminated area was increased; the final configuration is not a real tandem system); ✓ Electrolyte feeding system assessed; ⦿ Configuration of electrodes not suitable for tandem arrangements with a buried junction (photoanode // HER metal catalyst and photocathode // OER metal catalyst); ⦿ Operation under concentrated sunlight conditions not assessed.	• BiVO₄ photoanode; • Performance - 2 % STH efficiency; • Stability - Not clearly described;	160
2015	Louvered cell	Type II	• Demonstrated: - 2 PEC cell modules of (1.6 x 4.4) cm² - Possible to increase	✓ Gas separation mechanism through a Nafion membrane (only works in acidic media due to the electrode constraints); ✓ PV immersed in the electrolyte (tandem PE); ✓ Electrolyte feeding system was accessed through multi-physics modelling; ⦿ Configuration of electrodes not ideal for tandem arrangements (photoanode // photocathode); ⦿ Operation under concentrated sunlight was not assessed; ⦿ Dual side illumination (no information concerning the system transparency).	• Performance - 0.24 % STH efficiency; • Stability - 20 h.	161-163
2016-2020	Membrane-free PEC cell for alkaline water electrolysis in separate H ₂ and O ₂ cells	Type IV	• Demonstrated: - 1 and 100 cm² • Forecasted: - 5 x 9 array of (10 x 10) cm²	✓ H₂ and O₂ produced in separate hydrogen and oxygen cells; ✓ PV connection was not assessed, but the PV cell can be placed outside the PEC reactor, or immersed in the electrolyte using protective coatings or tandem PEs; ⦿ Electrolyte feeding system was not assessed; ✓ Configuration of electrodes suitable for tandem arrangements; ⦿ Operation under concentrated sunlight conditions was not assessed, but it was tested under natural sunlight in outdoor conditions.	• Ni foil and Pt-plated stainless-steel mesh electrodes; • Performance - 1 cm²: 7.5 % STH efficiency; - 100 cm²: 0.68 % STH efficiency. • Stability - 1 cm²: 1 h; 100 cm²: ca. 83 h.	130, 164, 165
2016-	CoolPEC cell	Type III	• Demonstrated: - 50 cm²	✓ Gas separation mechanism through an ion exchange membrane; ✓ PV cell placed behind the electrode reactor, or immersed in the electrolyte using protective materials or tandem PEs; ✓ Electrolyte feeding system fully optimized;	• α-Fe₂O₃ and dual CoPi/W:BiVO₄ photoanodes; • Performance	27, 72, 156

2019

- ✓ Configuration of electrodes ideal for tandem arrangements (photoanode $\perp$ HER catalyst and photocathode $\perp$ OER catalyst);
- ✓ Operation under concentrated sunlight was assessed in the SoCRatus setup.

- α -Fe₂O₃: 1 % STH efficiency;
- W:BiVO₄: 2 % STH efficiency;
- Stability
- α -Fe₂O₃: 1008 h.

2018-2020

CoolPEC module

Type III

- Demonstrated:
 - 200 cm², 1 x 4 array of 50 cm² PEC cells

- ✓ Gas separation mechanism through an ion exchange membrane;
- ✓ Electrolyte feeding system fully optimized;
- ✓ Configuration of electrodes ideal for tandem arrangements (photoanode $\perp$ HER catalyst and Photocathode $\perp$ OER catalyst);
- If multi-electrode windows are used instead of single 50 cm² PEs, the possibility of placing a PV cell at the back of PE is compromised.
- ✓ Operation under concentrated sunlight was assessed in the SoCRatus setup.

- 32 small nanostructured α -Fe₂O₃ PEs or single 50 cm² planar α -Fe₂O₃ PEs, connected in parallel;
- Performance
 - 2 mA·cm⁻² @ 1.45 V, 1 M KOH, ca. 6000 W·m⁻²;
- Stability
 - 4 days.

143

2019

Integrated PEC device (IPEC)

Type I

- Demonstrated:
 - 4 cm², 4 x 1 cm² III-V PV cells
 - Possible to increase

- ✓ Gas separation and proton conduction mechanisms through a membrane electrode assembly (consists of a proton-exchange nanoporous solid conductor, a Nafion 115 membrane coated with catalyst particles on each side, sandwiched between two gas diffusion layers and two bipolar flow plates);
- ✓ Electrolyte feeding system fully optimized;
- Configuration of electrodes may be suitable for tandem arrangements (electronic integration between the photoabsorber and electrocatalyst);
- ✓ Operation under concentrated sunlight considering thermal and mass transport optimization.

- Concept validated with triple junction InGaP/InGaAs/Ge PV solar cell;
- Performance
 - 0.88 A·cm⁻² – 17.2 % STH efficiency, ca. 474 kW·m⁻²;
- Stability
 - 2 h.

17, 166

The back-to-back PEC design containing the electrodes in a wired configuration (type I) is the most studied architecture for both lab- and large-scale applications -Table 1.3. This design is quite similar to the well-known alkaline electrolyzers (AEC), comprising a reservoir for the electrolyte wherein the electrodes are immersed, physically separated by an ion-exchange membrane, as shown in Figure 1.6. Over the past decade, different approaches were reported for scaling up this family of devices: i) in 2011 a 100 cm² “stacked” PEC reactor was reported for the first time by the Imperial College of London ^{153, 154}; ii) in 2014 UPORTO developed the 100 cm² “PortoCell”, which was further improved in 2016 ^{32, 156}; iii) in 2015 the European Union (EU) project ArtipHyction developed the largest PEC prototype to date, with an irradiated surface area of 1.6 m² ¹⁶⁰ and iv) in 2019 EPFL patented an integrated PEC (IPEC) device, whose concept was validated experimentally using a close electronic integration between the III-V-based photoabsorber (4 cm²) and IrRuOx-Pt-based electrocatalyst.^{17, 166} Although a great effort was pursued to successfully upscale PEC cells (Table 1.3), the arrangement of electrodes for a PEC-PV tandem configuration has always been a limiting factor to the efficient utilization of the solar spectrum, also requiring an optimized electrolyte flow pattern for efficient dissipation of heat and evolved gases.

The upgraded version of the “PortoCell” was the first PEC design that included an optimized flow pattern and simultaneously addressed ohmic losses across the electrolyte reservoir; still, this design presented some disadvantages under real operating conditions.¹⁵⁶ On the other hand, the ArtipHyction prototype was the first device that crossed the board between lab-scale cells and pilot-scale units; however, its viability was compromised by the low overall PEC performance: STH conversion efficiency of ca. 2 % with a 5 % decrease over 1000 h of continuous operation.¹⁶⁰ More recently, Haussener and her team constructed a thermally synergistic PEC-H₂ generator suitable for operation under concentrated sunlight, including an integrated reactant delivery/pre-heating flow field over the PV component for smart thermal management, and custom-designed conductive paths for close electronic integration.¹⁷ This device

demonstrated a power output of 27 W, and generated a current density of 0.88 A·cm⁻², while maintaining an efficiency of 17.12 %, under 474 kW·m⁻²; even so, this device can be operated up to a concentration factor of 1000. Despite yielding a considerably high performance, this device uses scarce and expensive materials. However, low-cost PEC-PV tandem systems based on perovskite-Si may be used with abundant electrocatalysts to turn the IPEC approach more competitive.

Type II PEC reactors are rarely reported; an example of this architecture was successfully demonstrated in 2015 by Walczak and his co-authors with the development of the so-called Louvered cell.¹⁶¹ In the Louvered prototype, planar macroscale tandem PEs are installed at a certain angle in a chamber; the PE compartments are separated by vertical ion-exchange membranes – Figure 1.6 (type II).^{161, 163} During the water splitting process, O₂ and H₂ are collected in compartments located at the top and at the bottom of the cell, respectively.^{161, 163} The overall efficiency of these PEC reactors is highly dependent on the performance of the tandem PEs but is equally important to ensure a proper ionic transport with low overpotentials. Moreover, the reactor design should be studied and optimized, e.g. through multi-physics modelling, to allow minimum ionic transport overpotentials, an efficient collection of evolved gas bubbles, and to maximize the amount of light that reaches the PE.¹⁶⁷

In a side-by-side design (type III), as the nomenclature suggests, CEs are placed side-by-side to the WE, perpendicular to the direction of the incident light; an ion exchange membrane is placed between electrodes on both sides to avoid gas mixture. Therefore, the side-by-side architecture is considered more feasible for large-scale H₂ production since it allows an open path for the sunlight to reach a tandem PE. Recently, UPORTO reported the “CoolPEC” cell, a type III design that was optimized for continuous operation, including improved key features: i) a PE that is simultaneously one window of the cell; ii) a feeding manifold for the electrolyte, assuring efficient gas bubbles detachment from the windows and efficient heat dissipation (crucial when the cell is operated under concentrated);

and iii) a narrow, easy-assemble and cost-efficient embodiment.²⁷ The “CoolPEC” cell presented a stable performance over 42 days (1008 h) in a continuous operation mode using a 50 cm² hematite photoanode that produced ca. 0.45 mA·cm⁻² at a constant bias potential provided by silicon heterojunction (SHJ) solar cells, under 1000 W·m⁻² and with constant electrolyte feeding at 45 °C.¹⁶⁸ This cell was also tested using 50 cm² dual CoPi/W:BiVO₄ photoanodes in assembled in a tandem arrangement with 2-series connected SHJ cells, showing ca. 1.7 mA·cm⁻².⁷² More recently, a 200 cm² modular device, comprising four 50 cm² CoolPEC cells, was demonstrated within this PhD work; the developed device was tested outdoor under homogenously concentrated solar radiation (up to 12.8 kW·m⁻²) provided by a LFR, and reached a maximum current density of ca. 4 mA·cm⁻².^{143, 169} Although the reported efficiencies for the side-by-side architecture are still below the target of 10 %, performance limitations can be overcome through the integration of highly efficient PEs, e.g. using the GaInP/GaInAs tandem absorbers that can yield a STH conversion efficiency of 16 %.¹⁷⁰

The fourth architecture, type IV, consists of membrane-free water splitting system implemented in separated hydrogen and oxygen cells, being the ion exchange mediated by an AE. This architecture, disclosed by Technion in a patent application filed in 2015¹⁶⁴ and reported by Landman *et al.* in 2017¹³⁰ and in 2020¹⁶⁵, is suitable for PEC systems using a photoanode in alkaline medium. In this work, Ni(OH)₂/NiOOH electrodes, commonly used in rechargeable alkaline batteries, were assembled as AEs. During electrolysis, the NiOOH electrode is charged in the oxygen cell, while the Ni(OH)₂ electrode is discharged in the H₂ cell. In Type IV devices, the oxygen produced by the photoanodes can be released to the atmosphere, eliminating the need for sealing the photopanel, while H₂ is produced at unilluminated close cells in a centralised place – Figure 1.6, avoiding the need for a large piping system for hydrogen collection. Separated cells are electrically connected using standard metal wire connections. This concept was successfully demonstrated in small-area cells (6.03 cm²) showing 7.5 % STH conversion efficiency¹³⁰, and was

recently upscaled to 100 cm² with dual hematite photoanodes, assembled in tandem with a Si PV module, showing ca. 0.552 mA·cm⁻² over 10 cycles of 8.3 h. Type IV devices incorporate important cost reduction strategies since the use of membranes is avoided and piping is shortened; even so, the STH conversion efficiency in large-area devices should be further improved, and the need of regularly replacing the AEs during the lifetime of the plant cannot be neglected.

1.5 USE OF CONCENTRATED SUNLIGHT FOR PEC WATER SPLITTING

Practical STH conversion devices do not rely only on yielding high efficiencies, but also on ensuring stable operation and on reducing the necessary operation area. Concentrating the solar radiation is considered a viable strategy for meeting those criteria, while reducing capital and operation costs, but it also brings additional challenges, namely due to the increased temperature load and continuous operation with high current density.^{17, 117}

At present, the use of solar concentrators in PEC systems remains almost unaddressed, mainly because large-scale PEC-H₂ production is still in an early stage of development and optimization, with few demonstrated devices. The closest approach to this topic is the use of solar concentrators in PV technologies. Indeed, over the last few decades, the integration of renewable energy sources in traditional systems resulted in the successful coupling of PV cells with AEC, where the PV cells feed the EC unit with the necessary power input to drive the water electrolysis.¹⁷¹ Both large-scale AECs and PV cells have been optimized, demonstrated and used for industrial H₂ production for many decades and, more recently, solar concentrators have been used to further improve the overall performance of the PV component.^{172, 173} In a similar way, integrating solar concentrators in PEC systems requires further optimization, but in a symbiotic approach, *i.e.* PEC devices need to be optimized to operate under concentrated sunlight and solar concentrator need to be redesigned to be compatible with material restrictions of PEC devices. Also, the operation under

an optimum concentration factor depends on the available solar irradiance (*i.e.* varies with the site location) and requires proper thermal management solutions, which should be optimized for each PEC device architecture.

Currently there is no standardized nomenclature in the literature for grouping solar concentrators.¹⁷⁴ Nevertheless, some authors have grouped solar concentrators in different categories, usually depending on the operational characteristic that better distinguishes the purpose to which they are used for. One option for categorizing solar concentrators considers the type of focal area, which can be linear or punctual.¹⁷⁵ This criterion is directly related to the concentration factor and temperature achieved in the receiver. Linear concentrators provide homogeneous light concentration along a planar surface or a line, allowing to reach moderate to high-temperature values in the receiver, usually, ranging from 100 to 500 °C.^{174, 176} On the other hand, punctual concentrators focus the sunlight in a single point, allowing to achieve very high temperature values in the receiver, usually above 500 °C.

Another option for categorizing solar concentrators addresses the way the solar radiation is focused on the receiver, being reflective or refractive.¹⁷⁷ More recently, Caron *et al.* suggested another categorization for solar concentrators suitable for planar PEC devices, based on the type of motion (fixed, translational and rotational) and on the type of tracking (stationary, one-axis and two-axis tracking).¹⁷⁸

Considering the four types of PEC device architectures, different solar concentrators can be coupled with PEC devices.¹⁷⁹ Coupling these two technologies can be made via two main assembly arrangements: i) externally, in separate structures, focusing the sunlight only in the PV component or in the tandem device, *i.e.* in both PV/PEC components; and ii) integrated in the device itself, *i.e.* comprised in the glass windows.¹⁸⁰ Figure 1.7 represents schematically the different types of solar concentrators currently available. Table 1.4 assesses

the compatibility of each solar concentrator depicted in Figure 1.3 with the PV and PEC technologies, based on multiple categorization criteria.

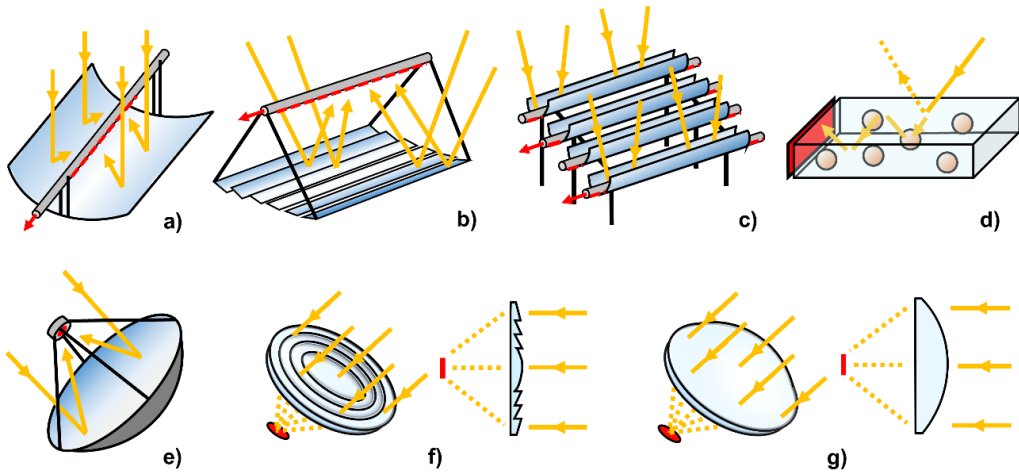


Figure 1.7. Schematic representation of the different types of solar concentrators: a) parabolic trough collector (PTC); b) linear Fresnel reflector (LFR); c) compound parabolic concentrator (CPC); d) luminescent solar concentrator (LSC); e) parabolic dish concentrator (PDC); f) Fresnel lens (FL); and g) convex lens (CL). The focal area in the receiver is highlighted in red.

Reflective concentrators with linear focus are the most common type of solar concentrators, including the parabolic trough collectors (PTC), the linear Fresnel reflectors (LFR), and the compound parabolic concentrators (CPCs). Being studied since the early nineteen-tens, parabolic trough collectors (PTC, Figure 1.7-a) are the most used linear solar concentrators, mainly due to its simple design and low-cost.¹⁷⁶ These concentrators work on a single axis and have a linear receiver unit. Basically, curved mirrors reflect the sunlight towards a dark-coated metallic tube (absorber), which is located just above the mirror and contains the recirculating working fluid.¹⁸¹ LFRs (Figure 1.7-b) are used since the mid-1960s and, like parabolic troughs, operate with a single-axis mirror.¹⁸² These concentrators essentially consist of different arrays of mirrors that focus the solar radiation in a linear central receiver, providing concentration ratios between 30 and 80. The solar receiver is located on the focal line, defined by

the tracking mirrors. These mirrors are positioned at different angles and the tracking system is installed at each line of mirrors to concentrate the sunlight on the fixed receiver.¹⁸³

Table 1.4. Main characteristics of the solar concentrators schematized in Figure 1.7 and the assessment of compatibility with PV and PEC devices.

Categorization		Solar concentrators (abbreviation)						
		PTC (a)	LFR (b)	CPC (c)	LSC (d)	PDC (e)	FL (f)	CL (g)
Working principle	Reflective	●	●	●	●	●	○	○
	Refractive	○	○	○	●	○	●	●
Focal area	Linear	●	●	●	●	○	○	○
	Punctual	○	○	○	○	●	●	●
Receiver	Planar	○	●	○	●	●	●	●
	Cylindrical	●	●	●	○	○	○	○
Compatibility	PV	●	●	●	●	●	●	●
	PEC	●	●	●	●	●	●	●
Association with PV/PEC	External	●	●	●	○	●	○	○
	Integrated	○	○	○	●	○	●	●
Main application	Fluid heating	●	●	●	○	○	○	○
	Power generation	○	●	○	○	●	○	○
	Glass / windows	○	○	○	●	○	●	●
	Coupling with PV	○	●	○	○	○	●	●
Defining operating parameter	Fluid temperature (°C)	350-400; up to 650	100-300; up to 600	80-250	NA*	NR**	NR**	NR**
	Concentration factor (x)	NR**	30-80	NR**	up to 100	up to 3000	60-260; up to 720	500; up to 900

* NA – Non-applicable

* NR – Non-relevant

Compound parabolic concentrators (CPCs, Figure 1.7-c) are also a mature technology, being used commercially for many decades, namely for PV applications, since they enable capturing the diffuse solar radiation together with the direct component. Among CPCs, the most studied and efficient type is the 2-D CPC trough, which allows collecting and concentrating all the rays within a specified acceptance angle (as depicted in Figure 1.7-c). More recently, novel

features have been added to this type of solar concentrators, namely lens-walled structures, allowing to have a larger acceptance angle and better optical efficiency. Also, customized 3-D CPCs, ideal for PV applications, represent a great improvement over traditional 2-D CPC troughs, yielding optical efficiencies higher than 90 %, considering the incident rays inferior to the acceptance angle.

Different types of reflective linear solar concentrators can be combined taking advantage of the unique design features of each one. The best-known example of this symbiotic association is the combination of LFRs with CPCs. In this case, the receiver of the LFR incorporates a secondary reflector, usually based on a 2-D CPC.¹⁸⁴

Due to the linear and cylindrical receiver configuration, reflective linear solar concentrators are mainly used for heating a recirculating fluid or for steam generation; therefore, they are not usually coupled to water electrolysis devices. Nevertheless, more recently, these solar concentrators have been redesigned for including double-axis tracking systems and special supports for holding linear-array reactors, used in modular EC and PEC devices. As result, these concentrators provide homogeneous concentrated sunlight in a rectangular focal plane (low to medium concentration range), with the advantage of having a small form factor.¹⁸⁵ The SoCRatus is a solar concentrator based on a LFR, developed by the Institute of Solar Research at DLR), equipped with 22 linear mirrors and a two-axis tracking system that concentrates the sunlight in a rectangular flat focus of $250 \times 10 \text{ cm}^2$, ideal for holding linear-array reactors.^{27, 186} This solar concentrator was successfully demonstrated for PEC water splitting, providing a PEC reactor with concentrated sunlight up to $17 \text{ kW} \cdot \text{m}^{-2}$.¹⁴³

Solar concentrators with a punctual focus are the other big group of solar concentrating devices, including reflective and refractive devices. Parabolic dish concentrators (PDCs, Figure 1.7-e) are probably the most well-known punctual solar concentrators. These devices have a simple design, comprising a parabolic reflective dish, usually equipped with a dual-axis solar tracking system and are

commonly used for power generation. The central receiver is located at the focal point¹⁸⁷, allowing to reach concentration ratios up to 3000. PV and PEC devices can be coupled to PDCs, if assembled out of the focal point, thus receiving concentrated solar radiation, but with a lower concentration ratio, compatible with the restrictions of materials used in PV and PEC devices.

Concentrating the solar radiation in a punctual focus area can also be achieved by simply using Fresnel lenses (Figure 1.7-e) or convex lenses (Figure 1.7-g). This technical solution is mainly used in smaller devices or modular devices comprising small individual cells. In fact, these type of lenses have been used in concentrated photovoltaic electrolyzers (CPVE) over some decades.¹⁸⁸ In CPVEs, lenses are typically used to focus the sunlight on a special tailored multi-junction solar cell, which is then connected to the anode of the electrolyser, usually a polymer electrolyte membrane (PEM) electrolyser.¹⁸⁹ Both types of lenses can also be directly coupled to PEC devices, directing the concentrated solar radiation to the photoactive electrode, or they can be integrated in the device itself, as front glass for both PEC or PV devices.¹⁹⁰ Price *et al.*¹⁹¹ demonstrated that using high-efficiency micro-PV cells embedded between a pair of plastic lens arrays allowed reaching a 200-fold increase in the power output comparatively to an unconcentrated cell, under an optical efficiency of 70%, for incidence angles of ca. 60 °, at a fixed latitude tilt. That work demonstrates that photo-conversion efficiencies up to 40 % can be achieved by simply incorporating arrays of convex plastic lenses in the front window and convex mirrors at the back, resulting in a compact and inexpensive design.

Luminescent solar concentrators (LSCs, Figure 1.7-d) are a distinct type of solar concentrating devices, with a different working principle comparatively to the two types previously presented. Typical LSCs basically consist of plastic optical waveguides doped with fluorophores, or glass pieces coated with active layers of emissive materials, which can absorb direct and diffused sunlight and then re-emit it at longer wavelengths. Total internal reflection propagates the luminescence towards a receiver (normally a PV cell), placed in the opposite

side of the device.¹⁹² LSCs combine the advantage of a reflective or refractive solar concentrator -collecting the sunlight from a larger area and focusing it onto a smaller area - while avoiding the disadvantages brought by the design of common solar concentrators (e.g. the need for direct sunlight tracking, and often restrictive parabolic-like shapes that require large surface areas), being ideal for integration in urban environments.¹⁹³ These devices were first reported in 1973 and, over the past decade, have been pointed as a cost-effective alternative to optics-based solar concentration systems aiming at enhancing the performance of stand-alone solar cells and allowing their integration into existing or newly constructed buildings, *i.e.* semi-transparent PV windows capable of transforming energy-passive façades into large-area energy generation units, a particularly appealing strategy towards nearly zero-energy buildings.^{194, 195} LSCs can also be coupled to PEC units, replacing one of the transparent windows. Additionally, if the emission wavelength of the LSC emitters is further matched with the spectral absorption peak of the photo-active receiver, the power output can be further increased.^{196, 197}

Concentrated photovoltaic electrolyzers (CPVEs) are considered a thriving way for low-cost and clean H₂ production from sunlight, and this technological synergy can be the starting point for developing concentrated photoelectrochemical cells (CPEC).¹⁹⁸ Based on modelling calculations and LCA analysis, Dumortier *et al.*¹⁹⁹ showed that the use of an integrated concentrated PV electrolyzer allows reducing the GHG of H₂ production up to seven times, comparatively to H₂ production through autocatalytic decomposition, non-concentrating PV electrolysis, or natural gas steam reforming. Also, the energy yield ratio – the ratio between the energy generated during the lifetime of the equipment and the energy that they incorporate – can be increased by four times, comparatively to standard electrolyzers.

In the past few years, conceptual designs of integrated CPVEs have been proposed and design guidelines based on performance modelling have already been presented. According to the literature, having an efficient thermal

management is the most critical design feature for assuring the expected performance increase due to the high photon flux.²⁰⁰ Some studies have revealed that at least 20 % of the total power cost comes from the water supply for cooling purposes. Still, for CPVEs, a significant part of the operational costs comes from the concentrators and from the tracking systems. Also, as previously explained, choosing efficient and stable absorbers and catalysts remains a mandatory requirement for low-cost H₂ production, since this is often considered the financial tailback of non-concentrator systems.²⁰¹

Like CPVEs, CPECs started to be subject of interest in the field. CPEC systems have a major advantage over CPVEs: the PV and the EC components are coupled in a single unit, which allows reducing the cost of the device and allows further improving the overall efficiency, since concentrated sunlight will be used by both components. Research work addressing the use of concentrated sunlight for PEC-H₂ production is strongly limited by the lack of commercially available PEC devices, particularly with an illuminated area higher than 50 cm².^{118, 131} In a pioneer work by Segev *et al.*²⁰², two different types of α -Fe₂O₃ PEs (50 nm polycrystalline dense film and 500 nm mesoporous layer with cauliflower structure) were subjected to concentrated simulated sunlight, ranging from 1 to 25 kW·m⁻². It was observed that the photocurrent generated by both 0.28 cm² samples increased linearly with the solar flux, while the photovoltage scaled logarithmically with the light intensity. More recently, a 200 cm² PEC module was demonstrated with a modified LFR, as part of the present PhD work.¹⁴³ This device was optimized for continuous operation under real concentrated sunlight and was tested with nanostructured α -Fe₂O₃ PEs, which generated a stable photocurrent density of ca. 2.0 mA·cm⁻² over four days, under solar irradiances up to 14 kW·m⁻². These results correspond to a measured H₂ production of 5.5×10^{-5} g_{H₂}·h⁻¹·cm⁻², the highest reported for a CPEC device based on a low-cost metal oxide semiconductor with an active area higher than 50 cm².

Particularly for combined CPV-PEC devices, splitting the solar spectrum is a promising strategy to further increase the solar conversion efficiency^{203, 204}, as reported by Bicer *et al.*²⁰⁵. Though the received portion of wavelengths decreased to 19 % due to the use of light splitters, the loss of power was compensated by the beneficial effect of concentrated sunlight, resulting in conversion efficiencies up to 15 %. Additionally, lower wavelengths were used by a Cu₂O photocathode for PEC-H₂ production.

CPEC devices allow reaching considerably higher photocurrent densities at lower applied potentials, comparatively to standard PEC systems, due to the increased photon flux; still, they result from the combination of two separated components, a PEC device and a solar concentrator. To overcome this limitation, concentrator integrated PEC (CIPEC) devices are an interesting approach, since they combine all components in a single unit.²⁰⁶ Therefore, the cost of solar-H₂ can be further decreased, since the construction area and the equipment infrastructure are simultaneously reduced.

The CIPEC approach has been investigated for PEC systems that use TiO₂ photoanodes, where quantum dots (QDs) LSCs are used for sensitizing narrow-bandgap TiO₂, thus improving both the photocurrent density and the photostability. Recently, Zhang *et al.* reported QDs-based LSCs with an optimal shell thickness of 1.6 nm employed in TiO₂ photoanodes that allowed reaching a current density of ca. 16.0 mA·cm⁻² (at 0.9 V_{RHE}), the highest value reported for PEC cells based on CdS/CdSe QDs; still, the stability was quite low, *i.e.* it showed 17 % photocurrent decrease after 4 h.²⁰⁷ The degradation is usually caused by the self-oxidation of QDs induced by ultraviolet radiation. Liu *et al.*¹⁹⁷ developed a new approach for integrating LSCs in PEC cells, aiming at having a standalone device. When QDs were coupled with a LSC, 84.6 % of the initial photocurrent density was retained after 23 h of continuous illumination.¹⁹⁷ The concept of integrated LSCs-PEC devices was already demonstrated in large-area devices. Meinardi *et al.* demonstrated a large-area Stokes-shift-engineered core/shell CdSe/CdS g-QDs LSC-PV device with negligible losses due to

reabsorption, yielding a 10.2 % efficiency, with an estimated effective concentration of 4.4.²⁰⁸ Also, Wu *et al.* recently demonstrated a large-area tandem LSC prototype ($> 230 \text{ cm}^2$) tuned for optimal solar-spectrum splitting that yielded an optical quantum efficiency of 6.4 % and solar-to-electrical conversion efficiency of 3.1 %.²⁰⁹

Another example of the CIPEC technology was addressed by the SHINE-Nanotera consortium's. This project aimed at developing a PEC device with integrated solar concentrator units for operating under medium-range solar concentration (ca. 20–50 times).²¹⁰ The solar concentrator used in this device embodies a self-tracking design, with an angular acceptance of $32^\circ (\pm 16^\circ)$ and an effective concentration up to 20; water microfluidics is used for thermal management.²¹¹ This smart system uses a dichroic mirror to split the solar radiation, where the transmitted part ($>750 \text{ nm}$) is absorbed by a black paraffin wax layer. Then, the paraffin melts and expands upwards, creating a coupling feature for the reflected light.²¹² Then, the focal spot changes and a different part of the actuator is activated, depending on the position of the sun throughout the day/season.

Simpler CIPEC devices can be developed by just replacing one window of a PEC reactor by a Fresnel or convex lens. The use of lenses with a short focus distance is compatible with planar PEC device architectures, providing a higher solar flux at moderate concentration factors, thus boosting the performance of the photoactive materials, but without requiring additional cooling systems. However, CIPEC devices designed for operation under high concentration factors usually require thermal management solutions.²¹⁰ Tembhurne *et al.*¹⁸⁰ developed a 2-D multi-physics model to investigate and simulate CIPEC devices subjected to highly concentrated sunlight, working at high temperatures. The calculation model allowed concluding that the decrease in the performance over the lifetime of the device due to degradation can be controlled and counterbalanced with proper thermal management, *i.e.* a 12 % degradation in STH efficiency can be compensated by increasing the mass flow rate of the

electrolyte by seven times. Very recently, an innovative CIPEC device, integrating thermal management, showed current densities of $0.88 \text{ A}\cdot\text{cm}^{-2}$, under concentration factors up to 474; even so, this device can be operated with concentration factors up to 1000.¹⁷ It was demonstrated that the aqueous electrolyte solution cools the illuminated semiconductor, preventing losses of photovoltage, while the electrocatalyst is heated, lowering the overpotential of the electrocatalytic reaction.

The upscaling of PEC devices that can be operated with concentrated sunlight must take advantage of the know-how acquired from other technologies that use concentrated sunlight to drive the water electrolysis. At present, thermochemical H_2 production is the most mature and widespread technology using concentrated solar power to promote water splitting. These systems usually use CPCs or heliostat solar towers, which provide the required high thermal input for the thermochemical- H_2 production cycles.²¹³ The first closed solar-only thermochemical- H_2 production plant was inaugurated on March 2008 in Almeria, Spain, equipped with a 100 kW continuous reactor, operating up to 40 cycles of constant H_2 production.²¹⁴ However, PEC devices are not compatible with such high solar inputs; alternatively, PEC- H_2 production plants should resemble those that currently exist for concentrated solar-driven AEC.¹⁷²

At industrial level, the energy required for promoting the water electrolysis is much higher than the theoretical value related to the energy of the reaction, mainly due to: i) ohmic losses, related to the resistive components of the cell, *i.e.* the electrodes, the electrolyte and the membrane; these overpotentials increase linearly with the generated current, but decrease with temperature; and ii) anodic and cathodic overpotentials, related to transport phenomena across the electrodes and to the kinetics of reactions. For overcoming these limitations, in PV-EC plants, PV modules are associated with LFRs, which provide concentration factors and generate a thermal input compatible with the modules.

Future PEC-H₂ production plants should present a similar layout as currently-operating CPV-EC plants, as follows ²¹⁵: i) an electrical station that comprises an inverter, a transformer, a rectifying cabinet, and a regulation unit; ii) a water pre-treatment unit, including sand and activated carbon filtration systems, a reverse osmosis system, and a mixing system for adding the electrolyte; iii) the PEC units (replacing the AEC), associated to solar concentrators; iv) a gas-liquid separation system, one for H₂ and another for O₂ (when O₂ is considered a valuable by-product; otherwise it can simply be released to the atmosphere); the remaining liquid, should be sent back to the PEC units; and v) a H₂ purification system, including de-oxidizer and drying sub-systems. Figure 1.8 schematizes a CPEC-H₂ production plant.

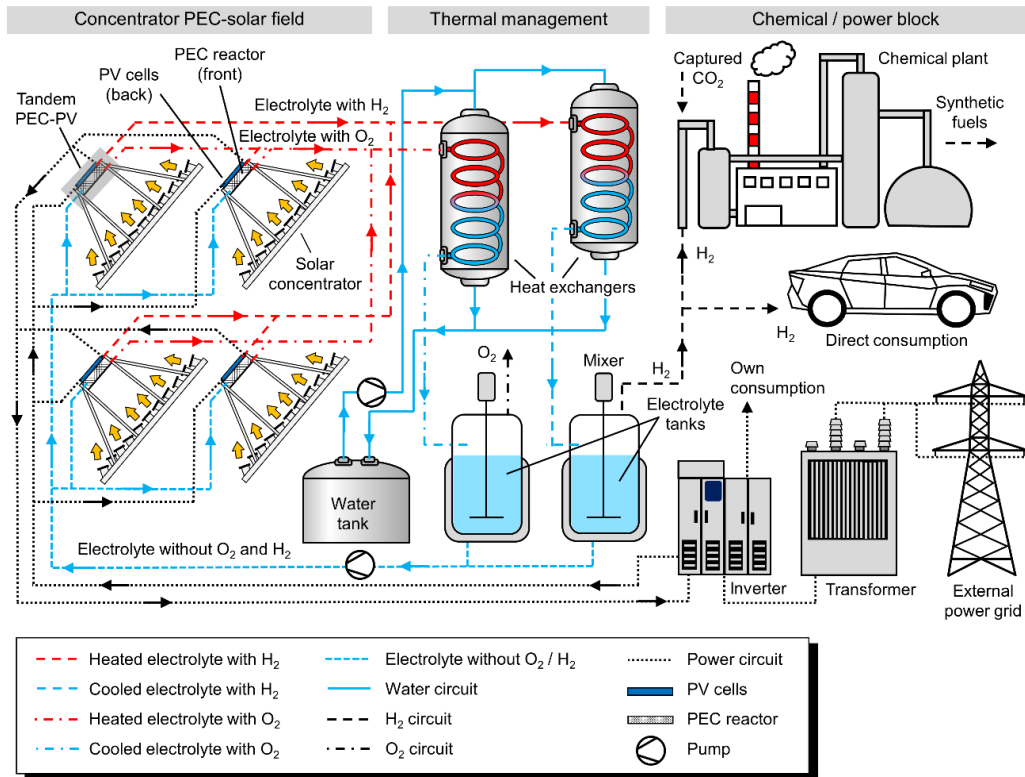


Figure 1.8. Schematic representation of a CPEC-H₂ production plant, comprising LFRs coupled to PEC-PV devices, with the complete liquid, gas and power flows.

1.6 COMPARATIVE OVERVIEW OF TECHNO-ECONOMIC AND LIFE-CYCLE ASSESSMENTS

Hydrogen is considered a versatile energy carrier, capable of addressing the fluctuating availability of solar, wind, water, and geological resources; however, to be considered a competitive option within the renewable energy market, its production should be affordable, reliable, safe, sustainable, and efficient.²¹⁶ At present, fossil fuels supply ca. 95 % of the global H₂ production, more specifically 48 % is produced from natural gas, 30 % from oil and 18 % from coal, which undermines the view that H₂ is a greener alternative to conventional systems.^{217, 218} As so, scientific efforts should be made for investigating more efficient, scalable, and low-cost technologies for producing H₂ from renewable sources.

Green-hydrogen has several economic advantages over other renewables: i) use in medium and high-temperature heating processes in the industry for which electricity is not effective; ii) distribution systems can be built on the existing natural gas infrastructure; iii) it is a valuable industrial chemical feedstock; iv) it can be used in fuel cell vehicles, which have quicker refueling than battery electric vehicles; and v) it can be stored in gaseous form for large scale applications, as a liquid, for air and space transportation, and stored in metal hydrides for small scale applications.²¹⁹ Complementarily, producing H₂ from renewable sources will have a direct effect on the environmental impact of the transportation and industry sectors.²²⁰ Several economic studies show that a well-developed H₂ infrastructure can only be achieved by increasing the capacity of H₂ production systems, especially for renewable-based systems. Attaining this goal will lead to the subsequent reduction in production costs and to the wide acceptance by the public, industry, and governments, which will support the investment on infrastructures.²²¹

At present, green-H₂ is produced mainly by mature and commercially available technologies, such as conventional electrolyzers, which incorporate non-abundant and expensive materials and are often operated with electricity from

the grid. Selecting the appropriate H₂-production method for future industrial plants is a massive challenge since few comparative studies have been made on this topic. Indeed, most environmental and economic assessment studies focus a specific technology or a case study of already existing plants. For the case of PEC-H₂, which is on its early development stage, adopting holistic approaches is vital for improving its competitiveness, namely by analyzing the main results of life-cycle and techno-economic studies performed over the last decade.

Life cycle assessment (LCA) is the most widely used tool for assessing the environmental impacts attributed to a product or a service, comprising three major stages: i) goal and scope definition, including the selection of the life cycle boundaries; ii) inventory data collection on material and energy flows, where emissions and consumption of resources are identified and quantified; and iii) estimation of the environmental impact of each life cycle step, normalization of the impact category indicators and grouping by weighting or significance.²²²

The most common type of LCA is the cradle-to-grave approach, which considers all steps of the life cycle, from the extraction of raw materials until the disposal/end-of-life. For energy systems, due to their complexity, a cradle-to-gate approach is more effective, usually including only the production and distribution of energy. Particularly for PEC-H₂, since commercial large-scale PEC devices are not available yet, LCA studies are based mainly on assumptions and extrapolations from the existing devices, which were developed for laboratory purposes. Sathre *et al.* performed a close approach to what could be an ideal prospective life-cycle inventory for PEC water splitting devices.^{223, 224} The authors report that large-scale PEC-H₂ production with a 10 % STH efficiency and a life span of 20 years (considering 1 GW·year⁻¹, equaling 610 t H₂·day⁻¹) would yield an energy payback time (EPBT) of 8.1 years, an energy return on energy invested (ERoEI) of 1.7, and a life-cycle primary energy balance of 500 PJ, considering 40 years of projected service life. If the STH efficiency is increased to 20 %, the EPBT can be further reduced to 3 years.²²⁴

Therefore, the STH conversion efficiency and the life span of the PEC cells are critical model parameters affecting the net energy metrics; in this context, parameters associated with the balance of systems (BOS), such as the construction and operation of liquid and gas infrastructure, play a much smaller role. Although Sathre's study only focused the net-energy parameters, other components of the life cycle were highlighted for quantifying the environmental impact of this technology, namely: i) fabrication of active materials; ii) production of the materials used in the embodiment; iii) assembly of the cell; iv) assembly of the module; v) operation of the module (including auxiliary equipment); and vi) end-of-life.

A major limitation of performing comparative analyses on LCA studies is the variety of reported impact categories, and lack of standardization in the way results are presented. As so, the comparative outlook presented in this work considers only the global warming potential (GWP, $\text{kg}_{\text{CO}_2\text{eq}} \cdot \text{kg}_{\text{H}_2}^{-1}$) and acidification potential (AP, $\text{g}_{\text{SO}_2\text{eq}} \cdot \text{kg}_{\text{H}_2}^{-1}$) as categories of environmental impact, since they are the most addressed indicators; the functional unit was defined as 1 kg of generated H_2 .

Assessing the economic viability of H_2 production methods is also crucial for having a holistic view on their competitiveness; a wide literature survey was done on the topic, aiming at understanding how competitive PEC- H_2 is against the other options.^{30, 31} Again, due to the lack of standardization of results and ambiguity in the definition of variables and criteria for the quantification of the economic performance, the present work only considers the payback time and the production cost (including the capital cost) as economic indicators for the comparative analysis. In short, the payback time of H_2 production systems describes how long a facility must operate to deliver the H_2 equivalent to the energy required for its manufacturing, construction, and decommissioning; it is calculated as the ratio between fixed energy inputs and the annual net energy output under full-scale steady-state operation.²²⁴ This parameter cannot be categorized as a life-cycle metric, since it does not account for the energy that

continues to be produced after the payback time is reached; therefore, the service life of the facility is not included in the calculations. The production cost is the second economic indicator selected for this work; in this case, it refers to the total cost needed to bring a H₂ production facility to a commercially operable status, combining individual purchase costs with installation factors, indirect costs (*i.e.* engineering, construction, contingency costs, taxes, etc.) and maintenance during the lifetime of the facility. The US Department of Energy targeted threshold cost of 5.70 € per kg of H₂.²⁵

Finally, it is essential to select the appropriate H₂-production methods that should be included in the comparative analysis, in other words, which are the technologies of interest to compare with PEC water splitting. At present, there is no specific taxonomy for grouping H₂ production methods, but one can assume a logical categorization depending on the main energy input, being classified as fossil-fuel- or renewable-based technologies.²²⁵ Fossil fuel-based technologies are more mature, widely developed and account for almost 95 % of current H₂ production.²¹⁸ Among them, steam methane reforming (SMR) and coal gasification are the most widespread; others include hydrocarbon pyrolysis and autothermal reforming. Despite accounting for only 5% of current H₂ production, renewable-based production is more diverse, and can be divided in two main categories: thermochemical and water splitting. Thermochemical H₂ production comprises biological processes (direct and indirect bio-photolysis, photo and dark fermentations, and multi-stage dark and photo-fermentation) and biogas reforming. On the other hand, water splitting technologies include electrolyzers (alkaline - AEC, proton exchange membrane - PEM, and solid oxide electrolysis cells - SOEC), supplied with electricity from the grid or from wind, hydro or solar-PV power plants), high-temperature electrolysis (HTE), usually integrated with nuclear power plants, and PEC water splitting coupled with or without solar concentrating devices. Figure 1.9 schematizes the taxonomy of H₂ production methods.

95% Current status of H ₂ production methods					5%
Non-renewable			Renewable		
Coal	Oil	Natural gas	Direct water splitting	Thermochemical processes	
Reforming			High temperature electrolysis	Photo/dark fermentation	
Gasification			PEC	Bio-photolysis	
			Electricity from the grid	Biomass gasification	
Alkaline/PEM electrolysis			Alkaline/PEM electrolysis	Biofuels reforming	
			Wind	Hydro	Solar
				Plasma arc decomposition	

Figure 1.9. Grouping and categorization of hydrogen production methods.

The present overview on LCA and techno-economic studies comprises specific H₂ production technologies, for which it was possible to collect enough data to perform a reasonable comparison, presented in detail in Table 1.5. A comparative outlook of environmental indicators and production costs of each H₂ production method is presented in Figure 1.10.

Table 1.5. Average values of global warming potential (GWP), acidification potential (AP), energy payback time (EPBT), production cost (PC) and efficiency for each H₂ production method, obtained from a literature survey on LCA and techno-economic studies.

	GWP kg _{CO2} eq. kg _{H2} ⁻¹	AP g _{SO2} eq. kg _{H2} ⁻¹	EPBT years	PC € kg _{H2} ⁻¹	Efficiency %
AEC	24.8 ²²⁶⁻²²⁸	27 ^{227, 229}	3.1 ²³⁰	7.2 ²³¹⁻²³⁵	74.2 ^{228, 234}
PV-EC	3.4 ^{219, 234, 236-238}	9.0 ^{219, 234, 236, 237}	9.4 ²³⁹	7.4 ^{198, 236, 240, 241}	21.1 ^{242, 243}
Wind-EC	0.9 ^{219, 228, 234, 236, 238, 244, 245}	3.7 ^{219, 228, 234, 236, 245}	6.4 ^{246, 247}	4.8 ^{236, 241, 247-249}	31.0 ^{241, 250}
SMR	10.9 ^{219, 228, 236, 245, 251-253}	14.2 ^{219, 228, 236, 245}	4.6 ²⁵⁴	3.3 ^{235, 236, 241, 248, 255}	65.5 ^{256, 257}
BGR	7.6 ^{236, 245, 252, 253}	4.9 ^{250, 255, 258}	8 ²⁵⁹	3.6 ^{236, 241, 260}	44.3 ²⁴¹
HTE	1.4 ^{234, 237, 245, 261, 262}	3.5 ^{234, 237, 245, 258, 261}	10 ²⁶³	4.5 ^{232, 240}	81.7 ^{264, 265}
Bio	4.3 ^{234, 237, 262, 266}	14.4 ^{229, 234, 237, 267}	4.8 ²⁶⁶	5.9 ^{233, 268, 269}	46.2 ²⁶⁶
PEC	1.1 ^{25, 234, 237}	1.5 ^{234, 237}	5.4 ^{223, 224, 270}	9.4 ^{25, 234, 240, 241, 271}	16.1 ^{79, 224}

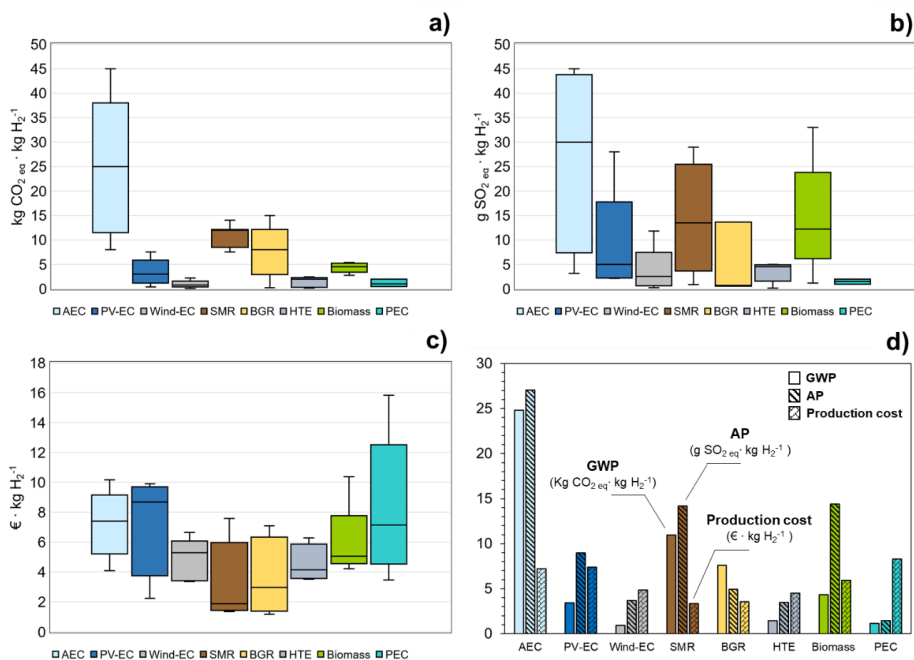


Figure 1.10. Results of LCA and techno-economic studies for different hydrogen production methods: a) global warming potential (GWP); b) acidification potential (AP); c) hydrogen production cost (PC); d) average value of GWP, AP and PC for each production method.

The obtained results clearly show that AEC is the H_2 production method with worst environmental performance, with a GWP of $24.8 \text{ kg}_{\text{CO}_2\text{eq}} \cdot \text{kg}_{\text{H}_2}^{-1}$ and an AP of $27 \text{ kg}_{\text{SO}_2\text{eq}} \cdot \text{kg}_{\text{H}_2}^{-1}$. It is important to note that these average values come from a significant variation between lower and upper limits, which is due to the highly variable nature of electricity from the grid; in many countries, the grid is supplied by fossil-fuel powered plants, which significantly hinders the environmental performance of AECs.²²⁷ Wind-electrolysis has the lowest GWP contribution, with $0.9 \text{ kg}_{\text{CO}_2\text{eq}} \cdot \text{kg}_{\text{H}_2}^{-1}$, whereas PEC water splitting has the lowest associated AP, with $1.1 \text{ kg}_{\text{SO}_2\text{eq}} \cdot \text{kg}_{\text{H}_2}^{-1}$. Overall, PEC water splitting is the H_2 production method with the lowest environmental impact, which agrees with other comparative studies.²¹⁶

Solar-based AEC is the currently available technology in operation that comes closer to future PEC-H₂ production plants. Therefore, a parallel comparison made with detailed LCA studies can provide key information on which components and which lifecycle stages have a higher contribution to the environmental impact. Koj *et al.* concluded that the anode and the cathode have the highest contribution for the AP, whereas the infrastructure of the production and the electrodes contribute equally to the GWP.²²⁷ This reinforces the need for choosing non-toxic, abundant, chemically stable materials, with a clean and non-complex fabrication for PEC water splitting. Koj *et al.* also concluded that operating an AEC-H₂ plant for 5 years has an impact on AP and GWP 9 times higher than the construction stage; as so, optimizing the operating parameters, such as maximum solar harvesting and thermal and power management, becomes critical for reducing the environmental impact of future PEC-H₂ production plants.

Table 1.6. Brief description, key benefits and challenges of the H₂ production methods selected for the comparative study.

Technology / abbreviation	Brief description	Pros / benefits	Cons / challenges
Steam methane reforming / SMR ^{272, 273}	Methane is first catalytically reformed at high temperatures, producing carbon monoxide and a syngas mixture. H ₂ is further produced through the water–gas shift reaction.	- Currently the most common and cost-effective method for H ₂ production.	- High emission of GHG; - High capital costs; - Coke deposition during the reaction.
Biogas reforming / BGR ²⁷⁴	Like fossil fuel-based SMR, but biogas is used as renewable resource for producing H ₂ (usually 55–65% CH ₄ , and 30–45% CO ₂).	- Biogas is a renewable source of methane; - Coupling with commercial digesters, landfills, or wastewater treatment plants.	- Feedstock quality; - Carbon capture and storage; - Low tolerance for impurities.
Alkaline electrolysis / AEC ²³¹	Direct current is provided to two electrodes immersed in a liquid electrolyte, usually concentrated KOH, resulting in the production of H ₂ at the cathode and oxygen at the anode. The two electrodes separated by a selective gas diaphragm.	- Mature and reliable technology; - Already optimized large-scale operation; - Constant power supply, preventing intermittent operation.	- High capital cost; - Corrosive operational environment; - Operation at high voltage (1.8 – 2.4 V); - Not necessarily clean when uses electricity from the grid; - Not suitable for dynamic operation; - Need of water purification (for preventing side reactions, such as chlorine formation).
High-temperature electrolysis / HTE ²⁶²	Water splitting occurs at high temperature (1000 – 1300 K) and the primary source (nuclear, concentrated solar power) generates both thermal and electrical inputs. High-temperature electrolysis typically uses yttria–stabilized zirconia as electrolyte.	- Coupling to existing nuclear power plants allowing large-scale production; - Free of GHG emissions.	- Few chemically stable materials for high temperature and highly reducing/oxidizing environment.

Photovoltaic electrolysis / PV-EC 273, 275	The conventional approach considers solar panels (c-Si) to generate electricity from sunlight, feeding an electrolyser with the appropriate voltage to split water. The PV power circuit (or battery) is sometimes connected to a DC–DC converter. Innovative approaches consider p- and n- semiconductors where one is in contact with air and the other is in contact with the liquid solution.	- Two mature technologies already optimized for large-scale operation; - The main energy source is renewable and clean.	- Two separate devices are required to drive water splitting (PV unit and electrolyser); - The system is limited by a single-bandgap PV cell; - Inability to use highly concentrated sunlight; - Intermittence of sunlight; - Aggregates the problems of the electrolyzer.
Photoelectrochemical / PEC 35, 143	The electrodes are in contact with an electrolyte in a single device where, at least, one is photoactive, converting incident photons to electron-hole pairs when exposed to sunlight, thus promoting the oxidation and reduction of water. H ₂ and O ₂ can be produced in the same compartment (internally divided by the ionic exchange membrane) or in physically separate compartments.	- Possibility of using concentrated sunlight; - Low-cost materials; - Operation at low temperature; - Plenty of room for optimization.	- Still in the early development stage; - Scalability and stability of PEs; - Operation in a corrosive environment (strong alkaline or acidic media).
Biomass / Bio 268, 276	Biomass is decomposed via thermochemical or biological processes to produce H ₂ . Common processes include slow and fast pyrolysis (heating at 650–800 K and 0.1–0.5 MPa, in the absence of air), gasification (biomass particles undergo partial oxidation at 1000 K, generating gaseous products and charcoal) and dark fermentation (biomass is converted into H ₂ by anaerobic bacteria).	- Abundant, renewable, and cheap feedstock, such as organic municipal waste.	- Formation of tar aerosols and ash in thermochemical processes (leading to slagging, fouling and agglomeration); - Use of expensive separation and purification units; - High reactor costs; - Substrate pre-treatment is crucial; - Biological processes can generate various undesirable subproducts, such as acetic, propionic and butyric acids as well as methanol, butanol and acetone.
Wind electrolysis / Wind-EC 248	Wind power plants (grid-connected or autonomous) feed the electrolyser (directly or through batteries).	- The main energy source is renewable; - High capital cost; - Aesthetic impact and noise.	- Intermittence of wind; - Aggregates the problems of the electrolyzer.

Regarding the economic performance, SMR remains the most competitive option, with a payback time of 4.6 years and a production cost of 3.3 €·kg_{H₂}⁻¹, though AEC has the lowest payback time, averaging only 3.1 years. Indeed, AEC is the firstborn H₂ production technology and has been optimized over two centuries. Still, due to the supremacy of fossil fuels in the energy market and the associated infrastructure, SMR delivers H₂ with the lowest production cost. HTE has the highest payback time, mainly because it is commonly associated with nuclear power plants, which demand a large initial investment. Unfortunately, this study shows that PEC water splitting generates H₂ with the highest cost, averaging 9.4 €·kg_{H₂}⁻¹; however, this result can be attributed to its early development stage, resulting in considerable expenses for producing and replacing PEs (which still have a low lifespan) and for manufacturing PEC panels (which still require the use of expensive and scarce materials, *i.e.* highly resistant polymers, noble metals).

After quantifying the impact categories for each H₂ production method, normalization was made using the ranking method, as follows ²³⁷:

$$ranking (method i) = \frac{\max - \bar{p}_{x,i}}{\max - \min} \times 10 \quad (8)$$

where $\bar{p}_{x,i}$ is the average value of the parameter x of the H₂ production method i ; ranking equal to 0 translates to poor performance and 10 indicates the ideal case (zero-cost and zero-emissions). The normalized results are presented in Figure 1.11. This figure complements the obtained results plotted in Figure 1.10, providing a complete overview of the H₂ production methods under study. PEC water splitting remains a promising option for sustainable H₂ production, scoring already a remarkable environmental performance, but lacking economic arguments.

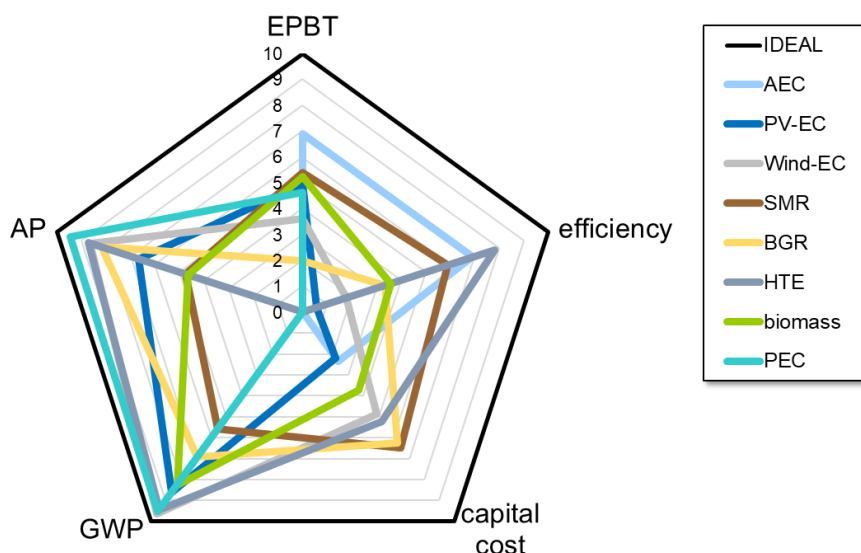


Figure 1.11. Overall performance comparison of hydrogen production methods.

Figure 1.11 clearly shows that more mature and widespread technologies, such as AEC and SMR, are financially safer, and more appealing to investors and H₂ consumers. This view reinforces the importance of scalability, a critical challenge for turning PEC water splitting viable at a commercial level, thus leading to its dissemination. Until then, wind-powered electrolysis is the H₂ production method that assures the best compromise between environment and economics for the upcoming years^{216, 228, 248}; the price of wind turbines is expected to have an annual decline of 4.0 %, and the capacity factor of wind-power is projected to have an annual increase of 0.7 %.²⁷⁷

Nevertheless, due to the geographically dispersed availability of wind, solar, and water resources, each case must be analyzed separately, despite its environmental and economic ranking; as an example, one can assume that wind-powered electrolysis would be a preferable option over PV-electrolysis in Nordic countries, such as Denmark, and the opposite would be verified in desert regions, like North Africa or the Arab peninsula. Overall, direct water splitting technologies (AEC, Wind-EC, PV-EC, PEC) have a better environmental performance whereas thermochemical and fossil fuel-based technologies show

a better economic performance.^{216, 234} However, the margin for reducing the environmental impact of fossil fuel-based technologies is very tight, whereas the margin for improving the economic performance of renewable-based H₂ production methods is huge, which represents a vital endorsement for future investments on green-H₂ infrastructures.

1.7 CLOSING REMARKS ON KEY CHALLENGES

Hydrogen is unmistakably recognized as a sustainable option for smart energy systems in the upcoming decades, mainly due to its advantages as an energy carrier and as industrial feedstock, while minimizing noise, air, soil and water pollution by replacing fossil fuel combustion processes in the transportation, building, and industry sectors.²⁷⁸ Still, to be considered a fully green alternative to the currently available technologies, H₂ must be produced from renewable sources in a cost-competitive, emission-free, and efficient way. Dincer *et al.*²⁷⁹ summarized the key requirements for future renewable-H₂ systems, as follows: i) increasing energy conservation along the lifespan of the production plant; ii) minimizing system losses, recovering, and reusing of generated heat and by-products (e.g. oxygen); iii) enhancing the use of renewable energies as primary source and integrating H₂ production with other existing clean technologies; iv) reducing the cost and the capacity of H₂ storage systems; and v) using smart-grid and smart-control tools to support the incorporation of green-H₂ technologies in the market while improving their efficiency, e.g. with weather forecast systems.

Green-H₂ already won the reputation of “key player” in future energy systems; still, a critical question remains: will PEC water splitting be able to compete with other green-H₂ production technologies?

Most studies on PEC-H₂ production agree that the major challenge for the near future is the scalability of PEC devices.^{15, 43, 243} To reach a similar H₂ output as PV-electrolysis, the active area of PEC devices has to be at least 50 times

larger.¹⁵ Additionally, efficient devices will require serious advances in the chemical stability of photoactive materials targeting 10000 h of reproducible performance; also, materials engineering at the nanoscale must be optimized for achieving reproducible structures across macroscopic areas. If these targets are not met in the next decade, long-term solar-H₂ technologies will tend to become a subset of PV-EC devices.²⁸⁰

Viable PEC architectures must deliver H₂ at a cost equal to or lower than available PV-EC systems and cannot be based on components that are also used to fabricate PV-EC devices. Indeed, decoupling the light-absorption and water splitting functions in solar-H₂ devices has fundamental advantages, arising from increased flexibility in the design, since each component (*i.e.* the light-absorber and water-splitting units) can be independently engineered and optimized, leading to higher modularity and lower electrolyte-degradation issues.²² For example, in PEC devices, thorough and clever design features are required for minimizing shading, light scattering and occlusion of electrocatalytic sites due to evolved gas bubbles. On the other side, PEC devices benefit from the integration of light absorbers with electrolysis technologies, with no peripheral electronics, especially in tandem architectures, which have higher theoretical efficiencies than silicon PV-electrolysers.²⁸ Catalysis in PEC water splitting can be integrated with the photoabsorber but, contrary to AEC, the catalyst used must be transparent, chemically stable, compatible with the photoabsorber, and also cost-competitive with the best available electrocatalysts.

Given thermodynamics and kinetic constraints, in terms of photoabsorption and catalysis efficiency, the best PEC-H₂ systems can only hope to match the best PV-electrolysers.²⁸¹ For that reason, and based on the comparative LCA and techno-economic results presented the previous section, the differentiating competitive factor will reside on the environmental and functional advantages of PEC water splitting, which are directly related to design and upscaling criteria. The use of decision support tools, such as decision trees, are an effective

strategy for overcoming the complexity involved in the development of innovative designs for PEC devices.⁴⁸ As an example, Figure 1.12 summarizes the decision tree used for conceiving the large-area modular PEC device developed within this PhD work.

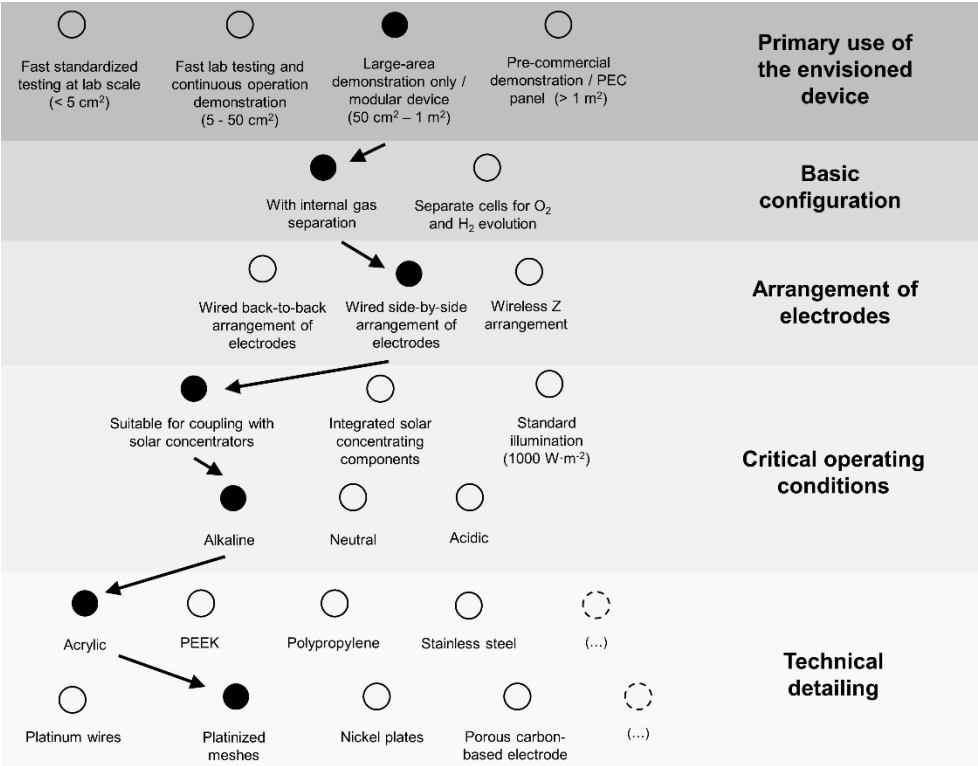


Figure 1.12. Hypothetical decision tree used for conceiving the large-area modular PEC device developed within the work plan of this thesis.

1.8 SCOPE OF THE THESIS

Hydrogen produced from renewable energy sources is expected to have a critical role in the energy market for upcoming decades. At present, photovoltaic and wind-powered electrolysis are the most efficient ways to produce renewable-H₂. However, techno-economic and life-cycle assessment studies show that PEC water splitting systems, with a 20-year lifespan, comprising PE with $\geq 1 \text{ m}^2$ capable of generating $10 \text{ mA}\cdot\text{cm}^{-2}$ at 1.23 V for at least 2920 h (8 working hours

over 365 days), can become the most competitive green-H₂ production technology. However, the lack of demonstrated large area PEC devices has delayed the entry of this technology in the energy market. Although great advancements have been achieved in the field of nanostructured materials, upscaling highly efficient PEs towards the expected dimensions of commercial PEC panels remains a massive challenge. Indeed, research efforts have been focused primarily on meeting efficiency targets, and the field still lacks upscaled PEs that are simultaneously highly efficient and stable.

This thesis aims at developing and demonstrating a large-area PEC device, suitable for tandem arrangements and able to be operated under concentrated sunlight, assembled with upscaled, efficient and stable PEs.

Chapter 1 makes an overview on large-area PEC water splitting, addressing promising semiconductor materials, relevant demonstrated large-area PEC devices and their combination with solar concentrators. This chapter also includes a comparative analysis of LCA and techno-economic studies made on the main H₂ production technologies. Finally, key challenges and opportunities for the PEC-H₂ production field are identified and briefly discussed.

Chapter 2 describes the optimization of a low-cost and scalable hydrothermal method for preparing highly efficient and stable nanostructured α -Fe₂O₃ PEs, including a long-term stability test performed with the optimal PE. The work comprised in this chapter was developed throughout the thesis.

Chapter 3 reports the development and optimization of an innovative 50 cm² PEC device that can host a tandem PE/PV cell, comprising design features never reported for large-area PEC devices. This chapter also comprises field tests conducted outdoor under concentrated sunlight and long-term stability with electrolyte recirculation under non-concentrated sunlight using a 50 cm² planar α -Fe₂O₃ PE. The outcomes of this chapter would be employed to develop a larger modular PEC device.

In Chapter 4 a disruptive approach was disclosed for overcoming the high electronic resistance imposed by large FTO-glass substrates. A segmented window was optimized for holding multiple PEs connected in parallel, and then demonstrated in the 50 cm² PEC device built in Chapter 3. The relevant findings of this chapter would also be used to improve the performance of the larger PEC device that would be developed ahead.

Chapter 5 describes a 200 cm² PEC module that combines the main achievements of chapters 2, 3 and 4, aiming at incorporating design features that enable the operation under concentrated sunlight and the separated collection of H₂ and O₂, while presenting versatility for using different membranes, CEs, electrolyte solutions and PEs (50 cm² one-piece, 50 cm² multi-piece, parallelly connected, and tandem PE/PV cells). The 200 cm² PEC module was demonstrated outdoor, in a continuous operation mode, under natural concentrated sunlight.

Finally, Chapter 6 reviews the main outcomes and conclusions of the present thesis and suggests recommendations for future work within the topic of upscaled PEC water splitting.

This thesis hopes to provide the field of PEC-H₂ production with relevant findings and pioneering technical solutions that can enhance the performance of large-area PEC devices, tackling all the three-pillar criteria – efficiency, stability, and scalability – required to turn this technology competitive in the energy market.

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CHAPTER 2

SPONGE-LIKE HEMATITE NANOCUBES FOR SOLAR
WATER SPLITTING EXCEEDING 1000 HOURS OF
STABLE PERFORMANCE

“What a week, huh?

Captain, it’s Wednesday.”

The Adventures of Tintin, Hergé

Adapted from a manuscript submitted for publication:

A. Vilanova, L Rodrigues, P Dias, T. Lopes and A. Mendes.

2 SPONGE-LIKE HEMATITE NANOCUBES FOR SOLAR WATER SPLITTING EXCEEDING 1000 HOURS OF STABLE PERFORMANCE

Hematite ($\alpha\text{-Fe}_2\text{O}_3$) is considered one of the most promising semiconductors to achieve commercially viable PEC- H_2 production. This metal oxide is abundant, non-toxic and can achieve a maximum theoretical solar-to-hydrogen (STH) efficiency of ca. 16% (corresponding to $12.6 \text{ mA}\cdot\text{cm}^{-2}$ at $1.23 \text{ V}_{\text{RHE}}$), presenting a notable chemical stability in standard PEC operating conditions. Solution based-methods are a simple, low-cost, and scalable technique that have been used to prepare highly efficient nanostructured $\alpha\text{-Fe}_2\text{O}_3$ PEs. The state-of-the-art PE was prepared with a hydrothermal method, delivering $6 \text{ mA}\cdot\text{cm}^{-2}$ at $1.23 \text{ V}_{\text{RHE}}$ (ca. 7% STH efficiency), corresponding to 50% of its theoretical limit; however, this PE demonstrated a stable performance over 100 h, still far from commercial ambitions.

The work developed within this chapter aimed at optimizing a hydrothermal method for preparing highly efficient and stable $\alpha\text{-Fe}_2\text{O}_3$ PEs. The stepwise approach implemented during the optimization process allowed identifying the experimental parameters with greater influence in the PEC performance of the PEs: i) concentration of fluoride ions in the precursor solution; ii) duration and temperature of the hydrothermal synthesis; and iii) the type of annealing.

Accordingly, the optimal preparation conditions were found to be: i) a F^- concentration in the precursor solution between 0.05 M and 0.075 M; ii) a hydrothermal synthesis performed at a constant temperature of 100 °C, over 6 h; iii) separate morphological and functional annealing, conducted at 550 °C for 2 h, and at 800 °C for 20 min, respectively. It was also found that performing an encapsulation with SiO_2 or TiO_2 between the annealing steps is crucial for preserving the porosity of the semiconductor.

The optimized $\alpha\text{-Fe}_2\text{O}_3$ PE presented a morphological structure comprising sponge-like nanocubes and showed a record-breaking stable performance, generating ca. $2.01\text{ mA}\cdot\text{cm}^{-2}$ at $1.23\text{ V}_{\text{RHE}}$ over 2014 hours (84 days) under uninterrupted illumination and without co-catalyst regeneration.

2.1 INTRODUCTION

Hematite ($\alpha\text{-Fe}_2\text{O}_3$) is one of the most promising semiconductors for achieving commercially viable PEC- H_2 production.¹ This metal oxide is a low-cost and abundant material, non-toxic and presents notable chemical stability in standard PEC operating conditions.² Unfortunately, research efforts have been focused primarily on meeting efficiency targets, and the field still lacks a $\alpha\text{-Fe}_2\text{O}_3$ photoelectrode (PE) that is simultaneously highly efficient and stable.³ Indeed, the ideal $\alpha\text{-Fe}_2\text{O}_3$ PE should meet the three-pillar criteria required for commercialization – efficiency, stability, and scalability, *i.e.*, it should be prepared with low-cost and scalable techniques, should achieve a STH efficiency of 10 %, and should present a stable performance for ca. 3000 hours (ca. 8 working hours over 365 days).

Hematite photoanodes can achieve a theoretical maximum STH efficiency of ca. 16% (corresponding to $12.6\text{ mA}\cdot\text{cm}^{-2}$ at $1.23\text{ V}_{\text{RHE}}$), given its bandgap of 1.9-2.3 eV, which is ideal for visible light harvesting.⁴ Despite presenting many advantages over other semiconductors, $\alpha\text{-Fe}_2\text{O}_3$ PEs comprise some drawbacks, namely: i) short diffusion length of 2–4 nm, mainly due to slow

mobility of holes (ca. $0.2 \text{ cm}^2 \cdot \text{V}^{-1} \text{ s}^{-1}$); ii) low water oxidation kinetics, which contributes to surface recombination, due to the accumulation of holes; iii) fast charge carrier recombination in the bulk; iv) low absorption coefficient (on the order of 10^5 cm^{-1}), requiring film thicknesses of at least 400–500 nm for optimal light absorption; and v) the need of an external bias to efficiently drive the water splitting reaction, due to the low conduction band position (ca. $0.4 \text{ V}_{\text{RHE}}$, at $\text{pH} = 0$) and the low photopotential.^{1, 5} According to several studies on $\alpha\text{-Fe}_2\text{O}_3$ PEs, most of these limitations can be overcome by implementing a 3-step approach during the fabrication procedure, based on: i) morphology control, ii) addition of dopants, and iii) surface control.^{1, 6}

Morphology control allows increasing the photocurrent density by enhancing the optical absorption, shortening the diffusion length of minority carriers, and improving the catalytic activity, through the enlargement of the surface area in contact with the electrolyte.⁷ Incorporating dopants, such as Si, Ti, Sn, or Pt, in the main morphological structure of the semiconductor, allows improving charge mobility and charge separation, while space-charge layers are shortened; this translates in a substantial increase in the generated photocurrent density, especially at lower potentials.^{8, 9} Finally, surface treatments are critical for improving the charge transfer at the semiconductor-liquid interface, which relates with the depletion region and the kinetics of the oxygen evolution reaction (OER).^{10, 11} Chemical and physical treatments, such as surface corrosion, directly affect the surface morphology of the semiconductor.^{2, 12} On the other hand, co-catalysts can be applied directly on the surface, leaving the morphology of the semiconductor unchanged, but playing a key role as bond-making and bond-breaking agents, passivating recombination sites and providing protection against photocorrosion.^{13, 14}

There is a vast range of published techniques to prepare $\alpha\text{-Fe}_2\text{O}_3$ PEs, such as solution-based methods, atomic layer deposition (ALD), spray pyrolysis (SP), among others.^{15, 16} Over the last few years, solution based-methods rose particular interest since they allow preparing PEs that successively displayed a

record-breaking performance.^{6, 17} Normally, α -Fe₂O₃ PEs prepared with this technique present a porous morphology, like nanorods, nanowires or worm-like protuberances, with a high surface area and with an ideal thickness of ca. 500 nm.¹ Additionally, solution-based methods require the use of simple and low-cost equipment, being easy to implement in most labs. The state-of-the-art α -Fe₂O₃ PE was prepared with a hydrothermal method, delivering an unprecedented photocurrent density of 6 mA·cm⁻² at 1.23 V_{RHE} (ca. 7% STH efficiency).¹⁷ Despite being already a remarkable achievement, this result corresponds to 50% of the theoretical limit for α -Fe₂O₃, offering still large room for improvement. This state-of-the-art PE demonstrated a stable performance over 100 h, still far behind of what is required for commercial applications. Stability-related problems are often considered the main drawback of PEs prepared with hydrothermal methods; the obtained nanostructures are quite fragile, *i.e.* they are easily damaged from mechanical erosion and from the uninterrupted release of evolved gases over many hours.¹⁷

Morphologies like compact films are much more stable and reproducible, but they typically achieve lower photocurrent densities, due to the reduced surface area and low porosity.¹⁸ The most stable α -Fe₂O₃ PE reported so far is an ultrathin α -Fe₂O₃ layer (ca. 19 nm) prepared by spray pyrolysis and reported by Dias *et al.*; this PE generated 1.05 mA·cm⁻² over 1000 h.¹⁹ This achievement was mainly attributed to the stepwise optimization of the spray pyrolysis technique, which allowed fully covering the FTO-glass substrate with a uniform morphology. Both Jeon *et al.* and Dias *et al.* highlight the importance of optimizing preparation techniques for achieving state-of-the-art PEs, but they also show the difficulty of addressing more than one key target – efficiency, stability, and scalability – at once. Developing a scalable and low-cost technique that allows obtaining highly efficient, reproducible, and stable α -Fe₂O₃ PEs remains then a massive challenge.

This chapter reports the optimization of a hydrothermal solution-based method for preparing efficient and stable sponge-like α -Fe₂O₃ nanocubes. The

preparation technique was optimized following a stepwise approach, addressing morphology control, doping, and surface treatments. Sponge-like $\alpha\text{-Fe}_2\text{O}_3$ nanocubes generated ca. $2.01 \text{ mA}\cdot\text{cm}^{-2}$ at $1.23 \text{ V}_{\text{RHE}}$ and presented a stable performance over 2014 hours (84 days). Figure 2.1 and Table 2.1 comprise a brief overview of published works on nanostructured $\alpha\text{-Fe}_2\text{O}_3$ photoanodes prepared by solution-based methods.

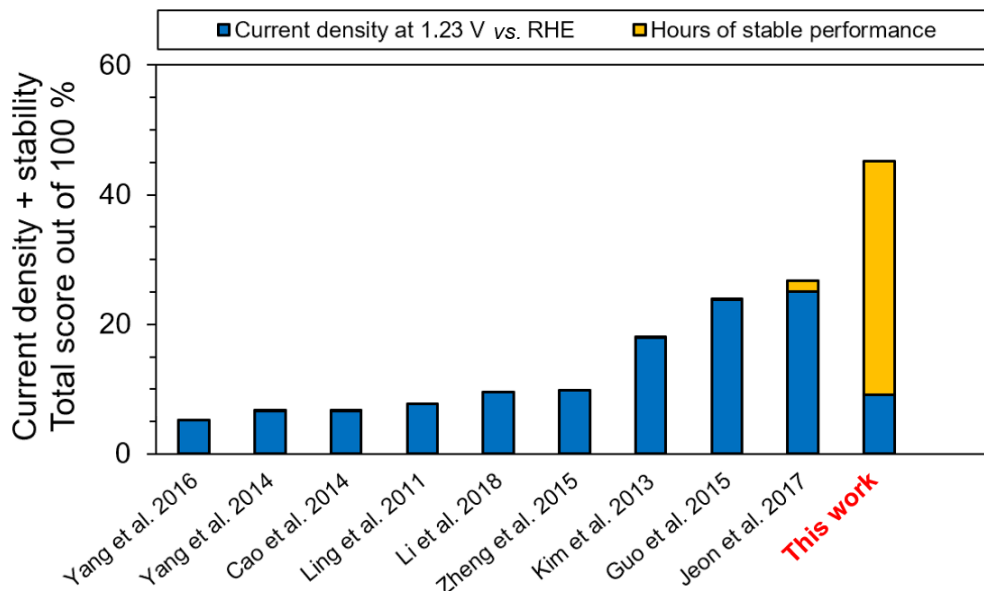


Figure 2.1. Short overview of published works on nanostructured $\alpha\text{-Fe}_2\text{O}_3$ photoanodes prepared by solution-based methods; each column of the chart corresponds to the overall performance of a specific $\alpha\text{-Fe}_2\text{O}_3$ photoanode, normalized for the current density measured at $1.23 \text{ V}_{\text{RHE}}$ and hours of stability, *i.e.* the total score out of 100 considers an equal 50 % contribution for each parameter; the upper limits considered for normalization were a current density of $12 \text{ mA}\cdot\text{cm}^{-2}$ (maximum theoretical value for hematite) and 2920 h of stable performance (8 hours over 365 days).

Table 2.1. Short overview of published works on nanostructured α -Fe₂O₃ photoanodes prepared by solution-based methods (ordered by current density measured at 1.23 V_{RHE}); the value presented alongside with the current density and stability corresponds to the score obtained out of the target defined for each parameter, *i.e.* a theoretical maximum current density of 12 mA·cm⁻² and 2920 h of stable performance (8 hours over 365 days).

Hydrothermal procedure	Thermal treatment	Surface Treatment / Catalysts	J_{photo} @ 1.23 / % (out of 12 mA·cm ⁻²)	Stability / % (out of 2920 h)	Main scientific contribution/ achievement	Ref. / Date
FeCl ₃ 0.15 M and NaNO ₃ 1.0 M; 100 °C up to 24 h	1-step annealing at > 390 °C, during at least 1 h		0 mA·cm ⁻² / 0 %	0 / 0 %	First reported hydrothermal method to prepare nanostructured α -Fe ₂ O ₃	²⁰ 2001
FeCl ₃ 0.15 M and NaNO ₃ 1.0 M; 95 °C / 4 h	Addition of SnCl ₄ drops to β -FeOOH; 2-setp annealing; 550 °C / 30 min; 800 °C / 20 min	Immersion in pure acetic acid for 5 min and annealing at 450 °C for 30 min	1.25 mA·cm ⁻² / 10.4 %	0 / 0 %	Suppression of electron–hole recombination by acid treatment; comparative study of different acidic solutions	¹² 2016
FeCl ₃ 0.15 M and NaNO ₃ 1.0 M; Ti(OBu) ₄ ; 95 °C / 50 min for un-doped and 13 h for doped structures	1-setp annealing; 550 °C / 3 h;	Underlayer and overlayer of bare α -Fe ₂ O ₃ prepared with the same procedure (FeCl ₃ 0.15 M and NaNO ₃ 1.0 M);	1.60 mA·cm ⁻² / 13.3 %	100 s / 0 %	Multi-layer PEs	²¹ 2014
FeCl ₃ 0.15 M and TiCl ₃ 9.3 mM; 100 °C / 4 h	2-setp annealing; 550 °C / 2 h; 650 °C / 15 min;		1.60 mA·cm ⁻² / 13.3 %	5 h / 0.2 %	Cathodic shift of 100 mV for water oxidation by surface corrosion	²² 2014
FeCl ₃ 0.15 M and SnCl ₄ ; 95 °C / 4 h	Addition of SnCl ₄ drops to β -FeOOH; 2-setp annealing; 550 °C / 2 h; 800 °C / 20 min	Surface corrosion promoted by immersion on HCl over 90 min	1.86 mA·cm ⁻² / 15.5 %	0 / 0 %	Multi-step high-temperature annealing and Sn diffusion through the substrate	²³ 2011

FeCl₃ 0.15 M, NH₄F 0.05 M, TiF₄ 0.2 % (w/w); 100 °C / 6 h	2-setp annealing; 550 °C / 2 h; 800 °C / 20 min	Encapsulation with SiO₂/TiO₂ Chemical etching with HCl 1.0 M; Co-Pi applied by PED	2.01 mA·cm⁻² / 16.7 %	2014 h / 71.9 %	Stable and reproducible performance	This work
FeCl ₃ 0.138 M and NaCl 0.8 M at pH 1.5 (adjusted with HCl); 95 °C / 1 h; 200 °C / 10 min	2-setp annealing; 550 °C / 2 h; 800 °C / 20 min	Chemical etching with a fluoruous aqueous mixture (2 M HF and 8 M NH ₄ F);	2.3 mA·cm ⁻² / 19.2 %	0 / 0 %	Ball-on-wire-array; silica encapsulation	²⁴ 2018
FeCl ₃ 0.15 M, NaF 2 mM, TiOCl ₂ 3μM; 100 °C / 10 h	1-setp annealing; 600 °C / 2 h;		2.35 mA·cm ⁻² / 19.6 %	0 / 0 %	Beneficial effect of adding fluoride ions to the precursor solution	²⁵ 2015
FeCl ₃ 0.15 M and Pt precursor (chloroplatinic acid); 100 °C / 6 h	2-setp annealing; 550 °C / 1 h; 800 °C / 20 min	Co-Pi PED	4.32 mA·cm ⁻² / 36 %	180 min / 0.1 %	Combination of Pt-doping with Co-Pi catalyst	⁶ 2013
Fe(OH)(Ac) ₂ 0.10 M, HF 0.10 M, o-anisidine 0.10 M and HAc 0.10 M; 180 °C / 70 min	Suspension of α-Fe ₂ O ₃ precipitates with Ru(acac) ₃ in ethanol, deposited by doctor blading; 700 °C / 5 h		5.7 mA·cm ⁻² / 47.5 %	42 min / 0 %	Deposition of [Ru(acac) ₃] β-FeOOH NRs onto FTO substrates via a doctor-blading	²⁶ 2015
FeCl ₃ 0.3 M, NaNO ₃ 2 M and 0.1 mL HCl (37%); 100 °C / 6 h	2-setp annealing; 550 °C / 1 h; 800 °C / 20 min	TiO ₂ overlayer, hydrogen annealing and Co-Pi PED	6.0 mA·cm ⁻² / 50 %	100 h / 3.6 %	Combination of hydrogen treatment and TiO ₂ overlayer	¹⁷ 2017

2.2 MATERIALS AND METHODS

2.2.1 PREPARATION OF SPONGE-LIKE HEMATITE NANOCUBES

Hematite PEs with an active area of $1.2 \times 2.0 \text{ cm}^2$ were prepared following a multi-step approach. First, FTO-glass substrates (Solaronix aluminoborosilicate TCO 10-10, 1.0 mm thick, $10 \Omega \cdot \square^{-1}$, $1.2 \text{ cm} \times 2.5 \text{ cm}$) were subjected to a stepwise cleaning procedure, described elsewhere.²⁷ Then, the cleaned FTO-glass substrates were placed tilted (at ca. 60°) inside a standard PTFE autoclave; the back side of the substrate (without FTO) and the area used for applying the electric contact were protected with Kapton tape. Then, a precursor solution of 0.15 M $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ($\geq 99 \%$, Sigma-Aldrich), 0.15 M NH_4F (96 %, Alfa Aesar) and Ti 0.2 %, Fe/Ti (TiF_4 crystalline 98 %, Alfa Aesar) was added to the autoclave –Figure 2.2-a. A hydrothermal treatment was conducted for 6 h inside an oven heated at 100°C to promote the growth of akaganeite ($\beta\text{-FeOOH}$) nanocubes on the FTO-glass substrates –Figure 2.2-b. The $\beta\text{-FeOOH}$ samples were taken from the autoclave at 100°C , immediately after the oven program ended, being rinsed abundantly with distilled water. The hydrothermal synthesis was followed by a first annealing step to promote the phase change from $\beta\text{-FeOOH}$ to $\alpha\text{-Fe}_2\text{O}_3$ (morphological annealing) – Figure 2.2-d; this temperature treatment was conducted in a small tubular oven, in air, heated up to 550°C ($10^\circ\text{C} \cdot \text{min}^{-1}$), over 2 hours. These samples were then subjected to an encapsulation procedure – Figure 2.2-c: i) silica encapsulation was obtained using an ethanolic solution containing a NH_4OH volume fraction of 6.5 % and a TEOS volume fraction of 1.5 %; $\alpha\text{-Fe}_2\text{O}_3$ PEs were immersed in this precursor and kept in the fridge at 5°C for 1 h; ii) TiO_2 encapsulation was performed according to the experimental procedure described by Miranda *et al.*²⁸; $\alpha\text{-Fe}_2\text{O}_3$ nanocubes were immersed in a 40 mM titanium(IV) chloride tetrahydrofuran complex ($\text{TiCl}_4 \cdot 2\text{THF}$, 97 %, Sigma-Aldrich) aqueous solution, and left at 70°C for 30 min, without stirring. A second annealing step was performed to the encapsulated $\alpha\text{-Fe}_2\text{O}_3$ aiming at inducing the formation of a sponge-like

morphology (functional annealing) – Figure 2.2-d; this temperature treatment was conducted in a small tubular oven in air, at 800 °C ($12\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$), over 20 min. An acid treatment was then applied on sponge-like $\alpha\text{-Fe}_2\text{O}_3$ samples for 1 h –Figure 2.2-e – using a 1.0 M aqueous solution of HCl. Finally, a Co-Pi co-catalyst was applied to the samples following a photo-assisted electrodeposition (PED) procedure Figure 2.2-f. In short, the $\alpha\text{-Fe}_2\text{O}_3$ samples were immersed in a 0.1 M potassium phosphate buffer solution (pH 7), and a bias potential of 0.2 V was applied during 30 s, under 1-sun illumination; these deposition conditions were found to be the ideal for this specific $\alpha\text{-Fe}_2\text{O}_3$ morphology. After the PED procedure, the PEs were rinsed with distilled water before the electrochemical characterization. During the optimization process, the order of some steps comprised in the procedure described above was changed, aiming at testing multiple experimental conditions. As an example, instead of performing separate morphological and functional annealing steps, a global annealing was performed; in this case, the encapsulation was performed on $\beta\text{-FeOOH}$ samples, after the hydrothermal synthesis, as sketched in Figure 2.2.

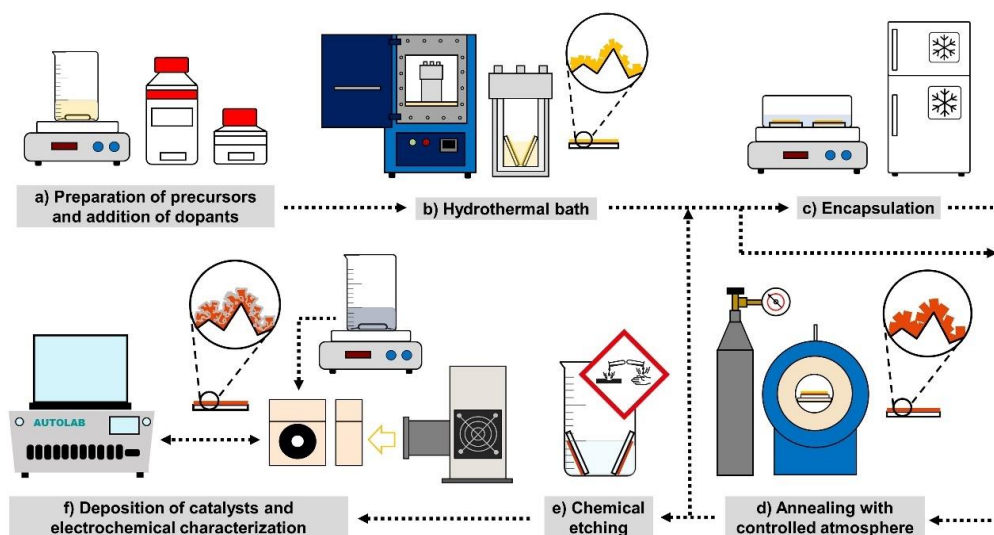


Figure 2.2. Multi-step procedure used to prepare sponge-like $\alpha\text{-Fe}_2\text{O}_3$ nanocubes.

2.2.2 ELECTROCHEMICAL CHARACTERIZATION

Electrochemical measurements were performed in a Cappuccino PEC cell. A standard three-electrode configuration was used, where $\alpha\text{-Fe}_2\text{O}_3$ PEs were operated as working-electrodes (WEs), a 99.9 % pure platinum wire (Alfa Aesar®, Germany) was used as counter-electrode (CE) and an Ag/AgCl/Sat KCl electrode (Metrohm, Switzerland) was used as reference electrode. The cell was filled with a 1.0 M KOH aqueous solution (25 °C, pH = 13.6) in which the electrodes were immersed. The photoanodes were front-illuminated, through the front opening of the cell, corresponding to an illumination area of 0.528 cm².

Photocurrent-voltage (J-V) measurements

J-V characteristic curves were obtained applying an external potential bias to the cell and measuring the generated photocurrent using an Autolab/PGSTAT302N workstation controlled by a Nova software package (Nova version 1.11). These measurements were performed at room temperature in the dark and under 1000 W·m⁻² of simulated sunlight, provided by a class B solar simulator, equipped with a 150 W Xe lamp (Oriel, Newport, USA) and an AM 1.5 G filter. The external bias was applied at a scan rate of 10 mV·s⁻¹ and reported as a function of the reversible hydrogen electrode (RHE), between 0.9 and 1.9 V_{RHE}.

Stability (J-t) measurements

Stability measurements were performed in the Cappuccino PEC cell, without electrolyte recirculation, under continuous simulated sunlight illumination (1000 W·m⁻², AM 1.5 G) at a constant potential of 1.23 V_{RHE}. The solar simulator was periodically calibrated using a c-Si photodiode (Newport, USA). The generated photocurrent density was monitored as a function of time using an Interface 5000E™ potentiostat (Gamry Instruments, USA). The photocurrent history was assessed over 2014 h. Distilled water was added to the cell every 24 hours, to compensate losses from evaporation.

2.2.3 SCANNING ELECTRON MICROSCOPY (SEM) CHARACTERIZATION

Morphology and surface topography characterization were made with top-view and cross-section SEM images obtained from a high-resolution scanning electron microscope (Quanta 400 FEG, FEI Company, USA), using an acceleration voltage of 15 keV and a working distance of about 10 mm between the in-lens detector and the sample.

2.3 RESULTS AND DISCUSSION

The preparation technique used to fabricate sponge-like α -Fe₂O₃ PEs was optimized following a stepwise approach. The first stage of the optimization process focused on the preparation steps that directly influence the morphology of the PE, *i.e.* the hydrothermal synthesis, the annealing, and the encapsulation Figure 2.2—a, -b, -c and -d. Nanostructured α -Fe₂O₃ PEs fabricated via solution-based methods are usually prepared with hydrothermal treatments, using a specific precursor solution added to an autoclave, which is placed inside a furnace programmed for the desired temperature and time conditions.

Usually, the solution added to the autoclave includes the β -FeOOH precursor, distilled water, and a dopant. After the hydrothermal synthesis, β -FeOOH nanoworms, nanowires, nanorods, or similar morphologies are grown on the FTO-substrate. Despite these structures display a high surface area, they have been described as quite fragile, therefore presenting low stability, which is the main drawback of α -Fe₂O₃ PEs prepared with this procedure. To overcome this limitation, fluorine can be added to the precursor solution for inducing the formation of nanocubes, instead of the aforementioned morphologies.^{7, 25} Therefore, the concentration of fluorine in the precursor solution was the first parameter optimized in this work – Figure 2.2-a. At this early stage of the optimization process, the experimental conditions of the hydrothermal treatment were fixed for 5 hours at 100 °C, and the concentration of fluorine was changed between 0.025 M and 0.1 M. Figure 2.3-a displays photos of the α -Fe₂O₃ PEs

prepared with different fluorine concentrations, with the corresponding top-view SEM images, whereas the plots of the corresponding J - V characteristic curves are displayed in Figure 2.3-b.

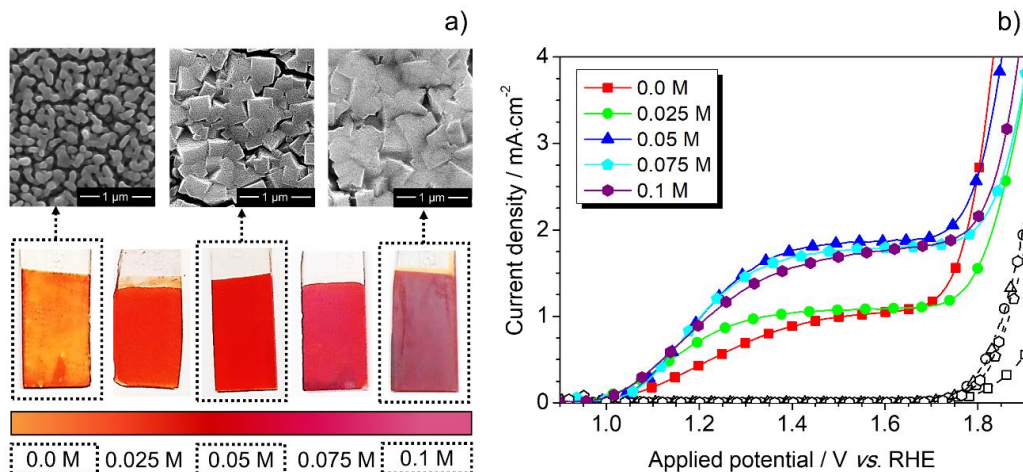


Figure 2.3. Influence of the concentration of fluorine (ranging from 0.0 M to 0.1 M) in the morphology and performance of α -Fe₂O₃ PEs prepared by a hydrothermal synthesis: a) top-view SEM images (mag. 75000 x) and pictures of the α -Fe₂O₃ PEs, after annealing (550 °C for 2 h and 800 °C for 20 min); b) J - V characteristics of the as-prepared α -Fe₂O₃ PEs, obtained in the dark (open symbols, dashed lines) and under 1000 W·m⁻² of simulated sunlight (filled symbols, solid lines), using a cappuccino PEC cell assembled in a three-electrode configuration and filled with 1.0 M KOH.

From Figure 2.3-a, it is apparent that the concentration of fluoride ions in the precursor solution directly influences the morphology of PEs. When the hydrothermal synthesis is conducted with low fluoride concentration (from 0 to 0.05 M), the resulting PEs present a reddish-orange colour. As the fluoride concentration increases, the colour of the PE becomes more reddish, until acquiring a darker colour with a purple-lighter tone for higher concentrations (> 0.075 M). This observation agrees with the literature.²⁵ SEM images from Figure 2.3-a also show that the presence of F⁻ ions in the precursor solution clearly induces the formation of nanocubes; when the precursor does not contain F⁻ ions, the resulting PEs present a morphology similar to nano-worms, which is

also in accordance with the literature. As the concentration of F^- ions increases, the formation of 300-400 nm wide nanocubes becomes clear, with very well-defined edges. SEM images also show that higher fluoride concentrations in the precursor results in a more compact film, with lower porosity and tortuosity, comprising agglutinated and not so sharp cubes.

The best performing $\alpha\text{-Fe}_2\text{O}_3$ PE was obtained using a precursor solution with a F^- ion concentration of 0.05 M –Figure 2.3-b. This $\alpha\text{-Fe}_2\text{O}_3$ PE generated $1.17 \text{ mA}\cdot\text{cm}^{-2}$ at $1.23 V_{\text{RHE}}$ and ca. $1.65 \text{ mA}\cdot\text{cm}^{-2}$ at the plateau. When the fluoride concentration is increased to 0.1 M the photocurrent density decreased to $1.03 \text{ mA}\cdot\text{cm}^{-2}$ at $1.23 V_{\text{RHE}}$ and decreased to $1.60 \text{ mA}\cdot\text{cm}^{-2}$ at the plateau. SEM images confirm this result, since $\alpha\text{-Fe}_2\text{O}_3$ PEs prepared with 0.05 M of F^- presented the best-defined cube shape and the highest porosity and tortuosity, corresponding to a higher surface area in contact with the electrolyte. These results also reveal that F^- concentrations $> 0.025 \text{ M}$ are required for obtaining $\alpha\text{-Fe}_2\text{O}_3$ PEs nanocubes, displaying better PEC performance comparatively to worm-like nanostructures, obtained when the precursor does not contain fluorine. As plotted in Figure 2.3-b, $\alpha\text{-Fe}_2\text{O}_3$ nano-worms generated ca. $0.51 \text{ mA}\cdot\text{cm}^{-2}$ at $1.23 V_{\text{RHE}}$ and ca. $0.95 \text{ mA}\cdot\text{cm}^{-2}$ at the plateau, agreeing with the literature; these results correspond to decreases of 130 % and 91 % in the generated photocurrent density at $1.23 V_{\text{RHE}}$ and at the plateau (ca. $1.45 V_{\text{RHE}}$), respectively.

Nanocubes promote light scattering, resulting in an opaquer PE, but with enhanced light absorption, boosting the PEC performance. Besides inducing the formation of nanocubes, the addition of fluorine to the precursor solution also promotes the incorporation of Ti ions in the $\alpha\text{-Fe}_2\text{O}_3$ lattice during the hydrothermal synthesis. This phenomenon was demonstrated by Zheng *et al.* with XPS data; the peak intensity of Ti2p was substantially higher for samples prepared with a precursor solution containing F^- ions.²⁵ Since the precursor solution used in the present work contained 0.2 % Ti/Fe (w/w), it is possible to infer that the presence of F^- ions enhanced the doping effect, improving the

transport of charge carriers across the semiconductor. This assumption is also addressed in the work of Zheng *et al.*; EIS analyses showed that samples prepared with precursors containing fluoride ions presented a lower charge transfer resistance and a higher Helmholtz capacitance, comparatively to α -Fe₂O₃ PEs prepared without fluorine.²⁵ Overall, for the specific case of hematite, porous nanocubes can be considered more promising than worm-like nanostructures, presenting higher porosity, tortuosity, and better light absorption and charge transport.⁷

After defining the ideal F⁻ concentration, the experimental parameters of the hydrothermal synthesis and the subsequent annealing were optimized –Figure 2.1-b, -c and -d. According to several published works describing the fabrication α -Fe₂O₃ PEs with solution-based methods, the hydrothermal synthesis should be performed between 95 °C and 100 °C and over a period between 4 and 10 hours.^{6, 17, 29, 30} The duration and the temperature of the hydrothermal synthesis affect the thickness, adhesion, feature size and shape of β -FeOOH nanostructures.

Nevertheless, Li *et al.* reported a disruptive approach for conducting the hydrothermal synthesis, which allowed obtaining a ball-on-wire-array hierarchical structure;²⁴ instead of performing the hydrothermal synthesis at a constant temperature for a long period, the authors opted for keeping the autoclave at 100 °C during 1 h and suddenly moving it to 200 °C during 10 min. This two-step approach enabled a serial growth of nanospheres with a diameter of ca. 500 nm over the 600 nm thick β -FeOOH nanowires, which represents a substantial increase in the surface area in contact with the electrolyte; the ball-on-wire α -Fe₂O₃ PE generated ca. 2.3 mA·cm⁻² at 1.23 V_{RHE}. This procedure allows significantly shortening the duration of the hydrothermal synthesis, which translates into a substantial reduction of fabrication costs, having particular interest when the development of a low-cost and scalable technique is intended. Therefore, that strategy was also assessed in the present work, by comparing the electrochemical performance of α -Fe₂O₃ PEs prepared with a 6 h

hydrothermal synthesis conducted at 100 °C with that delivered by α -Fe₂O₃ PEs prepared with a two-step procedure (100 °C during 1 h and 200 °C for 10 min) – Figure 2.4-a and -b.

Complementary to the assessment of the two types of hydrothermal procedures, two types of thermal treatments were investigated. Thermal treatments comprising two annealing steps are the most commonly used for preparing nanostructured α -Fe₂O₃ PEs through solution-based methods.^{6, 29, 31} The first annealing (morphological) is usually performed at a temperature between 500 °C and 550 °C, allowing a complete crystal phase transition from the yellow β -FeOOH to the orange-red hematite (α -Fe₂O₃). Then, a short annealing (functional) is performed at a higher temperature (700-800 °C), allowing the thermal activation of the α -Fe₂O₃ nanostructures, and promoting the migration of Sn from the FTO-glass substrate to the hematite lattice.^{32, 33}

When specific overlayers are applied on the semiconductor, namely protective scaffolds, performing thermal treatments with separate morphological and functional steps (allowing the PE to cool down in between), is a preferable approach, as reported by Brillet *et al.*³⁴ The authors demonstrated that applying a protective scaffold between the morphological and functional annealing allowed controlling the particle size and shape of the nanostructures that were grown after the first annealing. Such approach has particular relevance in the present work, since the pores of the nanocubes must be preserved after the functional annealing. Hence, the performance of α -Fe₂O₃ PEs prepared with a global thermal treatment was compared with that delivered by α -Fe₂O₃ PEs prepared by separated morphological and functional annealing, with the encapsulation made in between. In samples that were subjected to the single thermal treatment, the encapsulation was applied during the β -FeOOH phase, right after the hydrothermal synthesis. Figure 2.4 summarizes the comparative performance assessment of α -Fe₂O₃ PEs prepared with long and short hydrothermal syntheses, with global and two-step annealing and with TiO₂ and SiO₂ encapsulation.

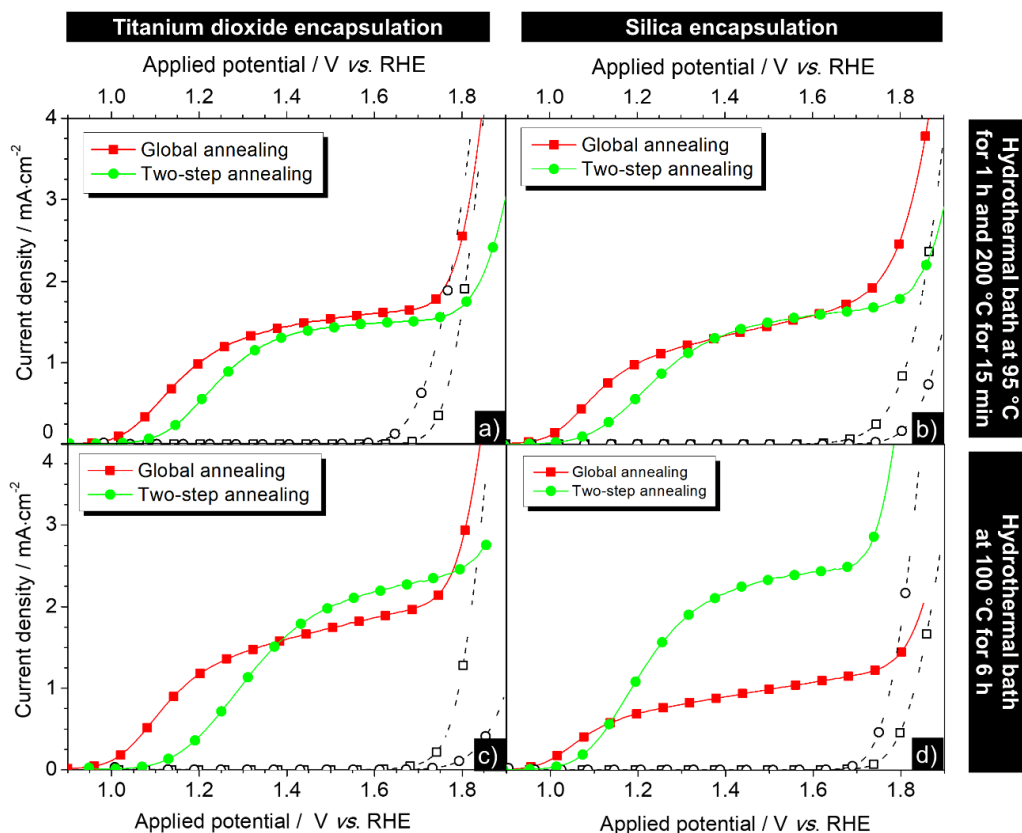


Figure 2.4. Comparative analysis of the electrochemical performance of sponge-like $\alpha\text{-Fe}_2\text{O}_3$ PEs prepared with a short two-step hydrothermal synthesis, followed by encapsulation with TiO_2 (a) or SiO_2 (b), and prepared with a long single-step hydrothermal synthesis combined with encapsulation of TiO_2 (c) or SiO_2 (d), subjected to a global thermal treatment (■) or to separate morphological and functional annealing (●). Plotted J - V curves were obtained in the dark (open symbols, dashed lines) and under $1000 \text{ W}\cdot\text{m}^{-2}$ of simulated sunlight (filled symbols, solid lines).

The results plotted in Figure 2.4 highlight that the duration and the temperature of the hydrothermal synthesis greatly influence the photocurrent plateau, whereas the type of thermal treatment strongly influences the onset potential. Figure 2.4 shows that performing a hydrothermal synthesis for a longer period at a constant temperature is preferable for reaching a higher photocurrent plateau. Although Li *et al.* were able to prepare $\alpha\text{-Fe}_2\text{O}_3$ PEs with increased surface area, high porosity and tortuosity, resulting from the hierarchical growth

of $\alpha\text{-Fe}_2\text{O}_3$ nanospheres on top of $\alpha\text{-Fe}_2\text{O}_3$ nanowires promoted by the sudden increase in the temperature of the hydrothermal synthesis, such approach was not effective in the present work.²⁴

SEM images revealed no substantial changes in the morphology of $\beta\text{-FeOOH}$ samples fabricated with the two types of hydrothermal procedures. This allows concluding that the presence of fluoride ions in the precursor solution inhibits the formation of other morphologies than nanocubes, independently from the experimental conditions of the hydrothermal synthesis.

Additionally, it was observed that more compact films comprising nanocubes with a smaller feature size are obtained when the temperature of the hydrothermal synthesis is suddenly increased. Several studies show that non-porous morphologies generate a lower photocurrent plateau, which supports the results obtained in this work.

Thermal treatments also have a major influence in the photocurrent density generated by the PE, since they induce significant changes in the morphology of the semiconductor. On the other hand, it is not expected that thermal treatments can cause significant changes in the onset potential, since those treatments do not directly affect the surface of the semiconductor and the water oxidation kinetics. However, the results plotted in Figure 2.4 indicate that performing a global thermal treatment instead of performing separate morphological and functional annealing caused a cathodic shift of ca. 100 mV on the onset potential. First, subjecting the samples to a sudden increase in the hydrothermal synthesis temperature may lead to the appearance of additional surface defects, which enhances light absorption. On the other hand, such unexpected behaviour might be explained by the strong interconnection between the different steps of the experimental procedure, particularly between the thermal treatment and the encapsulation. Protective overlayers were applied on the nanocubes before the functional annealing, targeting a $\alpha\text{-Fe}_2\text{O}_3$ morphology that presented a high surface area, porosity, and tortuosity, and

could be simultaneously resistant to photocorrosion and mechanical erosion. This strategy aimed at ensuring that the initial morphology, *i.e.* nanocubes with ideal feature size and with a high surface area, would not be damaged, or substantially modified, by the steep heating ramp and high temperature (800 °C) of the second annealing.

When a global thermal treatment is performed, *i.e.* the functional annealing is performed immediately after the morphological annealing, and samples are not cooled down to room temperature in between, the encapsulation has to be applied during the β -FeOOH phase. Consequently, during the global thermal treatment, part of the tetravalent species of the scaffold, such as Ti^{4+} or Si^{4+} , can migrate to the lattice of hematite, acting as dopants, while the remaining species can improve the charge transfer on the surface of hematite. These assumptions were investigated by Li *et al.* in a study that addressed the role of a TiO_2 overlayer combined with a thermal treatment in the performance of α - Fe_2O_3 nanorods.³⁵ Treated and non-treated samples presented a similar carrier density and flat band potential, indicating that the Ti doping effect was insignificant. Therefore, the authors attributed the performance increase to the surface states at the semiconductor-liquid junction, which leads to better charge separation and reduced electron-hole recombination.

Thermal diffusion of tetravalent species is a concentration- and time-dependent process, which relates to the thickness of the overlayer and with the annealing time; as so, performing a global annealing should favour both the migration of tetravalent species into the lattice of hematite and the gradual coverage of pores and channels created by water release, which supports the observed cathodic shift. Still, when this global thermal treatment is performed on β -FeOOH samples fabricated with a 6 h hydrothermal procedure, the photocurrent plateau decreased by ca. 20 % and by more than 100 % when the encapsulation is made with TiO_2 and SiO_2 , respectively (Figure 2.4-c and -d). Performing a hydrothermal treatment for a longer period at a constant temperature ≤ 100 °C enables the formation of a β -FeOOH layer with the ideal thickness, comprising

large nanocubes, which corresponds to an enhanced surface area. When the scaffold is applied on these structures before the morphological annealing, it covers the β -FeOOH template, partially suppressing the beneficial effect obtained by the ideal slow growth of pores. In the study conducted by Li *et al.* it is clearly highlighted that a thick TiO_2 overlayer can lead to the formation of a heterojunction between α - Fe_2O_3 and TiO_2 , which significantly limits the charge transport across the junction, hindering the overall PEC performance.³⁵ Therefore, the TiO_2 scaffold applied in this work followed the experimental procedure described by Miranda *et al.*, aiming at obtaining an ultrathin and highly transparent overlayer.²⁸ Thus, light trapping and obstruction of pores by TiO_2 was avoided. Additionally, using an ultrathin overlayer favours the migration of Ti^{4+} to the α - Fe_2O_3 lattice.

The highest photocurrent density values ($> 2 \text{ mA}\cdot\text{cm}^{-2}$) were obtained for α - Fe_2O_3 PEs prepared with a hydrothermal synthesis performed at 100°C , over 6 h and subjected to separated morphological and functional annealing. These experimental conditions were defined as the optimal for preparing the α - Fe_2O_3 PEs subjected to the subsequent stages of the optimization process, *i.e.* surface treatments and deposition of a co-catalyst. Also, these results confirm that when the encapsulation is applied between the morphological and functional annealing, the structural integrity of the nanocubes is better preserved. Consequently, after the functional annealing, the beneficial effects of increased porosity and tortuosity are amplified by the high active area of the nanocubes.

Once the baseline for preparing nanostructured α - Fe_2O_3 PEs was established, the obtained morphology was characterized by top-view and cross-section SEM images –Figure 2.5.

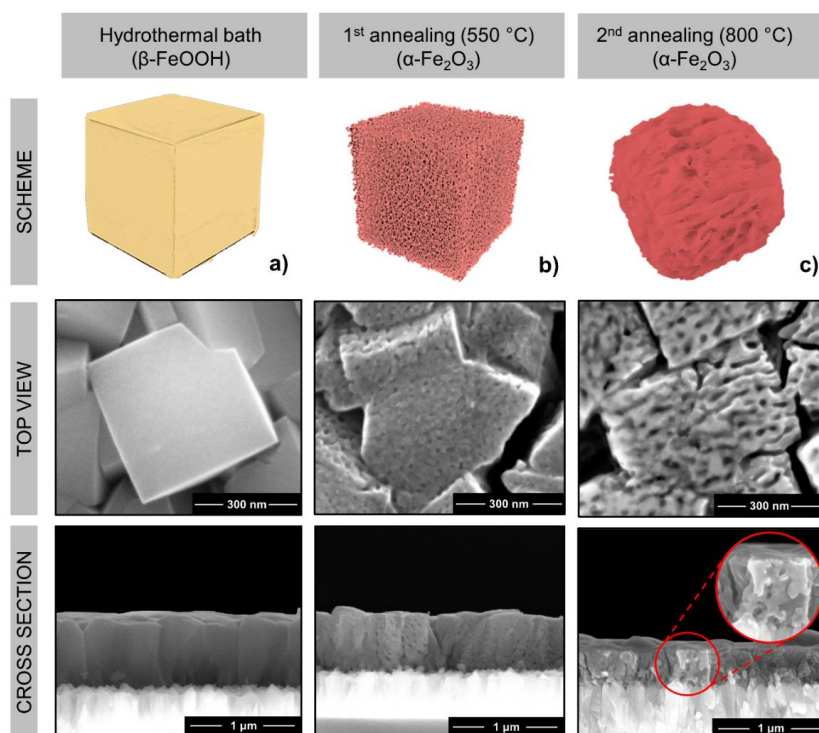


Figure 2.5. Schematic representation, top-view (mag. 350000 x), and cross-section (mag. 100000 x) SEM images of the sponge-like α -Fe₂O₃ nanocubes prepared with the optimal experimental conditions defined for the hydrothermal synthesis and subsequent annealing; a) β -FeOOH nanocubes obtained after the hydrothermal synthesis conducted at 100 °C during 6 h; b) porous α -Fe₂O₃ nanocubes obtained after the morphological annealing (550 °C, 2 h); c) sponge-like α -Fe₂O₃ nanocubes obtained after the functional annealing (800 °C, 20 min).

The hydrothermal procedure performed in this work allowed obtaining β -FeOOH samples comprising 380 nm wide nanocubes with well-defined sharp edges over the FTO glass substrate – Figure 2.5-a. As reported by Zheng *et al.*, the great affinity of fluorine to FeOOH induces the formation of nanocubes.²⁵ Indeed, worm-like β -FeOOH protrusions were obtained just by not adding NH₄F to the precursor solution, keeping the remaining parameters of the hydrothermal synthesis unchanged (Appendix 2-a). The first temperature treatment allowed obtaining porous α -Fe₂O₃ nanocubes – Figure 2.5-b; porosity was mainly attributed to the removal of water during the annealing. Also, the “dry mud”

appearance of the film (visible at lower magnification, Appendix 2-b) confirms the full removal of water from the agglutinated β -FeOOH nanocubes, which agrees with the literature. Finally, the second annealing performed at 800 °C allowed obtaining a 500 nm film containing sponge-like nanocubes (Figure 2.5-c), which, to the best knowledge of this thesis, is a morphology never reported for α -Fe₂O₃ PEs. Cross-section images reveal that these sponge-like nanostructures comprise several intrinsic channels, providing the α -Fe₂O₃ film with enhanced tortuosity, which greatly favours the transfer of photogenerated holes to the semiconductor/electrolyte interface. Interestingly, performing the functional annealing with a high heating rate ($> 10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$) allowed transforming the initial nanocubes into clusters of “rounded branched trunks”, with feature sizes of ca. 20-40 nm, which significantly reduces bulk recombination. Additionally, blank spaces comprised within the film were significantly enlarged. The reproducibility of the optimized technique was confirmed with top-view SEM images obtained for samples prepared in other batches; no morphological differences were identified, and it was confirmed that the α -Fe₂O₃ film was grown uniformly over the substrate (Appendix 2-c).

After obtaining the desired morphology, the performance of nanostructured α -Fe₂O₃ PEs, renamed as α -Fe₂O₃-NC (hematite NanoCubes), was further improved with two surface treatments. First, chemical etching was promoted on α -Fe₂O₃-NCs with silica encapsulation (α -Fe₂O₃-NC-S), using 5.0 M KOH. Then, surface corrosion was made with a 1.0 M aqueous solution of HCl on both α -Fe₂O₃-NCsS and α -Fe₂O₃-NC-T (hematite NanoCubes with Titanium dioxide encapsulation). Finally, a thin layer of a cobalt-phosphate catalyst was applied by PED on the best performing samples, renamed as Co- α -Fe₂O₃-NC-T and Co- α -Fe₂O₃-NC-S. Figure 2.6 summarizes the results obtained during this second stage of the optimization process.

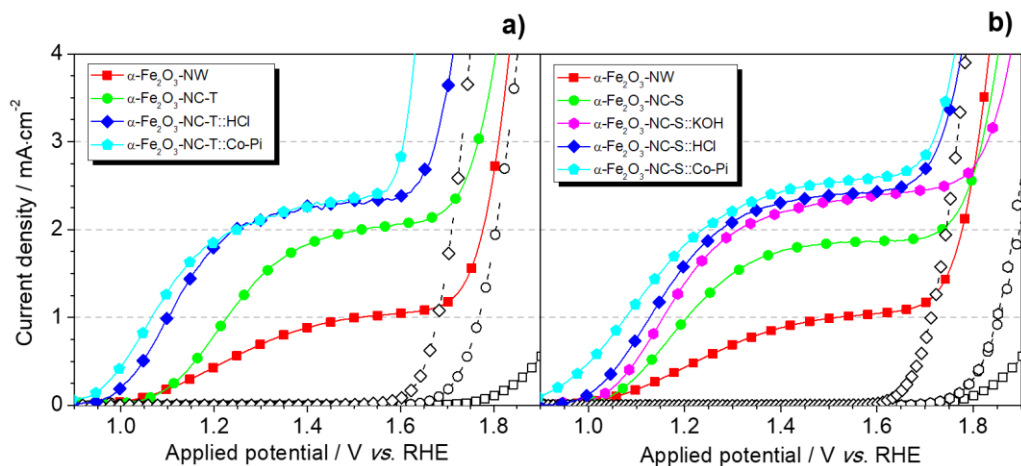


Figure 2.6. Stepwise optimization of nanostructured $\alpha\text{-Fe}_2\text{O}_3$ PEs with TiO_2 encapsulation (a) and SiO_2 encapsulation (b). For a better view of the complete optimization process, these figure includes J - V curves of: $\alpha\text{-Fe}_2\text{O}_3$ nanowires (NW, $\blacksquare$), prepared using a hydrothermal synthesis without F^- ions; $\alpha\text{-Fe}_2\text{O}_3$ nanocubes (NC, $\bullet$), prepared using a hydrothermal synthesis with F^- ions; $\alpha\text{-Fe}_2\text{O}_3$ NCs with SiO_2 encapsulation immersed in 5.0 M KOH ($\bullet$); $\alpha\text{-Fe}_2\text{O}_3$ NCs subjected to the acid treatment with 1.0 M HCl ($\blacklozenge$) treatment; $\alpha\text{-Fe}_2\text{O}_3$ NCs with a Co-Pi co-catalyst ($\bullet$). Plotted J - V curves were obtained in the dark (open symbols, dashed lines) and under $1000\text{ W}\cdot\text{m}^{-2}$ of simulated sunlight (filled symbols, solid lines), using a cappuccino PEC cell assembled in a three-electrode configuration and filled with 1.0 M KOH.

The adopted stepwise optimization strategy is clearly evidenced in Figure 2.6, since a gradual increase in the photocurrent density is observed for each step of the experimental procedure. The greatest current density improvement was obtained when fluorine was added to the precursor solution. As reported by Cao *et al.*, performing an acid treatment to Ti-doped $\alpha\text{-Fe}_2\text{O}_3$ PEs can promote a cathodic shift of ca. 100 mV on the onset potential, attributed to the suppression of the back reaction and passivation of surface states.²² Still, for the case of $\alpha\text{-Fe}_2\text{O}_3\text{-NC-S}$ PEs, an additional treatment is necessary for removing the SiO_2 scaffold, prior to the acid treatment. According to Brillet *et al.*, submerging the PE in a strong alkaline solution promotes a selective etching and allows removing the rigid scaffold, confirmed by XPS analysis.³⁴ In the present work,

α -Fe₂O₃-NC-S PEs were submerged in 5.0 M KOH for 10 min. As depicted in Figure 2.6-b, after removing the SiO₂ scaffold, the PE exhibited noticeable improvements both in the generated photocurrent density at 1.23 V_{RHE}, from 1.17 mA·cm⁻² to 1.65 mA·cm⁻², and at the plateau, from 1.81 mA·cm⁻² to 2.26 mA·cm⁻². These results confirm the effectiveness of the SiO₂ scaffold in preserving the surface area of α -Fe₂O₃-NC during the functional annealing.

The acid treatment was then performed on both α -Fe₂O₃-NCs-T and α -Fe₂O₃-NCs-S PEs. This surface treatment resulted in cathodic shifts of ca. 100 mV (Figure 2.6-a) and of ca. 50 mV (Figure 2.6-b) in α -Fe₂O₃-NCs PEs with TiO₂ and SiO₂ encapsulation, respectively. For α -Fe₂O₃-NCs-T PEs (Figure 2.6-a), the photocurrent density measured at 1.23 V_{RHE} increased from 1.05 mA·cm⁻² to 1.94 mA·cm⁻², and the photocurrent density measured at the plateau increased from 1.91 mA·cm⁻² to 2.29 mA·cm⁻², corresponding to improvements of 85 % and 20 %, respectively. Considering α -Fe₂O₃-NCs-S PEs (Figure 2.6-b), the acid treatment allowed obtaining improvements of 11 % and 4.4 % in the photocurrent density measured at 1.23 V_{RHE} and at the plateau, respectively. Despite this lower improvement in the photocurrent density, compared to α -Fe₂O₃-NCs-T PEs, Figure 2.6-b shows that the acid treatment greatly suppressed the dark current, which suffered an onset cathodic shift of ca. 150 mV. The increase in the generated photocurrent density after the acid treatment on α -Fe₂O₃-NCs-S PEs was somehow muffled by the previous chemical etching promoted by the highly concentrated potassium hydroxide solution. The later, directly affected the surface area of this PE by opening/enlarging the pores, covered by the SiO₂ scaffold, resulting in an increase in the photocurrent density more noticeable at the plateau than at lower potentials.

Finally, a cobalt-phosphate catalyst was applied on both α -Fe₂O₃-NCs-T and α -Fe₂O₃-NCs-S PEs by photoelectrodeposition (PED). Co-Pi has been widely studied as water oxidation co-catalyst for many semiconductors in PEC water splitting systems and was proven to be very effective on α -Fe₂O₃ PEs, promoting

a significant cathodic shift in the photocurrent density generated at lower potentials ($< 1.1 V_{\text{RHE}}$).^{36, 37} After the co-catalyst deposition, the photocurrent density measured at $1.23 V_{\text{RHE}}$ increased to $1.96 \text{ mA}\cdot\text{cm}^{-2}$ on $\alpha\text{-Fe}_2\text{O}_3\text{-NCs-T}$ PEs, and to $2.01 \text{ mA}\cdot\text{cm}^{-2}$ on $\alpha\text{-Fe}_2\text{O}_3\text{-NCs-S}$ PEs, corresponding to improvements of 1.0 % and 9.8 %, respectively. On $\alpha\text{-Fe}_2\text{O}_3\text{-NCs-T}$ PEs, the Co-Pi layer was deposited over the thin TiO_2 overlayer, whereas on $\alpha\text{-Fe}_2\text{O}_3\text{-NCs-S}$ PEs was directly applied on hematite (since the SiO_2 layer was already removed); as so, its beneficial effect was more noticeable in $\alpha\text{-Fe}_2\text{O}_3\text{-NCs-S}$ PEs. Co-Pi assist photogenerated holes to move away from recombination sites located at the surface; nevertheless, hole transfer from the oxidized Co-Pi to water is slow, and a fraction of the oxidized species can accumulate, inevitably reacting with photogenerated electrons, originating a plateau.³⁸ This justifies the negligible effect on the photocurrent plateau for both $\alpha\text{-Fe}_2\text{O}_3\text{-NCs-T}$ and $\alpha\text{-Fe}_2\text{O}_3\text{-NCs-S}$ PEs, reinforcing the initial assumption that morphology control is essential for improving the photocurrent plateau, whereas surface treatments and catalysts are crucial for cathodically shifting the onset potential.

Recent studies on semiconductors for solar water splitting have highlighted the importance of presenting stability measurements to demonstrate the feasibility of the developed material for viable PEC-H_2 production.^{3, 39} For the case of $\alpha\text{-Fe}_2\text{O}_3$ PEs, the work reported by Dias *et al.* is still considered a benchmark in the field.¹⁹ The developed $\alpha\text{-Fe}_2\text{O}_3$ PE presented a stable performance over 1000 h, generating *ca.* $1.05 \text{ mA}\cdot\text{cm}^{-2}$ and $1.45 V_{\text{RHE}}$ under $1000 \text{ W}\cdot\text{m}^{-2}$ of simulated sunlight. With the results reported by Dias *et al.*, the stability target instantly shifted from just a few dozen hours to two orders of magnitude above, entering into the thousands, which is acceptable from an industrial point of view. However, the $\alpha\text{-Fe}_2\text{O}_3$ PE reported by Dias *et al.* comprises a major drawback, related to the preparation technique. Spray pyrolysis allows preparing highly reproducible ultra-thin semiconductors, but with a compact morphology, with very low surface area and porosity.^{40, 41} For this reason, despite presenting an extremely stable behaviour, $\alpha\text{-Fe}_2\text{O}_3$ PEs prepared by spray pyrolysis will hardly generate photocurrent densities higher than $1.5 \text{ mA}\cdot\text{cm}^{-2}$ at $1.23 V_{\text{RHE}}$, even with

the use of expensive co-catalysts, which is unrealistic from a commercial perspective.

Nanostructured $\alpha\text{-Fe}_2\text{O}_3$ -PEs prepared via hydrothermal methods have already demonstrated a remarkable efficiency, reaching 50 % of its theoretical limit.¹⁷ However, nanostructured $\alpha\text{-Fe}_2\text{O}_3$ -PEs are usually poorly stable.^{6, 21, 42} On the other hand, these structures are often subjected to surface treatments and to the deposition of overlayers, making the stability of the PE dependent not only on the intrinsic properties of the semiconductor, but also on the properties of the materials deposited at the surface.⁴³ The work developed in this chapter aimed at tackling this issue, targeting the development of a highly stable nanostructured $\alpha\text{-Fe}_2\text{O}_3$ -PE. The multi-step annealing combined with the application of a protective overlayer were included in the experimental procedure envisioning not only high efficiency, but also, long-term stability. Also, sponge-like nanocubes should be mechanically more stable than nanorods, nanowires or similar structures. The stability of the developed Co- $\alpha\text{-Fe}_2\text{O}_3$ -NCs-S PE was assessed over more than 1000 hours. The photocurrent density generated at 1.23 V_{RHE} was continuously recorded under 1000 W·m⁻² of simulated sunlight, using a cappuccino PEC cell assembled in a three-electrode configuration. The obtained results are plotted in Figure 2.7.

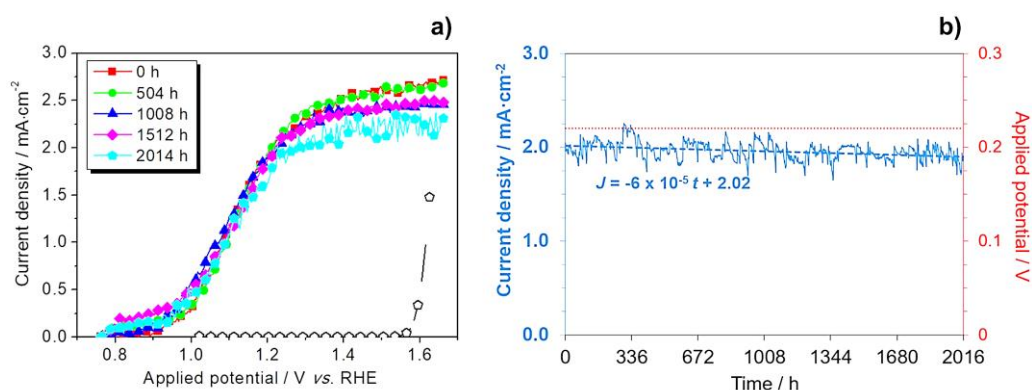


Figure 2.7. Long-term stability measurements: a) J-V characteristics of the Co- $\alpha\text{-Fe}_2\text{O}_3$ -NCs-S PE, assembled in cappuccino PEC cell with a 3-electrode configuration, filled

with 1.0 M KOH, under uninterrupted simulated sunlight ($1000 \text{ W}\cdot\text{m}^{-2}$), recorded before starting the stability test, 0 h (■), and after being operated for 504 h (●), 1008 h (▲), 1512 h (◆) and 2014 h (◆); b) photocurrent density history of the Co- α - Fe_2O_3 -NCs-S PE recorded at a constant bias of $1.23 \text{ V}_{\text{RHE}}$ and under simulated sunlight ($1000 \text{ W}\cdot\text{m}^{-2}$).

Figure 2.7 shows that the optimized sponge-like α - Fe_2O_3 -PE presented a fully stable performance over 2014 h under standard PEC operating conditions, continuously generating ca. $2.0 \text{ mA}\cdot\text{cm}^{-2}$ at a constant applied potential of $1.23 \text{ V}_{\text{RHE}}$, which is a record-breaking achievement. According to the linear fit made to the curve of the photocurrent history (Figure 2.7-b), a 10 % decrease on the recorded photocurrent (relatively to the initial value) would be achieved after 3516 hours, which meets the stability target for commercialization, *i.e.* 2920 h (corresponding to 8 working hours over 365 days). To the best knowledge of this thesis, this is also the first work reporting a metal oxide semiconductor with a co-catalyst capable of displaying a stable performance over more than 100 hours, without any maintenance procedure or catalyst regeneration performed in between. The closest approach to these experimental results was reported by Kuang *et al.*⁴⁴ The authors reported a stable particulate Mo:BiVO₄/Ni/Sn electrode that generated ca. $2.6 \text{ mA}\cdot\text{cm}^{-2}$ at $0.6 \text{ V}_{\text{RHE}}$ over 1100 h; however, stability measurements comprised eleven 100-hour runs, with electrolyte replacement between any two runs and *in situ* self-regeneration of the catalyst.

The noise observed in the photocurrent history plot was assigned to: i) accumulation of gas bubbles inside the cell, related to the absence of electrolyte recirculation; ii) sudden variations in the concentration of the electrolyte, attributed to the addition of distilled water every 24 hours to restore the initial liquid level; iii) electrolyte leakages from the cell, which sometimes caused the liquid level to drop below the top of the quartz window, affecting the illuminated area. Still, no significant changes were observed in the *J-V* measurements plotted in Figure 2.7-a, neither in the onset potential, nor in the photocurrent density recorded at the plateau. This is a preliminary indicator that the PE did not undergo any corrosion or erosion throughout the stability test, also indicating

that the obtained morphology is robust and enabled a good adhesion of the catalyst to the semiconductor.

By the time this dissertation it was not possible to perform any material analyses on the α -Fe₂O₃ PE after the stability test, essential for investigating any changes in the semiconductor promoted by the harsh operating conditions. Nevertheless, further material analyses should include: i) top-view and cross-section SEM analyses for investigating morphological changes in the PE, namely concerning the thickness and the pore size of the α -Fe₂O₃ film; ii) XPS analyses on fresh and aged samples, for investigating the presence of co-catalyst at the surface after the long-term test, and also for assessing the diffusion of Ti⁴⁺ and Si⁴⁺ into the lattice of hematite (promoted by the functional annealing); iii) ICP spectroscopy for checking any material detachment from the PE, namely through the quantification of iron and cobalt concentrations in fresh electrolyte and in the electrolyte used in the stability test. Depending on the equipment availability, it would also be interesting to subject a α -Fe₂O₃-NC-T PE to a similar long-term stability test, aiming at inferring which encapsulation procedure provides the PE with the best protection against corrosion and mechanical erosion. In the case this stability test could be performed, electrolyte recirculation should be promoted to investigate the effect of erosion.

This work shows that there is still plenty room for improving the performance of α -Fe₂O₃-NC PEs, which can be strategically accomplished with the implementation of a DoE study, as previously done by Dias *et al.*¹⁹ The thickness of the α -Fe₂O₃ film is a relevant parameter that should be included in a hypothetical DoE study. Even so, the work developed in this chapter is a solid contribution for future optimization studies since it allowed answering to two essential requirements of DoE analyses: i) defining the lower and upper limits of each experimental parameter subjected to optimization; ii) acquired knowledge and experience with the preparation technique. Furthermore, EIS and IMPS analyses should be performed during the optimization process for better identifying and understanding the key factors that may influence the PEC performance of these sponge-like α -Fe₂O₃ PEs.

2.4 CONCLUSIONS

This chapter aimed at optimizing a low-cost and scalable hydrothermal method for preparing highly efficient and stable nanostructured α -Fe₂O₃ PEs. The stepwise approach implemented in this work allows concluding that the experimental parameters with greater influence the PEC performance are: i) concentration of fluoride ions in the precursor solution; ii) duration and temperature of the hydrothermal synthesis; and iii) the type of annealing. The optimal preparation conditions were found to be: i) a F⁻ concentration in the precursor solution between 0.05 and 0.075 M; ii) a hydrothermal synthesis performed at a constant temperature of 100 °C, over 6 h; iii) separate morphological and functional annealing, conducted at 550 °C for 2 h, and at 800 °C for 20 min, respectively, allowing the PE to cool down in between. It was found that performing an encapsulation with SiO₂ or TiO₂ between the annealing steps is crucial for preserving the porosity of the semiconductor. Top-view and cross-section SEM images revealed that the α -Fe₂O₃ PE fabricated with this set of experimental conditions comprises 500 nm thick highly porous sponge-like nanocubes with feature sizes of ca. 20-40 nm, a morphology never reported before. This new morphological structure allowed improving the photocurrent density by more than 100 % when compared with similar morphologies reported in the literature.⁷

Porous sponge-like α -Fe₂O₃ nanocubes were subjected to different surface treatments. Performing an acid treatment on α -Fe₂O₃ PEs with TiO₂ encapsulation allowed obtaining improvements of 85 % and 20 % in the photocurrent density generated at 1.23 V_{RHE} and at the plateau, respectively; this acid treatment promoted a cathodic shift of ca. 100 mV on the onset potential. On the other hand, removing the silica scaffold was the surface treatment with greatest influence on the performance of α -Fe₂O₃-NC-S PEs; this treatment allowed obtaining improvements of 41 % and 25 % in the photocurrent density generated at 1.23 V_{RHE} and at the plateau, respectively. For these PEs, the acid treatment did not have a significant impact on the performance. The optimal

sponge-like $\alpha\text{-Fe}_2\text{O}_3\text{-NC-S PE}$, decorated with a Co-Pi co-catalyst, generated $2.01\text{ mA}\cdot\text{cm}^{-2}$ at $1.23\text{ V}_{\text{RHE}}$, $2.49\text{ mA}\cdot\text{cm}^{-2}$ at the plateau, and $2.6\text{ mA}\cdot\text{cm}^{-2}$ before the dark current onset.

One of the main contributions of the present work is the unprecedented stable performance exhibited by the as-prepared photoanode. The optimal sponge-like $\alpha\text{-Fe}_2\text{O}_3\text{ PE}$ presented a fully stable performance over 2014 h under standard PEC operating conditions, continuously generating ca. $2.0\text{ mA}\cdot\text{cm}^{-2}$ at $1.23\text{ V}_{\text{RHE}}$, without catalyst regeneration. A 10 % decrease on the recorded photocurrent is expected to be achieved after 3516 hours of continuous operation, meeting the stability target for commercialization, *i.e.* 2920 hours (8 working hours over 365 days).

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CHAPTER 3

OPTIMIZED PHOTOELECTROCHEMICAL TANDEM CELL FOR SOLAR WATER SPLITTING

“Lithium-ion batteries are not the solution, they are just one little help that gives you, young engineers, some time to find a proper solution for energy storage at an industrial scale.”

John Bannister Goodenough,

The Voice of Industry, Porto, Portugal, 2018



Reprinted from peer-reviewed article:

A. Vilanova, T. Lopes, C. Spenke, M. Wullenkord and A. Mendes, *Energy Storage Materials*, 2017, **13**, 175-188.

3 OPTIMIZED PHOTOELECTROCHEMICAL TANDEM CELL FOR SOLAR WATER SPLITTING

In the field of PEC-H₂ production most studies focus on developing efficient nanostructured materials and less attention is given to the optimization of PEC devices. However, the reactor design greatly influences the overall performance of these devices and it is a key element to turn PEC hydrogen generation competitive and marketable.

In this work, a 50 cm² tandem PEC-PV cell, named CoolPEC cell (compact, optimized, open light PEC cell), was designed and optimized for continuous operation comprising improved key features: i) an open path for the sunlight to reach a PV cell placed at the back of the PEC cell; ii) a PE that simultaneously is one of the windows of the cell; iii) an integrated manifold to feed the electrolyte. CFD simulations were performed to improve the reactor design assuring good heat dissipation and an efficient collection of evolved oxygen and hydrogen in separated compartments.

The CoolPEC cell presented a stable performance over 42 days (1008 h) in a continuous operation mode. The 50 cm² hematite PE produced ca. 0.45 mA·cm⁻² at a bias potential of 1.6 V provided by two silicon heterojunction (SHJ) solar cells, under 1000 W·m⁻² and with constant electrolyte feeding at 45 °C. SEM, EDS and ICP analyses confirmed that the hematite PE was resistant to the accelerated corrosion promoted by the operating conditions.

3.1 INTRODUCTION

Water electrolysis is a well-known process, optimized over two centuries. PEC devices for solar water splitting incorporate key design features adapted from commercial electrolyzers, so it is quite helpful to visit the water electrolysis field, to understand how it has evolved and which are the main technological advancements –Figure 3.1. The water electrolysis field was born in 1789 when Jan Rudolph Deiman and Adriaan Paets van Troostwijk used an electrostatic machine to feed electricity to gold electrodes immersed in water in a Leyden jar.¹ In 1800 William Nicholson and Anthony Carlisle reported for the first time hydrogen produced from electrolysis of water –Figure 3.1-a.² By 1902 more than 400 industrial plants were producing hydrogen via water electrolysis.² Since then, alkaline electrolysis turn out to be the selected technology for hydrogen production (Figure 3.1–b).³ Polymer electrolyte membrane (PEM) electrolyzers appeared in 1960s (Figure 3.1–c) with the advantages of having a faster response to the power input and delivering hydrogen at high pressure, but requiring the use of more complex reactors and expensive materials.⁴ Currently, commercial electrolyzers of both types could reach efficiencies up to 80 %.⁵

In more recent decades, with the development of increasingly efficient and cheaper photovoltaic (PV) technologies ⁶⁻⁸, the concept of combined photovoltaic-electrolysis arose (Figure 3.1–d). Hydrogen produced from solar water splitting is considered a low-cost and clean route for storing the solar energy, promising to display a solar-to-hydrogen (STH) conversion efficiency of 12 %.⁹ Combined PV-electrolysis consists basically of coupling a photovoltaic cell (Figure 3.1– f, g and h) to an electrolyser where electrolysis occurs in a two-step process: i) photon-to-electric conversion and ii) electric-to-chemical conversion.¹⁰ By the time this work was developed, crystalline silicon PV cells could reach efficiencies up to 27.6 %.¹¹ Indeed, solar energy is the most abundant renewable energy source and it is able to supply present and future world needs for energy.¹² At any instant, the solar power striking the Earth's surface is equal to 1.08×10^{14} kW, corresponding to 7 500 times the world's

present annual primary energy consumption. Combined PV-electrolysis enables converting this energy source into a fuel that can be easily stored and transported.¹³ Still, combining these highly efficient solar cells to an efficient electrolyser results in expensive devices due to the need for power conditioning equipment and losses from lateral collection and transmission of electricity.¹⁴ To overcome this limitation integrated PV-electrolysers appeared as an interesting alternative (Figure 3.1–e).¹⁵ This technology incorporates a PV cell and one of the electrodes in a single panel that can be immersed in the electrolyte. In these systems power-conditioning equipment is eliminated and transmission losses are greatly reduced.^{10, 16} To date, the best integrated PV-electrolysis system achieved a 48-h average STH efficiency of 30 %.¹⁷ Still, the added complexity from the dual-function panels limits the up-scale development and compromises the overall efficiency improvements.⁴

In 1972, Fujishima and Honda reported for the first time the use of a PEC cell for water splitting (Figure 3.1–m); this unbiased pioneer device was equipped with a *n*-type TiO₂ PE (PE) operating under UV light and displayed a quantum efficiency of 10 %.¹⁸ In a PEC cell the functions of a solar cell and electrolyser are combined in a single device, which is favorable in terms of packaging and overall system costs.¹⁹ Single water splitting devices are usually divided into biased and unbiased systems.^{20, 21} PEC devices with no additional bias comprise single and multiple photo-system arrangements and can be divided in two main categories: i) monolithic systems (Figure 3.1–j) and ii) separated electrode systems (Figure 3.1– k and l).¹⁶ Still, even the best-performing semiconductors used in PEC cells require an external bias to efficiently carry out the water splitting reaction. To address this challenge tandem cells, combining a wider-bandgap and stable PE (1.8–2.4 eV) with a smaller-bandgap PV-cell (1.0–1.5 eV), started to emerge –Figure 3.1–i.^{16, 22} Power management units can be used to further increase the STH efficiency of PEC-PV devices up to 21 %, which exceeds the total conversion efficiency of PV-electrolysis systems producing the same amount of hydrogen.²³ Using high solar flux concentrations is also a possible route to improve the performance of semiconductors by enhancing the

photocurrent and/or reducing the applied bias.^{24, 25} So far, the best-performing PEC-PV device ($1.5 \times 1.5 \text{ cm}^2$) reached 7.1 % STH conversion efficiency, using photon-recycling hybrid conductive distributed Bragg reflectors (cDBRs).²⁶

Presently, most PEC reactors reported in the literature were developed for testing new PEs at lab scale.²⁷ Among these devices, “Cappuccino” PEC cell (EPFL, Switzerland) and PortoCell (UPorto; Portugal) are probably the most widely used.^{28, 29} “Cappuccino” cell (Figure 3.1-n) has a compact design and the small distances between the electrodes minimize ohmic losses. More recently, “PortoCell” (Figure 3.1-o) was developed for hosting PEs up to $10 \times 10 \text{ cm}^2$, close to the expected dimensions of commercial PEs in a PEC panel.³⁰ Despite incorporating several advancements, this cell still lacks important design features to be operated in a continuous mode with tandem PEs and under concentrated sunlight.

A PEC reactor for hosting a tandem PE/PV cell needs to display an open path from the front to the back window for allowing a PV cell to be installed at the back. Counter-electrodes (CEs) should be placed side-by-side to the working-electrode (WE), but separated by an ion exchange membrane to avoid gas mixture. Cost-efficient PEC reactors should be narrow and easy to assemble. Developing a PE that can be simultaneously a window of the cell is critical for keeping the costs low. The glass substrate needs to have a conductive path between the conductive side in contact with the electrolyte and the non-conductive side. A metallic frame screwed to the cell allows making the electrical contact between the PE and the current collector. The sealed area should match the active area of the PE, thus preventing the bare FTO to contact the electrolyte; if FTO contacts the electrolyte, the dark current onset decreases, limiting the performance of the cell.³¹ These improved key features included in the proposed PEC cell design are represented in Appendix 3-a.

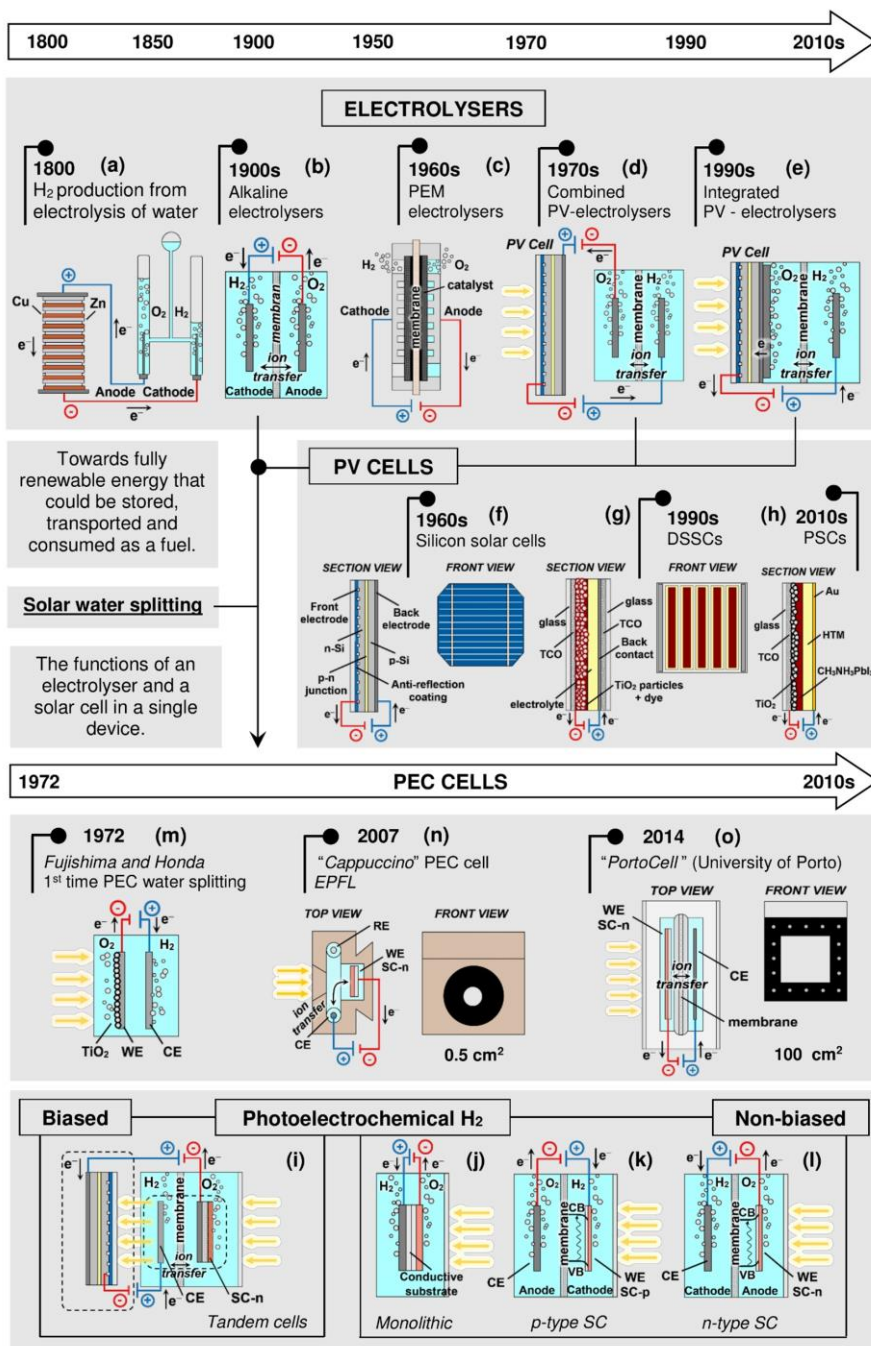


Figure 3.1. Short overview on electrolyzers, photovoltaic cells and PEC cells: chronological development and different combinations between them.

This chapter addresses the challenge of designing, building, optimizing, and assessing a 50 cm² tandem PEC-PV cell. According to Nielander *et al.* this solar fuel generator belongs to the family of photovoltaic-biased photoelectrosynthetic cells (PV-PES)³²; still, in the present study the envisioned device was named as tandem PEC-PV. A CFD software was used for optimizing the reactor design. The stability and performance of the PEC-PV cell was assessed over 1000 h under continuous solar illumination and with electrolyte recirculation. As previously mentioned in the introduction, the optimization of α -Fe₂O₃ PEs was made throughout the entire work plan of this PhD. Unfortunately, when the work comprised in this chapter was performed, the optimization of the experimental procedure for fabricating nanostructured α -Fe₂O₃ PEs was at its early stage. As so, preparing a 50 cm² nanostructured α -Fe₂O₃ PE would represent a massive task, especially in what concerns the homogeneity of the fabricated semiconductor across the large-area substrate. Also, by the time there was no evidence that a large-area nanostructured α -Fe₂O₃ PE could be stable over dozens of hours under standard PEC operating conditions. Finally, there was no available autoclave in the hosting lab for preparing 50 cm² nanostructured α -Fe₂O₃ PEs. Therefore, α -Fe₂O₃ prepared by spray pyrolysis was the selected semiconductor for preparing a stable and reasonably efficient 50 cm² PE, taking advantage of the acquired knowledge and background of the hosting lab with this preparation technique. Nevertheless, the developed PEC cell can be assembled with any type of PE, including tandem PEs.

3.2 EXPERIMENTAL

3.2.1 MODEL AND SIMULATION

CFD (Computational Fluid Dynamics) is a powerful way of modelling fluid flow, heat transfer, and related processes.^{33, 34} Ansys® Workbench Academic 16.0 was used to perform the required calculations and to assist designing the new PEC reactor. The electrolyte flow path inside the cell body was optimized

targeting good heat dissipation – it was assumed a maximum solar irradiance of 17-sun – and efficient collection of evolving gas bubbles at the top of the cell, preventing their accumulation across the light path. The mesh was built considering only the electrolyte volume inside the acrylic embodiment. A three-dimensional unstructured finite-volume method was used to simulate the PEC reactor considering an incompressible flow. Ansys Fluent uses the vector equations for 3D Cartesian coordinates from the Navier-Stokes equations, considering the velocity u expanded as $u = (u_x, u_y, u_z)$. Since the fluid was assumed incompressible, the fluid density ρ is constant for any fluid element, the continuity equation becomes:

$$\frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} + \frac{\partial u_z}{\partial z} = 0 \quad (1)$$

The realizable k - ϵ model was selected to simulate the fluid turbulence. The transport equations for k and ϵ can be written as:

$$\frac{\partial}{\partial t}(\rho k) + \frac{\partial}{\partial x_j}(\rho k u_j) = \frac{\partial}{\partial x_j} \left[\left(\mu + \frac{\mu_t}{\sigma_k} \right) \frac{\partial k}{\partial x_j} \right] + G_k + G_b - \rho \epsilon - Y_M + S_k \quad (2)$$

and

$$\frac{\partial}{\partial t}(\rho \epsilon) + \frac{\partial}{\partial x_j}(\rho \epsilon u_j) = \frac{\partial}{\partial x_j} \left[\left(\mu + \frac{\mu_t}{\sigma_\epsilon} \right) \frac{\partial \epsilon}{\partial x_j} \right] + \rho C_{1\epsilon} S_\epsilon - \rho C_{2\epsilon} \frac{\epsilon^2}{k + \sqrt{\nu \epsilon}} + C_{1\epsilon} \frac{\epsilon}{k} C_{3\epsilon} G_b + S_\epsilon \quad (3)$$

where

$$C_1 = \max \left[0.43, \frac{\eta}{\eta + 5} \right], \quad \eta = S \frac{k}{\epsilon}, \quad S = \sqrt{2 S_{ij} S_{ij}}$$

and μ is the fluid viscosity, k is the kinetic energy of turbulence, ϵ is the dissipation rate, G_k represents the generation of turbulence kinetic energy due to the mean velocity gradients, G_b is the generation of turbulence kinetic energy due to buoyancy, Y_M represents the contribution of the fluctuating dilatation in

compressible turbulence to the overall dissipation rate, C_2 and $C_{1\epsilon}$ are constants and σ_k and σ_ϵ are turbulent Prandtl numbers for k and ϵ .

Ansys Fluent solves the energy equation in the following form:

$$\frac{\partial}{\partial t}(\rho E) + \nabla \cdot (\vec{v}(\rho E + p)) = \nabla \cdot \left(k_{eff} \nabla T - \sum_j h_j \vec{J}_j + (\bar{\tau}_{eff} \cdot \vec{v}) \right) + S_h \quad (4)$$

where k_{eff} is the effective conductivity and $\vec{J}_j$ is the diffusion flux of species j . The first three terms on the right-hand side of the equation represent energy transfer due to conduction, species diffusion and viscous dissipation, respectively. S_h includes the heat of chemical reaction and any other volumetric heat sources defined by the user. In equation (4),

$$E = h - \frac{p}{\rho} + \frac{v^2}{2} \quad (5)$$

where sensible enthalpy is defined for incompressible flow as

$$h = \sum_j Y_j h_j + \frac{p}{\rho} \quad (6)$$

When a fixed temperature condition is applied at the wall, the heat flux to the wall from a fluid cell q is computed as:

$$q = h_f(T_w - T_f) + q_{rad} \quad (7)$$

where h_f is the fluid-side local heat transfer coefficient, T_w is the wall surface temperature, T_f is the local fluid temperature and q_{rad} is the radiative heat flux. When a heat flux boundary condition is defined at a wall, Fluent uses Equation (7) and the user input of heat flux to determine the wall surface temperature adjacent to a fluid cell as:

$$T_w = \frac{q - q_{rad}}{h_f} + T_f \quad (8)$$

Steady state conditions were considered for temperature simulations using the energy model with solar ray tracing. The solar flux was only applied to the front wall. When the combined convection and radiation boundary conditions are chosen, the heat flux to the wall is computed as:

$$q = h_{ext}(T_{ext} - T_w) + \epsilon_{ext}\sigma(T_{\infty}^4 - T_w^4) \quad (9)$$

where h_{ext} is the external heat transfer coefficient (defined by the user), T_{ext} is external temperature (defined by the user), ϵ_{ext} is the emissivity of the external wall surface (defined by the user), σ is the Stefan-Boltzmann constant, T_w is the surface temperature of the wall and T_{∞} is the temperature of the radiation source on the exterior.

The main input data used in CFD simulations are presented in Table 3.1.

Table 3.1. Values selected as main input parameters used in CFD simulations.

Velocity-inlet	
x-velocity	0 m·s ⁻¹
y-velocity	0 m·s ⁻¹
z-velocity	1.06 m·s ⁻¹ ; 0.53 m·s ⁻¹ (*)
Specification method	Intensity and hydraulic diameter
Turbulent intensity	5 %
Hydraulic diameter	1 x 10 ⁻² m
Temperature	298 K; 318 K (*)
Radiation model	
Model	Solar ray tracing
Direction vector for sunlight	x
Direct solar irradiation	1 000 kW·m ⁻² ; 17 000 W·m ⁻² (*)

Diffuse solar irradiation	200 W·m ⁻²
Spectral fraction	0.5
Convergence criteria	
Continuity	1 x 10 ⁻⁵
x-velocity	1 x 10 ⁻³
y-velocity	1 x 10 ⁻³
z-velocity	1 x 10 ⁻³
Energy	1 x 10 ⁻⁵

3.2.2 PREPARATION OF HEMATITE PES

In the envisioned PEC cell, the PE is simultaneously the front or the back window. This feature requires having a conductive path between both sides of the commercial FTO glass substrate. A conductive silver paste (Ferro GmbH GSSP SP 1963) was manually printed on both sides of the substrate edges as illustrated in Appendix 3-b. The silver paste was then sintered and annealed at 500 °C before the α -Fe₂O₃ deposition.

Hematite thin films were prepared by spray pyrolysis due to its high stability and reproducible performance³⁵. FTO glass substrates (120 mm x 70 mm; Solaronix TCO 22-7) with the silver paste frame already sintered, were pre-treated with TEOS (tetraethyl orthosilicate), as described elsewhere³⁶. The glass substrates were first heated at 450 °C and then ca. 20 mL of a diluted TEOS solution (99.9 %, Aldrich; 10 % volume in ethanol) were hand-sprayed with a glass atomizer. After the TEOS pre-treatment, α -Fe₂O₃ thin films were applied by spray pyrolysis. The experimental setup used in this work is depicted in Appendix 3-c. In short, substrates were placed over a heating plate (18 x 18) cm² at 450 °C. The spray nozzle placed 30 cm over the glass substrates was fed by an automatic syringe pump (Cronus Sigma 2000 Dual Syringe Pump) delivering discrete volumes of 1 mL at 12 mL·min⁻¹ of a solution containing 10 mM of Fe(acac)₃ (99.9+ %, Aldrich) in EtOH (99 %, Aga). The time gap between sprays was 45 s and the total solution volume applied was 70 mL. During the deposition, a constant air flow was directed to the substrate from the spray head. The

α -Fe₂O₃ PEs were then annealed for 30 min at 500 °C before being cooled down to room temperature.

3.2.3 J–V MEASUREMENTS BEFORE THE STABILITY TEST

The photocurrent–voltage (*J–V*) characteristic curves presented in Figure 3.3-a and -b were obtained by applying an external potential bias to the cell and measuring the generated photocurrent using an Autolab/PGSTAT302N workstation controlled by Nova software package (Nova version 1.11). Photocurrent–voltage measurements were performed in the dark and under simulated sunlight, AM 1.5 G (1000 W Xe lamp, 1000 W·m⁻², 25 °C) calibrated with a c-Si photodiode, at a scan rate of 10 mV·s⁻¹. The working- and counter-electrodes were individually connected to the workstation. Only a 3-electrode configuration was considered and Metrohm Ag/AgCl sat. KCl was used as reference electrode.

3.2.4 TEST FACILITY SoCRATUS

SoCRatus is a solar concentrator unit developed by the Institute of Solar Research, German Aerospace Center (DLR) equipped with 22 linear mirrors and a two-axis tracking system that concentrate the sunlight in a rectangular flat focus of 250 x 10 cm² up to 20-sun.^{37, 38} The developed PEC cell was installed in the SoCRatus unit together with the two electrolyte cycle loops, the heat exchangers and the GC, as illustrated in Appendix 3-d. Evolved H₂ and O₂ leave the cell together with the two exiting electrolyte streams. These gases are collected separately at their respective electrolyte tanks. A nitrogen stream carries the evolved gases to a GC for assessing their flowrate and purity. Temperature, pressure, flow rate, pH and O₂ and H₂ concentrations are determined and processed by the data acquisition and control system.

3.2.5 TEST BENCH FOR THE LONG-TERM STABILITY TEST

The long-term stability test was performed using the setup schematically presented in Appendix 3-e. Pictures of the test bench are available in Appendix 3-f. The developed PEC cell was operated with an in-house made $\alpha\text{-Fe}_2\text{O}_3$ PE (50 cm², ca. 20 nm thick). Platinized-Ti meshes (Umicore, F-type mesh) were used as CEs, separated from the PE by an anion exchange membrane (Fumatech Fumasep[®] FAA-3-PK-100). To supply the $\alpha\text{-Fe}_2\text{O}_3$ PE with the necessary bias potential of ca. 1.6 V, two 50 cm² silicon heterojunction (SHJ) solar cells prepared by PVcomB from HZB (Helmholtz-Zentrum Berlin) were connected in series. An Autolab/PGSTAT302N workstation controlled by Nova software package (Nova version 1.11) was used to continuously monitor the photocurrent produced by the semiconductor. The PEC-PV cell was placed over a metallic support aligned with the centre of the solar simulator. Continuous simulated solar irradiance of 1000 W·m⁻² was provided by a Sulphur plasma lamp (system AS 1300 V 2.0, Plasma International GmbH), calibrated with a c-Si photodiode. Continuous electrolyte feeding (ca. 0.2 L·min⁻¹) was promoted by a peristaltic pump (Watson Marlow 323). A water bath (Julabo F12 EH) was used to keep the electrolyte at a constant temperature of ca. 45 °C.

3.3 RESULTS AND DISCUSSION

3.3.1 PRELIMINARY TESTS

Recent studies have increasingly mentioned the importance of up-scaling PEs from few square centimetres towards practical dimensions (≥ 50 cm²).³⁹ This requires solving engineering challenges associated with large-area tandem PEC-PV systems, namely ohmic losses in the electrolyte and in the semiconductor film.^{40, 41}

CEs placed side-by-side to the PE represent additional ohmic losses in the electrolyte, comparatively to the zero-gap configuration where CEs are located

at the back of the PE. Ohmic losses at the electrolyte can be estimated for a solution with a known conductivity and assuming a one-dimension linear model:

$$\eta = \rho \cdot \frac{l}{A} \cdot I \quad (10)$$

where η is the overpotential, ρ is the electrolyte resistivity, I is the recorded current, l is the distance between electrodes and A is the cross-section of the electrolyte container. These ohmic losses can also be experimentally estimated using the experimental PEC cell working just with two platinized-Ti meshes to promote the water electrolysis in 1.0 M aqueous solution of KOH, with a conductivity of $199 \text{ mS} \cdot \text{cm}^{-1}$ – Figure 3.2.

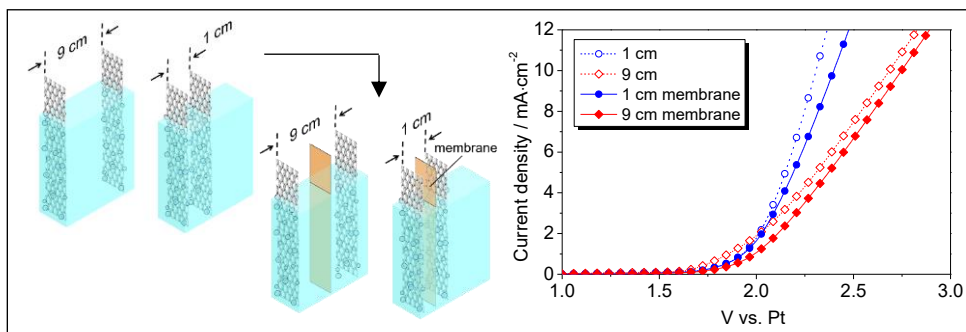


Figure 3.2. Electrodes of platinized-Ti immersed in 1.0 M KOH and anion exchange membrane (Fumatech Fumasep® FAA-3-PK-100): a) experimental configurations for obtaining the J - V curves in hydrolysis mode; b) J - V curves.

Increasing the distance between the two electrodes from 1 cm to 9 cm resulted in an overpotential of 297 mV at a current density of $8.1 \text{ mA} \cdot \text{cm}^{-2}$ (current density corresponding to the target of 12 % STH). This result agrees with the estimating value based on eq. (10), 283 mV. Since in the PEC-PV cell positive and negative electrodes are separated with an ionic exchange membrane for avoiding gas mixing, the additional charge transport overpotential should be also assessed. The selected membrane displayed an overpotential of 73 mV @ $8.1 \text{ mA} \cdot \text{cm}^{-2}$ when the platinized-Ti meshes were placed 1 cm away from each other.

For assessing the ohmic losses at the FTO conductive substrate, two sets of experiments were conducted – Figure 3.3. Two $10 \times 10 \text{ cm}^2$ bare $\alpha\text{-Fe}_2\text{O}_3$ PEs (ca. 20 nm thick, prepared by spray pyrolysis) were stepwise cut, first decreasing the length and then decreasing the width. The PEs were immersed in 1.0 M KOH and front-illuminated (AM 1.5 G, $1000 \text{ W}\cdot\text{m}^{-2}$, 25°C). Two platinized-Ti meshes were used as CEs, placed side-by-side to the PE. The distance between the CEs and the PE was 0.5 cm in all measurements.

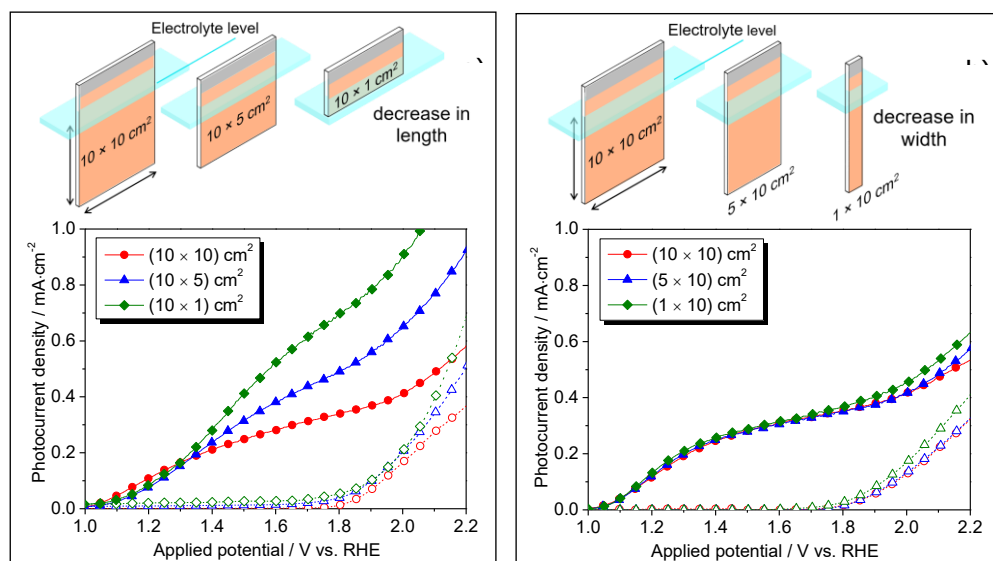


Figure 3.3. J - V characteristic curves of $\alpha\text{-Fe}_2\text{O}_3$ prepared by spray pyrolysis obtained in a 3-electrode configuration under dark conditions (dashed lines) and under simulated sunlight ($1000 \text{ W}\cdot\text{m}^{-2}$, solid lines): a) PE cut horizontally; b) PE cut vertically.

As the width-to-length ratio became higher (Figure 3.3-a) the generated photocurrent increased. When the distance that electrons needed to travel to reach the current collector is shortened, ohmic losses reduce significantly. An overpotential of 0.6 V vs. RHE was obtained for an increase of 9 cm in the length of the PE. However, this high overpotential is not only related to the electrical resistance imposed by the FTO substrate (in this case, $7 \Omega\text{sq}$). Ohmic losses due to recombination phenomena are amplified when electrons need to travel longer paths to reach the current collector.^{42, 43} Therefore, the electronic

resistance should not be calculated as a proportional relation between the electronic path in the substrate and the recorded photocurrent. Nevertheless, for large-area PEs, the distance between the central point of the substrate and the current collector should be as small as possible to reduce the electrical ohmic overpotentials. On the other hand, as the width-to-length ratio became smaller no significant differences were observed in the recorded photocurrent (Figure 3.3-b). These experiments were used for designing the 50 cm² PE, schematically represented in Appendix 3-g.

3.3.2 CFD-DRIVEN OPTIMIZATION

Ansys® Workbench Academic 16.0 was used to design the fluid body inside the cell and simulate the flow path. Following a stepwise approach by changing the diameter and location of inlets and outlets it was possible to obtain an optimized design that allowed generating the upward uniform flow path –Figure 3.4-a. A manifold incorporating several diffusers was designed for feeding the electrolyte. A transparent acrylic plate (2 mm thick) was placed at the middle of the WE compartment to enhance the fluid flow towards the outlets. This design allows a uniform upward flow, as pictured in Figure 3.4-b.

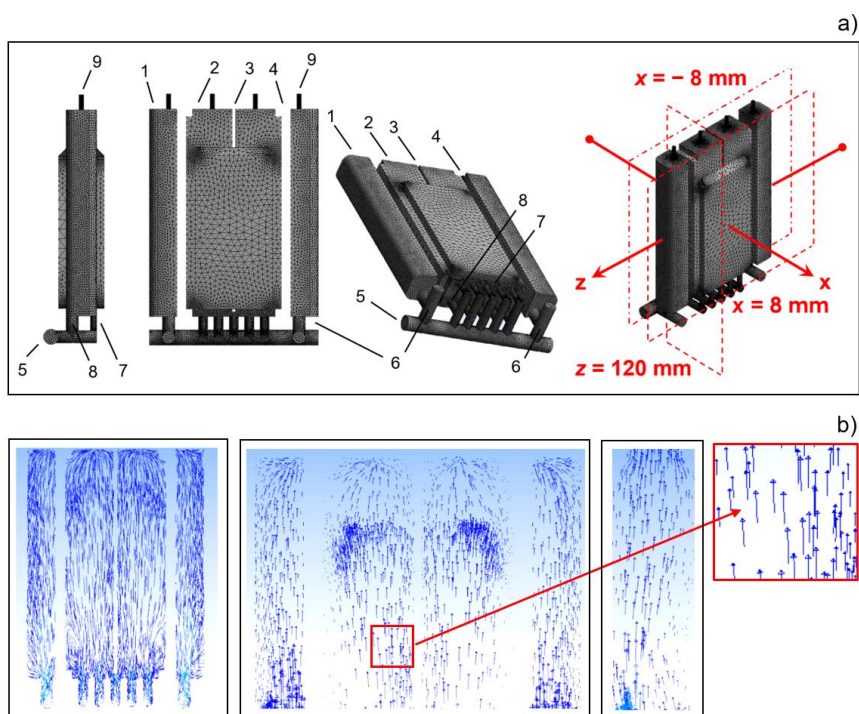


Figure 3.4. Optimized design for the electrolyte container: a) fluid body inside the reactor: 1 – CE compartments; 2 – WE compartment; 3 – housing-area for the internal acrylic plate dividing the WE compartment; 4 - housing-area for the membrane holder; 5 – main electrolyte inlet ($\varnothing = 10$ mm); 6 – inlets of the CE compartments ($\varnothing = 8$ mm); 7 – inlets of the WE compartment close to the front window ($\varnothing = 4$ mm); 8 – inlets of the WE compartment close to the back window ($\varnothing = 6$ mm); b) fluid flow pathlines in the sectional plane close to the back window ($x = -8$ mm) [left-side], in the sectional plane close to the front window ($x = -8$ mm) [middle] and in the middle of the CE compartment ($z=120$ mm) [right-side].

Based on the optimized electrolyte geometry (Figure 3.4-a) the PEC reactor was designed – Appendix 3-h. The embodiment was manufactured using acrylic (Perspex®, from Lucite®) –Figure 3.5. This polymer assures good resistance to the electrolytes normally used and a very acceptable range of operating temperatures – from 0 °C to 65 °C.⁴⁴ Two acrylic parts hold the ionic exchange membrane against the platinized-Ti meshes (CEs), in a close zero-gap configuration. Specific housing-areas in the front side allow screwing a protective

shield (Appendix 3-i) for operation under concentrated sunlight, preventing the cell from overheating and protecting the main components from degradation. The manufactured device was named CoolPEC cell (compact, optimized, open-light PEC cell). Images of the cell with a scale bar are provided in Appendix 3-j.

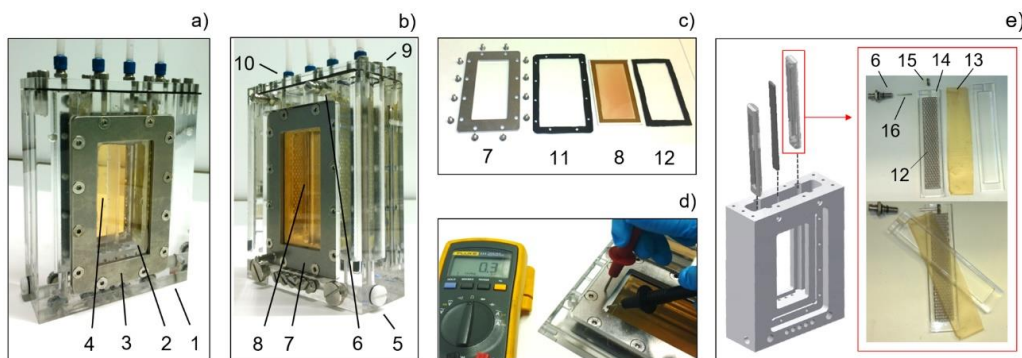


Figure 3.5. CoolPEC cell: a) front side; b) back side; c) main elements for assembling the PE (back window); d) conductivity test between the conductive printed and sintered layer and the stainless-steel frame; e) detailed view of the support that holds the ionic exchange membrane and the CE. 1 – acrylic embodiment; 2 – front window (synthetic quartz); 3 – front stainless steel frame; 4 – internal acrylic plate dividing the WE compartment; 5 – main electrolyte inlet; 6 – external screw (current collector for the CE); 7 – back stainless steel frame; 8 – back window (PE); 9 – acrylic cap; 10 – electrolyte outlet; 11 - internal gasket; 12 - external gasket; 13 – Platinized-Ti mesh; 14 – ionic exchange membrane; 15 – acrylic holders; 16 and 17 – metal connectors between the Pt-Ti mesh and the external screw.

3.3.3 MODEL VALIDATION

The CoolPEC cell allows generating an optimized electrolyte flow path towards the outlets with small stagnant flow zones observed in a quite restricted part at the bottom, as shown in Figure 3.4-b. To experimentally assess the optimized flow path generated with CFD simulations two sets of tests were performed – Figure 3.6.

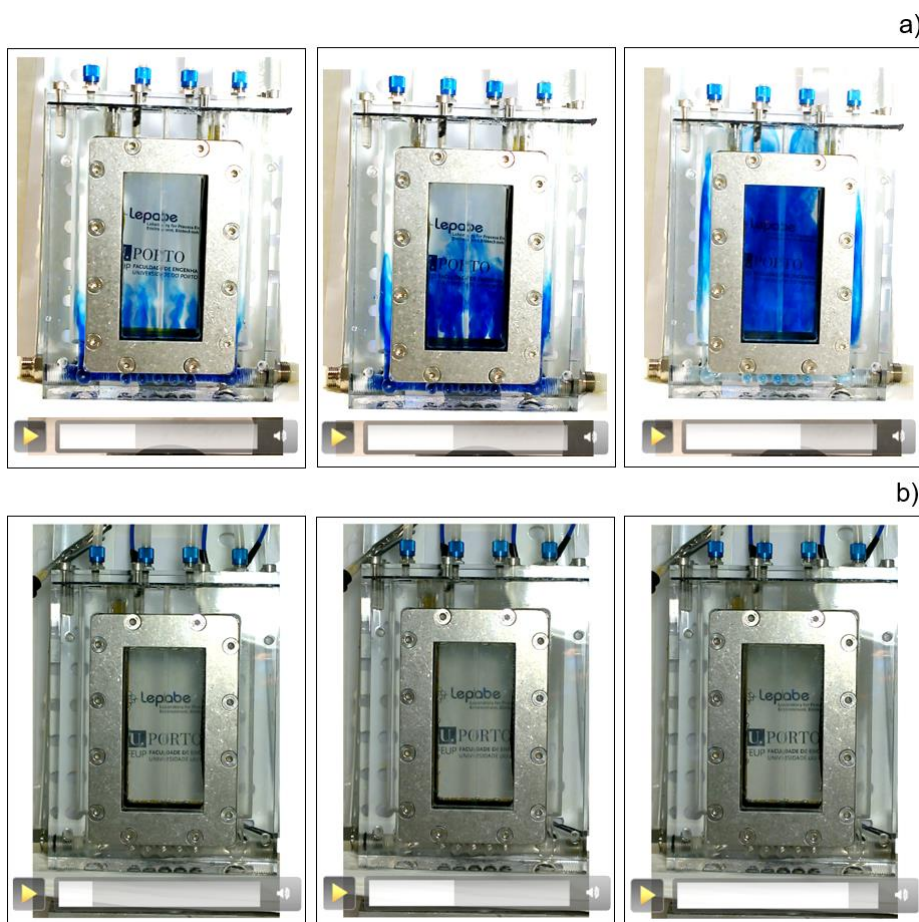


Figure 3.6. Experimental tests to assess the optimized electrolyte flow path: a) tracer test performed with a blue dye and distilled water with a feeding flow rate of $0.5 \text{ L} \cdot \text{min}^{-1}$ pictured at different instants after the injection of the dye (from left to right, 3 s, 6 s and 12 s); b) forced gas evolution at $5.4 \text{ mA} \cdot \text{cm}^{-2}$ with 1.0 M KOH and a feeding flow rate of $0.5 \text{ L} \cdot \text{min}^{-1}$ pictured at different instants after the water electrolysis was promoted (from left to right, 2 s, 20 s and 45 s).

First, a tracer experiment was performed with continuous water feeding at $0.5 \text{ L} \cdot \text{min}^{-1}$ —Figure 3.6-a. After being injected in the main feeding stream, the tracer followed a continuous upward path towards the outlets, which is in accordance with CFD results (Figure 3.4-b). No relevant stagnant areas could be identified.

In a second set of tests, the efficient collection of evolved gas bubbles at the top was assessed –Figure 3.6-b. Two platinized-Ti meshes and a bare FTO glass window (7 Ω square, 2.2 mm thick) were used as cathode and as anode, respectively, to perform the water electrolysis at 5.4 mA·cm⁻² (corresponding to a STH efficiency of 8 %, an ambitious target for upscaled PEs) in 1.0 M aqueous solution of KOH. Despite the intense flow of evolved gases there was no visible accumulation of bubbles inside the CoolPEC cell. This test was also performed with a non-optimized PEC cell (Appendix 3-k and Appendix 3-l). Considerable accumulation of bubbles occurred few seconds after the water electrolysis onset, which would cause a significant decrease in the performance of the PEC-PV cell. To quantitatively demonstrate this negative effect, a c-Si PV cell was placed in the back of the FTO glass and water electrolysis was promoted on both cells under simulated sunlight (Figure 3.7-a). Comparative results for the non-optimized cell and the CoolPEC cell are presented in Figure 3.7-b.

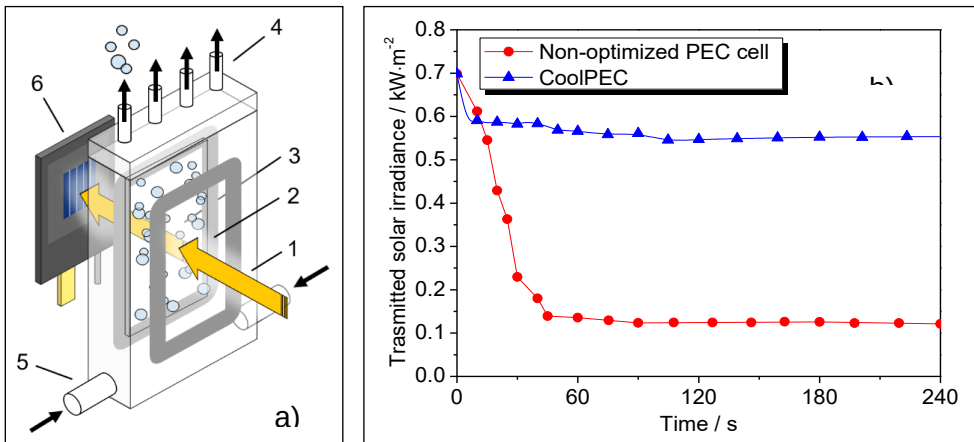


Figure 3.7. Assessment of light trapping due to bubbles accumulation inside the PEC cell; a) schematic representation of the setup used to conduct the experiment; 1 – simulated sunlight (1000 W·m⁻²); 2 – front window (synthetic quartz); 3 – back window (FTO glass, 2.2 mm, 7 Ω square); 4 – electrolyte outlet; 5 – electrolyte inlet; 6 – Si calibrator used to monitor the solar irradiance reaching the outer surface of the back window; b) solar irradiance reaching the external surface of the back window monitored over 4 min with the PEC cell operating at 5.4 mA·cm⁻² with 1.0 M KOH and a feeding flow rate of 0.5 L·min⁻¹: (●) “non-optimized cell” PEC cell; (▲) CoolPEC cell.

In the non-optimized cell, ca. 82 % of the solar irradiance initially measured at the outer surface of the back window (before water electrolysis was promoted) was lost due to the accumulation of gas bubbles, whereas in the CoolPEC cell this value was just ca. 17 %.

The proper separation of evolving gases was experimentally assessed determining the concentration of H_2 and O_2 in both electrolyte streams using a GC. Two platinized-Ti meshes and a bare FTO glass window ($7\ \Omega$ square, 2.2 mm thick) were used as cathode and as anode, respectively, to perform the water electrolysis at $5.4\text{ mA}\cdot\text{cm}^{-2}$ (8 % STH efficiency, at $1.45\text{ V}_{\text{RHE}}$) in a 1.0 M aqueous solution of KOH. The CEs were physically separated from the WE using an anionic exchange membrane (Fumatech Fumasep® FAA-3-PK-100). Figure 3.8-a and-b plot the main operating parameters recorded over 7 h. The feeding flow rate and the tilt position of the cell were changed to simulate different operating scenarios.

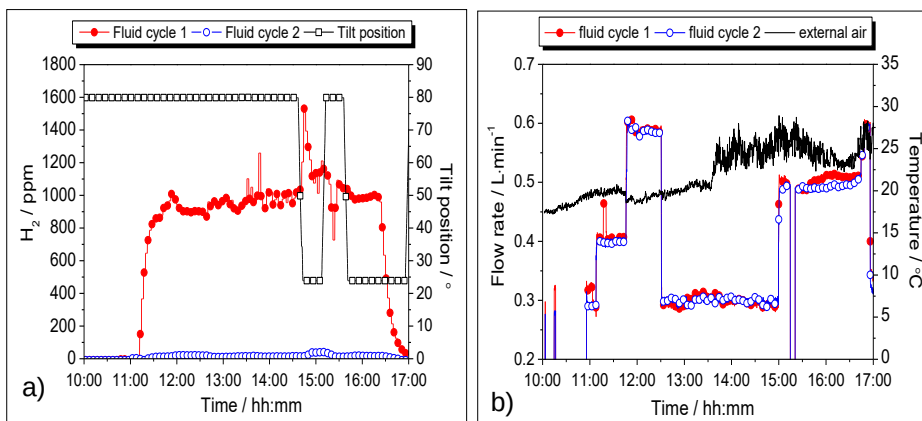


Figure 3.8. Hydrogen flow produced by the CoolPEC cell operated as an electrolyser working at $5.4\text{ mA}\cdot\text{cm}^{-2}$, for different feeding flow rates and tilt angles: a) evolved H_2 flowrate; (●) H_2 collected in the CE compartments (fluid cycle 1); (○) H_2 collected in the PE compartment (fluid cycle 2); b) electrolyte flow rate monitoring at the inlets; (●) fluid cycle 1 – electrolyte inlet 1 and outlets from the CE compartments; (○) fluid cycle 2 – electrolyte inlet 2 and outlets from the PE compartment.

Field tests showed that the CoolPEC cell can safely operate at different tilt positions, avoiding gas mixture inside, independently from the feeding flow rate (Figure 3.8-b). When the tilt position was suddenly changed from 80° to 25°, a crossover peak occurred with *ca.* 41 ppm of H₂ being collected in the WE compartment.

As mentioned, the photocurrent density increases with concentrated sunlight ^{24, 45}. An optimized electrolyte flow path is crucial to assure efficient temperature control and good heat dissipation under such operating conditions. The CoolPEC cell owes its name to the self-cooling ability when operating under concentrated sunlight. This feature was assessed with CFD simulations considering two scenarios: i) standard operating conditions, 17 kW·m⁻² with a total feeding flow rate of 1 L·min⁻¹ at 25 °C and the outside air at 25 °C; ii) cost-saving conditions, 17 kW·m⁻² with a total feeding flow rate of 0.5 L·min⁻¹ at 45 °C and the outside air at 25 °C. Heat dissipation under concentrated sunlight was also assessed with field tests in the SoCRatus. The electrolyte temperature was continuously recorded at the outlets. The temperature in the embodiment was recorded in four specific points (Figure 3.9-b).

Considering the standard scenario (Figure 3.9-a, top), a maximum difference of 1°C is observed between the inlets and outlets with a maximum temperature of *ca.* 40 °C being reached at the upper corners in the internal part of the front window. In the cost-saving scenario, when the electrolyte enters the cell at 45 °C (Figure 3.9-a, bottom), a maximum difference of 3 °C is observed between the inlets and the outlets. A maximum temperature of *ca.* 58 °C is reached in the fluid at the upper corners and in the middle of the internal part of the front window.

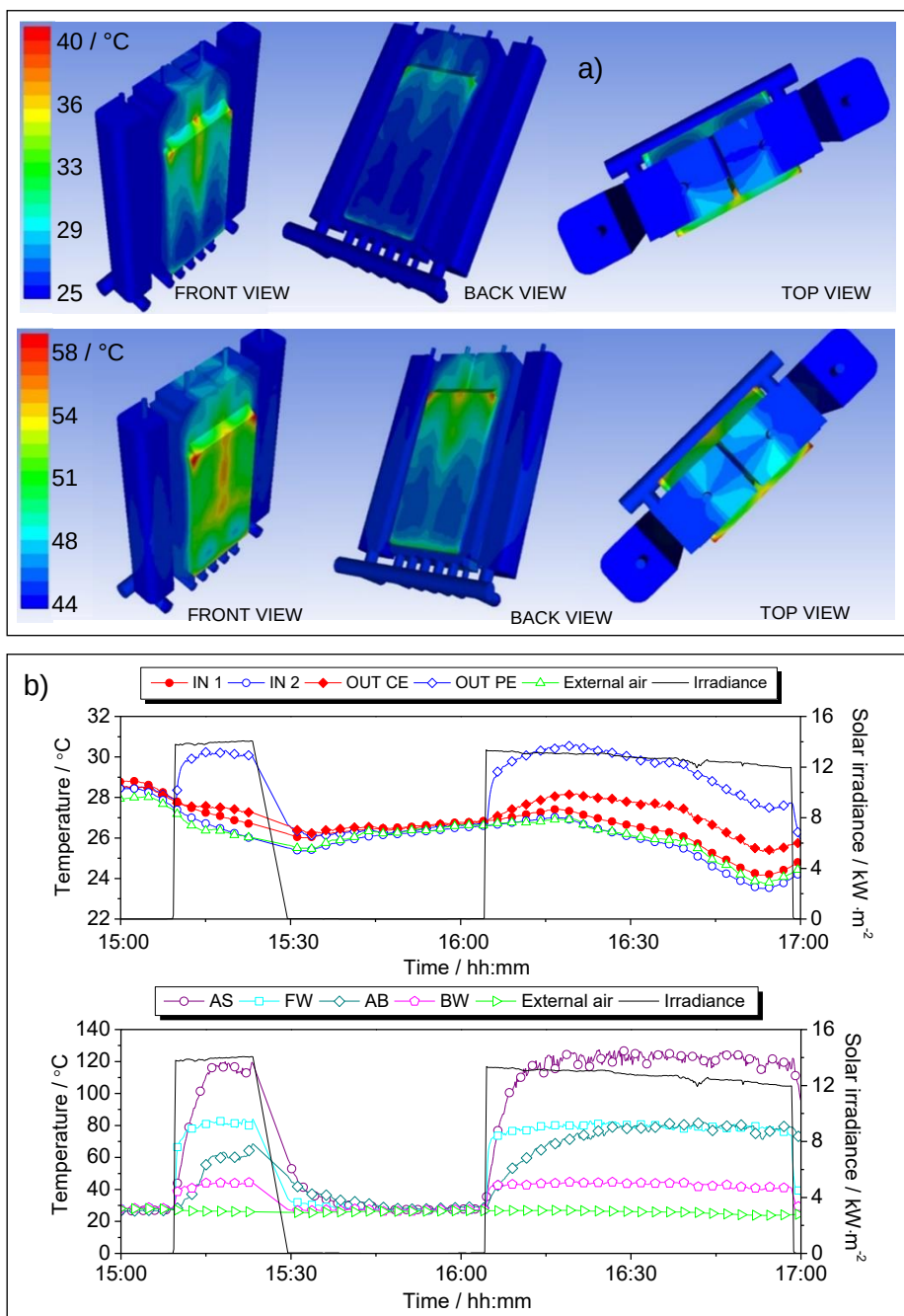


Figure 3.9. Heat dissipation under concentrated sunlight: total temperature contours of the electrolyte inside the CoolPEC cell under 17 kW·m⁻² considering an outside air temperature of 25 °C with electrolyte feeding of 1 L·min⁻¹ at 25 °C (top) and electrolyte feeding of 0.5 L·min⁻¹ at 45 °C (bottom); b) temperature monitoring of the electrolyte

circuit (top) and in the cell embodiment (bottom) under concentrated sunlight with a constant electrolyte temperature of 25 °C and a constant feeding flow rate of 0.5 L·min⁻¹: (●) IN1 – electrolyte inlet 1; (○) IN2 – electrolyte inlet 2; (◆) OUT CE – electrolyte outlets for the CE compartments; (◇) OUT PE – electrolyte outlets for the PE compartments; AS (○) – back side of the aluminium shield; (□) AB– acrylic body; (◇) FW– front window; (◇) BW– back window.

In accordance with CFD simulations, under concentrated sunlight, a slight increase in the electrolyte temperature was experimentally observed in the PE compartment –Figure 3.9-b. A maximum difference of 4 °C was recorded between the inlets and the outlets due to the solar input. The aluminium shield (Appendix 3-i) protected the cell from overheating; a maximum value of ca. 80 °C was recorded on the external side of the front window and ca. 40 °C was recorded on the external side of the back window. These measurements confirm that the CoolPEC cell can safely operate under concentrated sunlight.

Another set of field tests was conducted to assess the effectiveness of CoolPEC cell to maintain a specific electrolyte temperature inside under concentrated sunlight. The feeding flow rate was gradually changed from 0.4 L·min⁻¹ to 0.6 L·min⁻¹. The initial electrolyte feeding temperature was 45 °C and it gradually changed to 25 °C –Figure 3.10. Under concentrated sunlight (ca. 15-sun) the electrolyte temperature slightly increased at the PE compartment. The maximum temperature difference recorded between the inlets and the outlets was ca. 4 °C with electrolyte feeding at 25 °C and ca. 3 °C with electrolyte feeding at 45 °C. These results show that the CoolPEC cell can keep a desired operating temperature for the foreseen feeding flow rate and for the solar irradiance ranges considered.

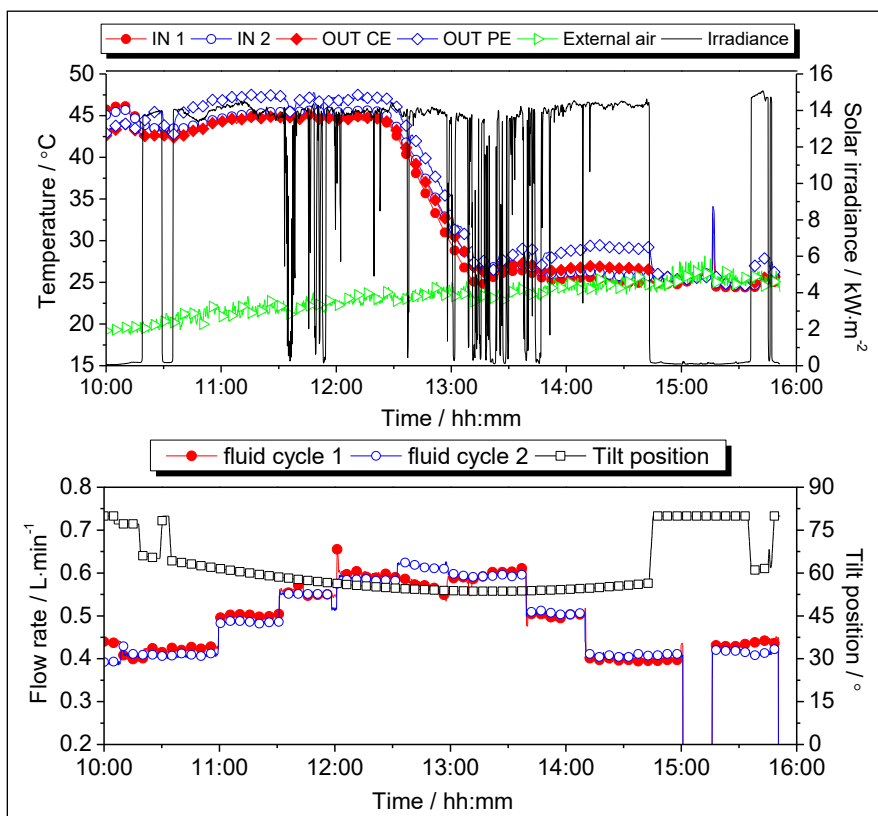


Figure 3.10. Temperature control in the CoolPEC cell operating under concentrated sunlight with variation of the feeding flow rate and tilt position in the SoCRatus: (●) IN 1 – electrolyte inlet 1; (○) IN 2 – electrolyte inlet 2; (◆) OUT CE – electrolyte outlets for the CEe compartments; (◇) OUT PE – electrolyte outlets for the PE compartments. (●) fluid cycle 1 – measured at electrolyte inlet 1; (○) fluid cycle 2 – measured at electrolyte inlet 2.

The innovative features implemented in the CoolPEC cell, first modelled in terms of efficient collection of evolved gases and temperature control using a CFD simulator, were validated experimentally. These features allow enhancing the PEC performance independently from the semiconductor material and from the PE arrangement, including tandem PEs²⁰.

3.3.4 LONG-TERM STABILITY TEST

Long-term stability of semiconductors has been considered a topic of high relevance in recent studies within the solar water splitting field.^{46, 47} Preparing highly stable PEs is a crucial target to achieve commercial viability of PEC devices. Dias *et al.* reported a stable $\alpha\text{-Fe}_2\text{O}_3$ PE operating at ca. $1.05\text{ mA}\cdot\text{cm}^{-2}$ and 1.45 V vs. RHE over 1000 h under $1000\text{ W}\cdot\text{m}^{-2}$ of simulated sunlight⁴⁸. Still, in this study continuous electrolyte feeding was not considered and the surface area under illumination was only ca. 0.5 cm^2 .

In the present study, the CoolPEC cell was continuously operated using a tandem PE-PV over 42 days (1008 h); the photocurrent density history over 1008 h is plotted in Figure 3.11-a. The performance of the $\alpha\text{-Fe}_2\text{O}_3$ PE and PV components was monitored at specified instants, first over periods of 12 h, then 48 h and finally 72 h. After these periods J - V curves were obtained for both components. Figure 3.11-b plots the performance of these two components obtained at the initial instant (0 h) and at the end of the test (42 days = 1008 h).

According to Figure 3.11-a the CoolPEC cell remained stable over 42 days delivering an average photocurrent density of ca. $0.45\text{ mA}\cdot\text{cm}^{-2}$. Although the illuminated area in the PE increased by a factor of ca. 100, the obtained current density was decreased only by half compared with the data by Dias *et al.*⁴⁸ The noise of the recorded photocurrent was assigned to the periodic interruptions of the current reads to obtain the J - V curves. The initial photocurrent decay was assigned to the generation of long-lived holes during the formation of a space charge layer, which can oxidize water on a timescale of around 1 s .³⁷ According to Figure 3.11-b no significant changes were observed neither in the photocurrent measured at 1.6 V nor in the dark current onset potential (ca. 1.8 V).

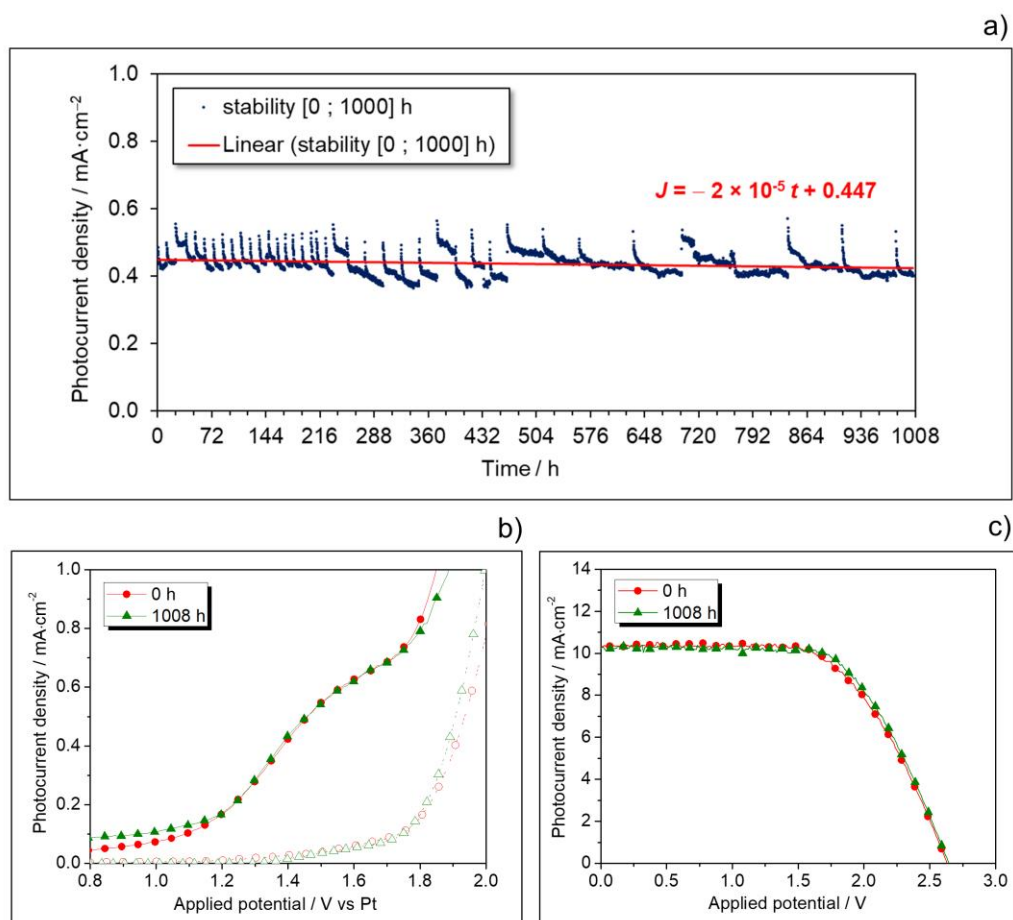


Figure 3.11. Long-term stability measurements: a) photocurrent density history of the α - Fe_2O_3 PE obtained under a constant bias of 1.6 V and simulated solar irradiance ($1000 \text{ W}\cdot\text{m}^{-2}$); b) J-V characteristics of the 50 cm^2 α - Fe_2O_3 photoanode, before starting the stability test, 0 h ($\bullet$), and after operating 1008 h ($\blacktriangle$), obtained in a 2-electrode configuration under dark conditions (dashed lines) and under simulated sunlight ($1000 \text{ W}\cdot\text{m}^{-2}$, solid lines) in 1.0 M KOH; b) J-V characteristics of two 50 cm^2 silicon heterojunction (SHJ) solar cells connected in series before starting the stability test, 0 h ($\bullet$), and after operating 1008 h ($\blacktriangle$) under simulated sunlight, ($1000 \text{ W}\cdot\text{m}^{-2}$).

Corrosion in the α - Fe_2O_3 film was investigated by SEM (scanning electron microscopy) and EDS (energy-dispersive X-ray spectroscopy) analyses (FEI Quanta 400FEG) – Figure 3.12.

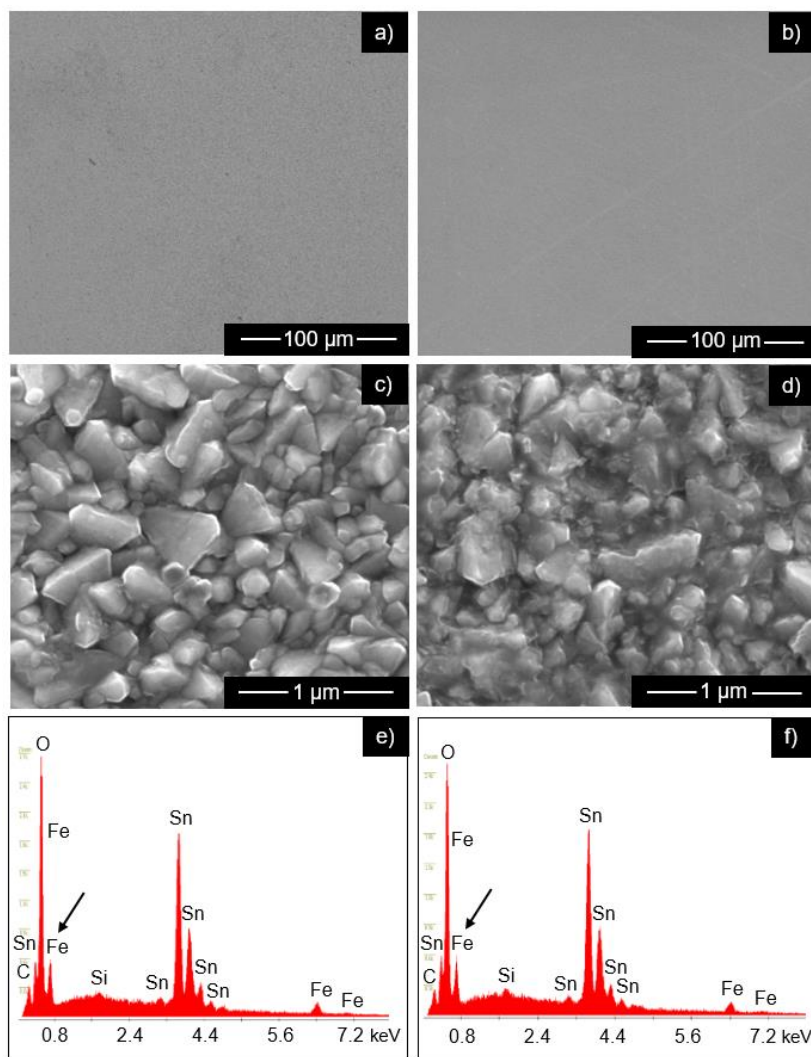


Figure 3.12. Top-view SEM images and EDS analyses of the α -Fe₂O₃ film prepared by spray pyrolysis before [left-side] and after [right-side] the stability test (1008 h); a) and b) mag. 1000 x; c) and d) mag. 100000 x; e) and f) EDS analyses.

According to Figure 3.12-a) and b), both fresh and aged samples of the 50 cm² α -Fe₂O₃ photoanode presented crystals with an organized surface that fully covered the underneath FTO structure. Absence of corrosion in the aged sample is confirmed based in Figure 3.12-c and -d since no significant differences

between the fresh and aged PE are observed, apart from accumulation of some electrolyte residues in the aged sample. Also, the EDS analyses show no differences between fresh and aged samples –Figure 3.12-e) and f). SEM and EDS analyses were made on distinct areas of the 50 cm² PE and very similar results were obtained; moreover, no α -Fe₂O₃ free areas were found in the aged PE – Appendix 3-m.

X-ray diffraction (XRD) analyses (Figure 3.13) were made to a fresh α -Fe₂O₃ sample and to a sample collected from the PE tested over 1008 h.

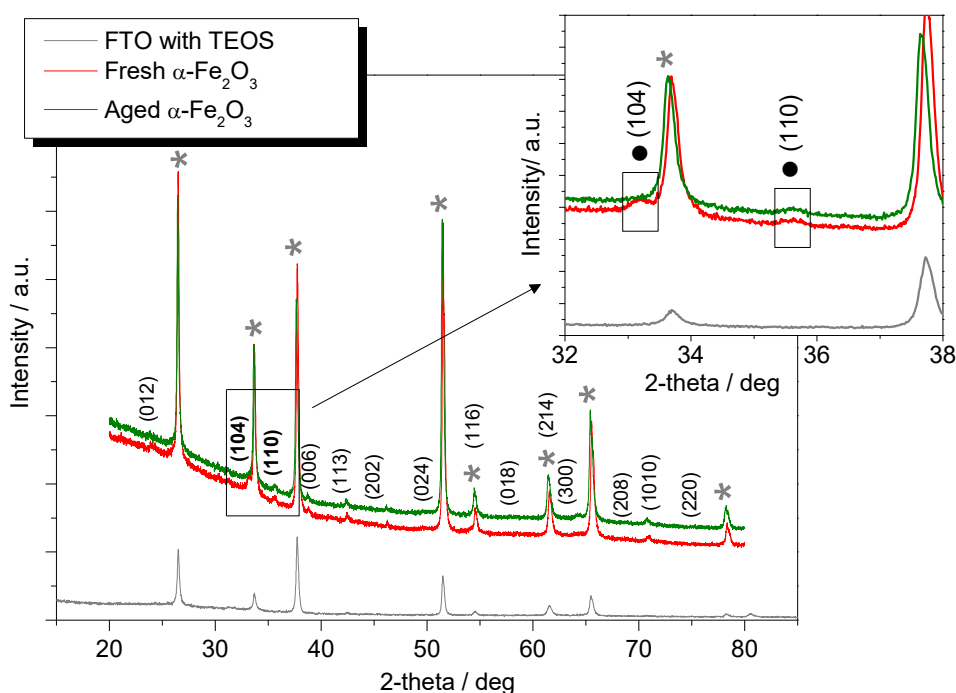


Figure 3.13. XRD spectra of the iron oxide thin film on F:SnO₂ conducting glass prepared by spray pyrolysis before (fresh sample – red spectra) and after (aged sample – green spectra) performing the stability test over 1000 h. The FTO glass substrate (FTO + TEOS Substrate – grey spectra) corresponds to the SnO₂ signals. Main peaks from the substrate are labeled with “**” and from the α -Fe₂O₃ phase with “*”. On the right side is a zoom-out of the left side from 32° to 38°.

Before testing (red line), the α -Fe₂O₃ film presented a preferential crystallographic orientation along the (104) and (110) planes. After the stability tests there was a significant decrease in the intensity of the peak along the (104) plane; no significant changes were observed in the peak along (110) plane. Therefore, the preferential orientation along the (110) plane should be responsible for the PEC performance of the α -Fe₂O₃ film since the decrease in the intensity of the peak along (104) plane did not have any noticeable influence in the photocurrent density nor in the photopotential of the PE. The (110) diffraction peak indicates the strong preferential crystal growth along the C-axis perpendicularly to the FTO glass substrate.^{49, 50}

XPS analyses were also made to a fresh α -Fe₂O₃ sample and to a sample collected from the PE tested for 1008 h. XPS spectra are available in Appendix 3-m. According to the obtained spectra, no significant changes are observed. Appendix 3-n shows the presence of α -Fe₂O₃ at the surface and down up to 5-10 nm in both samples. The obtained peaks agree with what is reported in literature.⁵¹ The underneath area of Fe 2p peaks are also similar for the two samples.

The electrolyte used in the stability test was analysed by inductively coupled plasma (ICP) spectroscopy to confirm no material detachment occurred from the α -Fe₂O₃ film. Iron concentrations lower than 50 μ g/L were detected in the control sample (fresh electrolyte) and in the electrolyte used over 42 days, indicating no corrosion of α -Fe₂O₃.

After completing the stability test, the PEC-PV cell was disassembled, and it was confirmed that none of the constructive elements undergone degradation.

3.4 CONCLUSIONS

The main objective of this chapter was to design, build and assess a new PEC-PV cell with a photoactive area of 50 cm². The developed device, named CoolPEC cell, comprises three improved features: i) an open path for the sunlight to reach the PV cell placed at the back of the PEC cell; ii) a PE that is simultaneously one window of the cell and iii) an optimized electrolyte feeding system arranged in a manifold configuration. CFD simulations were performed to optimize the fluid flow path inside the cell, assuring good heat dissipation and efficient collection of evolved gas bubbles. The cell was built and submitted to several tests using a α -Fe₂O₃ PE. The flow path generated by the simulator was validated using a tracer experiment.

Field tests performed in a continuous operation mode allowed concluding: i) evolved H₂ can be collected separately from O₂; ii) the developed device can be safely operated under concentrated sunlight in a continuous mode assuring efficient heat dissipation; iii) the electrolyte temperature inside the cell can be kept at a desired value independently from the tilt position and the feeding flow rate. These features stand for any PE.

The performance of the CoolPEC cell was assessed under non-concentrated sunlight (1000 W·m⁻²) in a long-term stability test using an in-house prepared α -Fe₂O₃ PE. The 50 cm² PE remained stable over 42 days (1008 hours) delivering a photocurrent density of ca. 0.45 mA·cm⁻² at 1.6 V provided by two SHJ solar cells. SEM, EDS and ICP analyses confirmed the stability of the α -Fe₂O₃ film. XRD analyses allowed to conclude that α -Fe₂O₃ plane (110) is the main responsible for the water splitting.

The obtained results in this initial phase of the work plan proved to be extremely encouraging and promising for the tasks that lie ahead, allowing to answer to two of the most challenging aspects in the field of PEC-H₂ production: stability and scalability. Moreover, these results show that the route for turning this

technology commercially appealing is neither not as long nor as difficult as many studies have considered it to be.

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CHAPTER 4

LARGE-AREA PHOTOELECTROCHEMICAL WATER SPLITTING USING A MULTI- PHOTOELECTRODE APPROACH

“Man turns to geometry as plants turn to the sun: it is the same need for clarity; all cultures have been illuminated by geometry, whose shapes awaken in the spirit a sense of accuracy and absolute evidence.”

Nadir Afonso



Reprinted from peer-reviewed article:

A. Vilanova, T. Lopes and A. Mendes, *Journal of Power Sources*, 2018, **398**, 224-232.

4 LARGE-AREA PHOTOELECTROCHEMICAL WATER SPLITTING USING A MULTI- PHOTOELECTRODE APPROACH

In the field of PEC-H₂ generation, constructing an efficient and stable upscaled device remains a major challenge. One of the main limitations to achieve this goal is the difficulty in preparing efficient large-area nanostructured photoelectrodes. This work reports a segmented support for holding up to eight photoelectrodes connected in parallel, with an active area of 3.2 cm² each, and tested in the CoolPEC cell. CFD results show that the use of internal separators between electrodes is needed to avoid parasitic ionic paths and additional overpotential losses. Inside the cell, an optimized electrolyte flow path is guaranteed through the internal separators; each internal plate is strategically perforated to assure flow circulation, preventing the accumulation of evolved gases. *J-V* measurements performed in 2- and 3-electrode configurations show that when eight α -Fe₂O₃ PEs are operated in parallel neither the photocurrent density nor the photovoltage are affected; without the internal separators a current loss of ca. 15 % is observed. This work also demonstrates that the negative effect of an underperforming PE in the overall performance of the cell decreases exponentially with the number of PEs connected in parallel.

4.1 INTRODUCTION

TCO-coated glass, such as FTO-coated glass, is commonly used as substrates for making PEs for PEC water splitting^{1, 2}. These substrates allow using tandem PEs/PV cells, which is considered the most feasible arrangement for reaching the required STH efficiency targets^{3, 4}. Overcoming the high ohmic losses in large-area PEs due to the electronic resistance imposed by this type of substrates is a key requirement to bring upscaled PEC cells to the commercial market⁵. Hankin *et al.*⁶ demonstrated that the performance of PEC reactors that use large PEs is significantly affected by the geometry of the electrode, especially for lengths >0.1 m. Some promising approaches have been proposed to overcome this challenge, namely the use of conductive lines across the substrate to reduce the electronic path until the current collection point⁷. Although this approach can be easily implemented in solar cells, its implementation in PEs for PEC cells is more complex. Since the PE is immersed in an electrolyte, metal lines need to be protected against corrosion^{8, 9}. However, it is difficult to guarantee the full coating protection of the lines, which may lead to corrosion problems and to the waste of more active area for an effective protection⁵.

Although PEC-H₂ produced from solar water splitting has been pointed as a quite competitive and promising option for the energy sector^{10, 11}, the lack of a commercial PEC prototype is often considered the main obstacle to accurately demonstrate the advantages of this technology^{12, 13}, despite the large number of reported PEC lab cells^{14, 15}. Although great advancements have been achieved in the field of nanostructured materials, upscaling highly efficient PEs towards the expected dimensions of commercial PEC panels is still a massive challenge^{16, 17}. Most lab equipment used to prepare highly efficient semiconductors is not suitable for large area substrates ($\geq 50 \text{ cm}^2$), which compromises the upscaling process^{18, 19}. Record-performing PEs usually have few square centimetres^{20, 21} and the demonstration of their applicability in large-area devices is still missing^{15, 22}. This chapter addresses an innovative

approach to overcome the main constraints of upscaling PEs for PEC-H₂ production (Appendix 4-a). A segmented support was developed for holding multiple PEs connected in parallel, used as PEC cell window. Therefore, highly efficient nanostructured PEs with small dimensions can be prepared using the state-of-the-art equipment and then connected in parallel to fulfil large-area requirements. As previously explained, the optimization of nanostructured α -Fe₂O₃ PEs was carried out throughout the work plan of this PhD. By the time the work comprised in this chapter was performed, the procedure for preparing highly efficient nanostructured α -Fe₂O₃ PEs was not sufficiently optimized for enabling the preparation of, at least, eight stable and reproducible PEs; also, there was still no available autoclave in the hosting lab for preparing multiple nanostructured α -Fe₂O₃ PEs in a single batch, with the required dimensions for the experiments performed in this chapter. Therefore, α -Fe₂O₃ prepared by spray pyrolysis was the selected material for preparing eight stable and reproducible PEs, taking advantage of the acquired knowledge and background of the hosting lab on this preparation technique.

4.2 EXPERIMENTAL

4.2.1 PREPARATION OF α -Fe₂O₃ PHOTOELECTRODES

Hematite (α -Fe₂O₃) PEs were prepared by spray pyrolysis technique, following the procedure developed by the hosting lab and reported elsewhere ²³. First, a TEOS (tetraethyl orthosilicate) pre-treatment was applied to the FTO glass substrates (120 mm x 70 mm; Solaronix TCO 22-7) ²⁴. Briefly, 20 mL of a diluted TEOS solution (99.9 %, Aldrich; 10 % volume in ethanol) were hand-sprayed to the substrates heated at 450 °C using a glass atomizer. Then, the pre-treated substrates were placed on a heating plate, 30 cm below the spray nozzle, and heated at 475 °C (corresponding to a measured surface temperature in the substrate of 425 °C). An automatic syringe pump (Cronus Sigma 2000 Dual Syringe Pump) was used to feed the spray nozzle with the precursor solution containing 10 mM of Fe(acac)₃ (99.9+ %, Aldrich) in EtOH (99 %, Aga). During

the spray pyrolysis deposition, a constant air flow directed to the substrates was assured. Discrete volumes of 1 mL were sprayed onto the substrates at $12 \text{ mL} \cdot \text{min}^{-1}$ considering a time gap of 45 s between sprays and a total volume of 70 mL. Finally, the $\alpha\text{-Fe}_2\text{O}_3$ thin films were annealed for 30 min at 550°C and cooled down to the room temperature.

4.2.2 J-V MEASUREMENTS

J-V measurements were performed in an Autolab/PGSTAT302N workstation controlled by Nova software package (Nova version 1.11). Briefly, an external bias potential was applied to the cell and the generated photocurrent was recorded. *J-V* characteristic curves were obtained in the dark and under simulated sunlight conditions, (Sulphur plasma lamp system AS 1300 V 2.0, Plasma International GmbH, $500\text{-}2500 \text{ W} \cdot \text{m}^{-2}$, 25°C) calibrated with a c-Si photodiode. When the cell was assembled as a 3-electrode setup, an Ag/AgCl sat. KCl reference electrode (Metrohm) was used. Scan rates of $30 \text{ mV} \cdot \text{s}^{-1}$ and $10 \text{ mV} \cdot \text{s}^{-1}$ were selected for measurements in two- and three-electrode configurations, respectively. A schematic representation of the test bench used to perform *J-V* measurements is available in Appendix 4-b.

4.3 THEORY/CALCULATION

4.3.1 MODEL AND SIMULATION

Ansys® Workbench Academic 18.2 was used for assisting the design of the segmented support that holds the PEs and for modelling electrochemical reactions, fluid flow and tracer diffusion inside the PEC cell. The stepwise optimization of the electrolyte flow path inside the cell aimed at promoting the efficient collection of evolved gases at the top, thus avoiding the accumulation of bubbles across the light path. CFD (computational fluid dynamics) simulations were performed considering a three-dimensional unstructured finite-volume method and incompressible flow. The calculation mesh was generated for the

inner volume of the acrylic embodiment, which corresponds to the electrolyte volume. To simulate electrochemical reactions inside the CoolPEC cell ²⁵, the electrochemical option in Fluent was enabled. The reaction rate was determined using the Butler-Volmer equation ^{26, 27}:

$$i_{F,r} = i_{0,r} \prod_{k=1}^N \left(\frac{Y_{k,r}}{Y_{k,r}^{ref}} \right)^{\gamma_{k,r}} \left[\exp\left(\frac{\alpha_{a,r} F \eta_r}{RT}\right) - \exp\left(\frac{-\alpha_{c,r} F \eta_r}{RT}\right) \right] \quad (1)$$

where $i_{F,r}$ is the current density, $i_{0,r}$ is the exchange current density, N is the total number of chemical species, $Y_{k,r}$ is the mass fraction of species k , $Y_{ref}^{k,r}$ is the reference mass fraction of species k , $\gamma_{k,r}$ is the dimensionless power of species k , $\alpha_{a,r}$ and $\alpha_{c,r}$ are the anodic and cathodic transfer coefficients, respectively, F is the Faraday constant ($96487 \text{ C}\cdot\text{mol}^{-1}$), R is the universal gas constant ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$), T is the absolute temperature and η_r is the overpotential. The anodic reaction occurs in the direction where electrons are produced, while the cathodic reaction occurs in the direction where electrons are consumed. The electric current is proportional to the species production/consumption rate in an electrochemical reaction, according to the Faraday's law:

$$S_{Faradaic,i}^r = \frac{(v_{i,r}'' - v_{i,r}') M_{W,i}}{n_r F} i_{F,r} \quad (2)$$

where $S_{Faradaic,i}^r$ is the species production/consumption rate, $v_{i,r}'$ and $v_{i,r}''$ are the stoichiometric coefficients of the k^{th} species as reactant and product in the reaction r , respectively, $M_{W,i}$ is the species molecular weight and n_r is the total number of electrons produced by the electrochemical reaction r .

Finally, in a liquid electrolyte, the electric current as a net flux of charged species is computed as:

$$i = F \sum_k z_k N_k = F \left(- \sum_k z_k D_k \nabla c_k + u \sum_k z_k c_k - \nabla \varphi \sum_k z_k^2 m_k F c_k \right) \quad (3)$$

where N_k is the flux density of species k generated by species diffusion, species convection and migration in the electric field, u is the velocity of the flow field, c_k is the concentration of species k , D_k is the diffusion coefficient of species k and m_k is the mobility of species k ²⁷. For these simulations the stoichiometric coefficients were inserted in accordance with the O₂ evolution reaction (OER, anode) and the H₂ evolution reaction (HER, cathode), as follows:



The governing equations of the simulation model for the fluid flow are described elsewhere ^{25, 27}. The main input data used in CFD simulations are presented in Table 4.1.

Table 4.1. Values selected for the main input parameters used in CFD simulations.

Velocity-inlet	
x-velocity	0 m·s ⁻¹
y-velocity	0 m·s ⁻¹
z-velocity	0.106 m·s ⁻¹
specification method	intensity and hydraulic diameter
turbulent intensity	5 %
hydraulic diameter	1 x 10 ⁻² m
temperature	298 K
mass fraction of OH ⁻	0.017 (*)
mass fraction of H ₂ O	0.983 (*)
Tracer specifications	
density	998.2 kg· m ⁻³
viscosity	0.001 kg· m ⁻¹ s ⁻¹
mass diffusivity	5 x 10 ⁻¹⁰ m ² · s ⁻¹
Convergence criteria	
continuity	1 x 10 ⁻⁴
x-velocity	1 x 10 ⁻⁴

y-velocity	1×10^{-4}
z-velocity	1×10^{-4}
Radiation model	
Model	Solar ray tracing
Direction vector for sunlight	x
Direct solar irradiation	$17\,000 \text{ W}\cdot\text{m}^{-2}$
Diffuse solar irradiation	$200 \text{ W}\cdot\text{m}^{-2}$
Spectral fraction	0.5
Electrochemical reactions	
anodic transfer coefficient	0.288
cathodic transfer coefficient	0.422
exchange current density	$0.0001 \text{ A}\cdot\text{m}^{-2}$
equilibrium potential (anode)	0.401 V (**)
equilibrium potential (cathode)	-0.829 V (**)
electrolyte conductivity	$12.7 \text{ S}\cdot\text{m}^{-1}$
diffusivity of OH^-	$5.26 \times 10^{-5} \text{ cm}^2\cdot\text{s}^{-1}$

(*) For an electrolyte solution of KOH 1.0 M

(**) Considering $\text{pH} = 13.6$

4.3.2 CALCULATION OF THE HYDROGEN PRODUCTION RATE

In the work developed within this chapter, the amounts of evolved gases were not experimentally quantified. Even so, since bare $\alpha\text{-Fe}_2\text{O}_3$ PEs were used in the cell, considerably high faradaic efficiencies (> 0.99) would be expected²⁸. According to previous works, under similar experimental conditions negligible losses are related to parallel or parasitic reactions^{29, 30}. Therefore, the H_2 flowrate can be estimated from the current assuming a faradaic efficiency of 100 %:

$$I = nFAQ_{\text{H}_2} \quad (6)$$

where I is the photocurrent density ($\text{A}\cdot\text{m}^{-2}$), n is the stoichiometric coefficient of the H_2 generation reaction, F is the Faraday constant ($96\,485\text{ C}\cdot\text{mol}^{-1}$), A is the active area (m^2) and Q is the H_2 flowrate ($\text{mol H}_2\cdot\text{s}^{-1}$).

4.4 RESULTS AND DISCUSSION

4.4.1 CFD-DRIVEN OPTIMIZATION

The CoolPEC cell, a home-designed PEC cell, was chosen for testing the new segmented support ²⁵. The later was designed for holding up to eight PEs with a maximum active area of $1.6 \times 2.2\text{ cm}^2$, corresponding to a total photoactive area of ca. 28 cm^2 . As reported in chapter 3, the CoolPEC cell was developed and optimized for generating a uniform upward electrolyte flow, assuring proper heat dissipation and effective collection of evolved gas bubbles in a continuous operation mode. When multiple PEs are operated in parallel, immersed in the same electrolyte volume, internal separators are needed between PEs to minimize parasitic ionic paths and additional overpotential losses ³¹. This was assessed by simulating the electric potential and current vectors inside the electrolyte reservoir when the cell works at a constant potential of 1.45 V – Figure 4.1. CFD results of the mass fraction contours of OH^- are available in Appendix 4-c.

As depicted in Figure 4.1, internal separators are essential to prevent undesired electric paths, generated when PEs with different performances are connected in parallel. In fact, the asymmetric electric field of these PEs, placed nearby in the multi-electrode window, creates a non-uniform flow of reactant species (OH^-) which hinders the performance of the cell ³². However, these internal separators disturb the optimized flow path, generating fluid turbulence and creating undesired stagnant areas. To address this challenge, a stepwise simulation approach was followed, using Ansys® Workbench Academic 18.2, where holes made in each separator were optimized – see Appendix 4-e– until reaching the desired flow pattern, as illustrated in Figure 4.2.

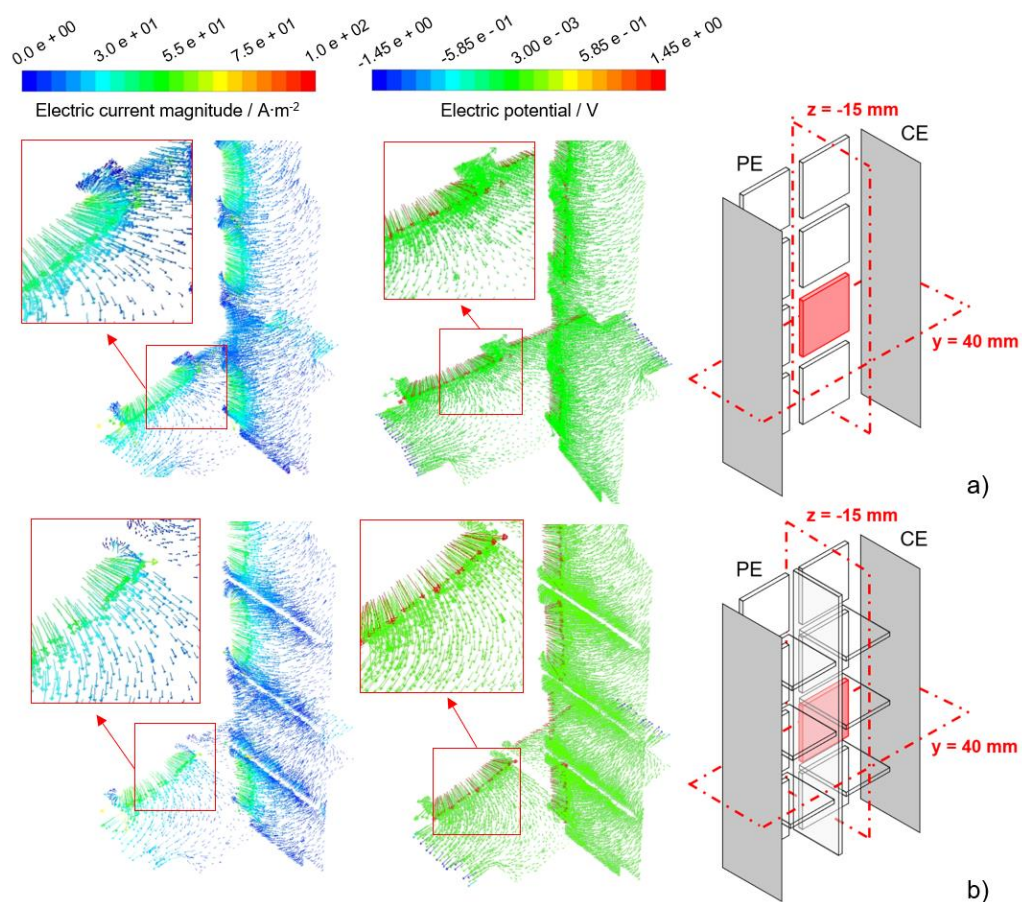


Figure 4.1. Vectors of electric current and electric potential inside the CoolPEC cell considering a feeding flow rate of $500 \text{ mL} \cdot \text{min}^{-1}$ and an underperforming PE – highlighted in red; a) CoolPEC cell without internal separators; b) CoolPEC cell with internal separators. Current densities of $5 \text{ mA} \cdot \text{cm}^{-2}$ and $1 \text{ mA} \cdot \text{cm}^{-2}$ @ 1.45 V were assumed for the healthy and for the underperforming PEs, respectively. Sectional planes $z = -15 \text{ mm}$ and $y = 40 \text{ mm}$ were used to visualize these results (see Appendix 4-d).

The new design including perforated acrylic plates between the PEs allows having a continuous upward flow, preserving the main flow path lines inside the CoolPEC cell. Also, near the surface of the PEs the fluid velocity is considerably lower, as shown in the zoomed areas of Figure 4.2. This guarantees the desired separation between electrodes, minimizing polarization losses.

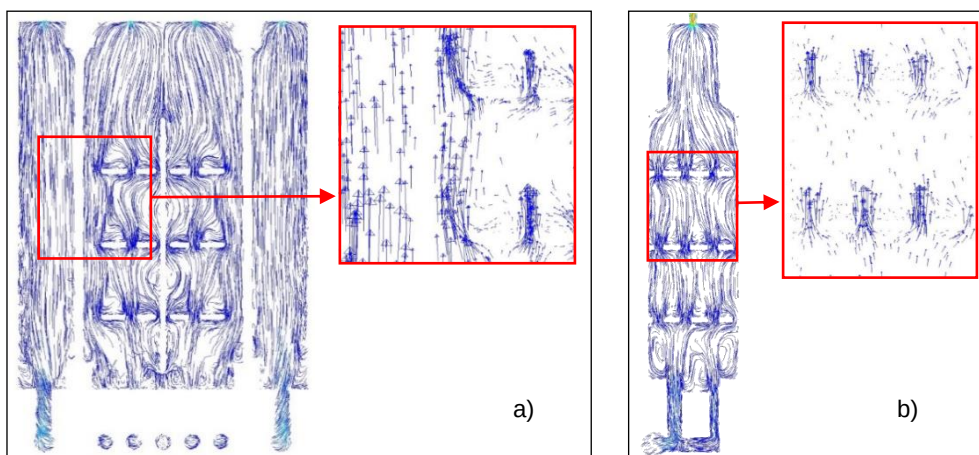


Figure 4.2. Fluid flow path lines and velocity vectors inside the CoolPEC cell with the segmented support considering a feeding flow rate of $500 \text{ mL} \cdot \text{min}^{-1}$: a) horizontal sectional plane close to the middle of the working-electrode compartment ($x = -3$ mm); b) vertical sectional plane in the middle of the working-electrode compartment ($z=12$ mm). The location of the sectional planes is presented in Appendix 4-d.

The segmented support was manufactured using acrylic (Perspex[®], from Lucite[®]) –Figure 4.3-3. The electrical path between the conductive side in contact with the electrolyte and the non-conductive side of each PE is made through copper tape (3M conductive copper foil tape) –Figure 4.3-2. External screws allow making the contact between the copper tape (back side of each PE) and the current collector –Figure 4.3-7. A picture of a $\alpha\text{-Fe}_2\text{O}_3$ PE with a scale bar is provided in Appendix 4-f.

PEs are connected in parallel using low resistance cables with alligator clips Figure 4.3-15. The assembly of the PEs is schematically represented in Appendix 4-g. A single cable connects the PEs to the potentiostat. Highly resistant silicone sealing paste (*Sellaceys*, transparent acetic silicone) was used to seal the acrylic support to the housing area of the back window. Additional images of the cell assembled with the segmented support are available in Appendix 4-h.

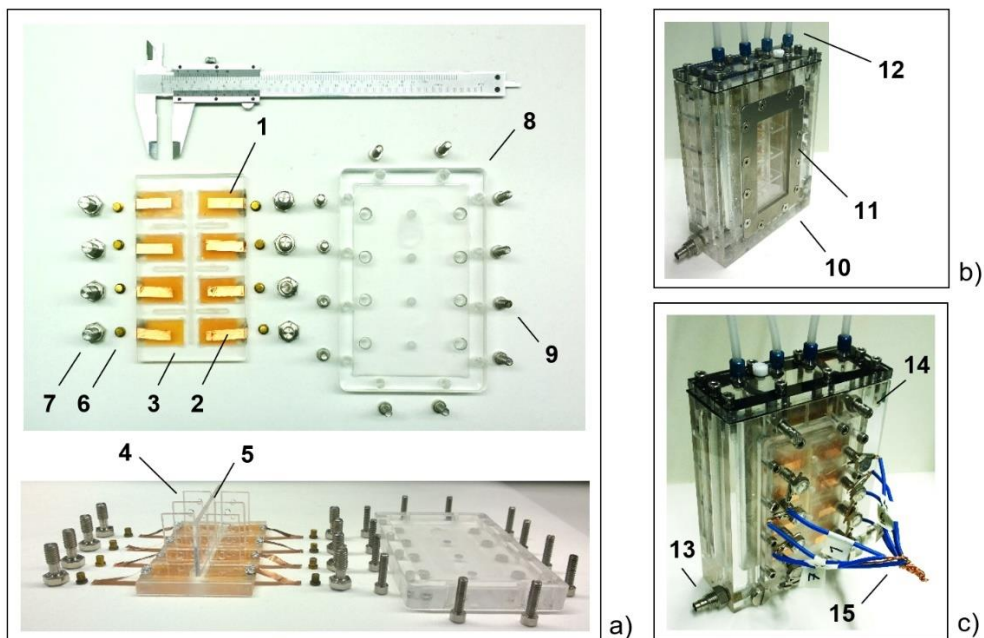


Figure 4.3. Assembly of the segmented support in the back side of the CoolPEC cell: a) main elements of the segmented support (back window); b) front side; c) back side; 1 - α -Fe₂O₃ PE; 2 – copper tape; 3 – acrylic support for the PEs; 4 – drilled internal separators; 5 – middle separator (acrylic); 6 – contact for the back side of the acrylic support; 7 – external screw (current collector of the PEs); 8 – acrylic holder for the back side; 9 – back screws for the acrylic holder; 10 – acrylic embodiment of the CoolPEC cell; 11 – front metal frame (front window); 12 – electrolyte outlet; 13 – electrolyte inlet; 14 – external screw (current collector for the CE); 15 – low resistance cables to connect multiple PEs in parallel.

4.4.2 MODEL VALIDATION

As mentioned, the drilled internal separators were designed to preserve the optimized electrolyte flow path. Two sets of tests were performed to experimentally assess the results obtained with the CFD software. First, a tracer experiment was conducted for a feeding flowrate of $0.5 \text{ L} \cdot \text{min}^{-1}$ – Figure 4.4.

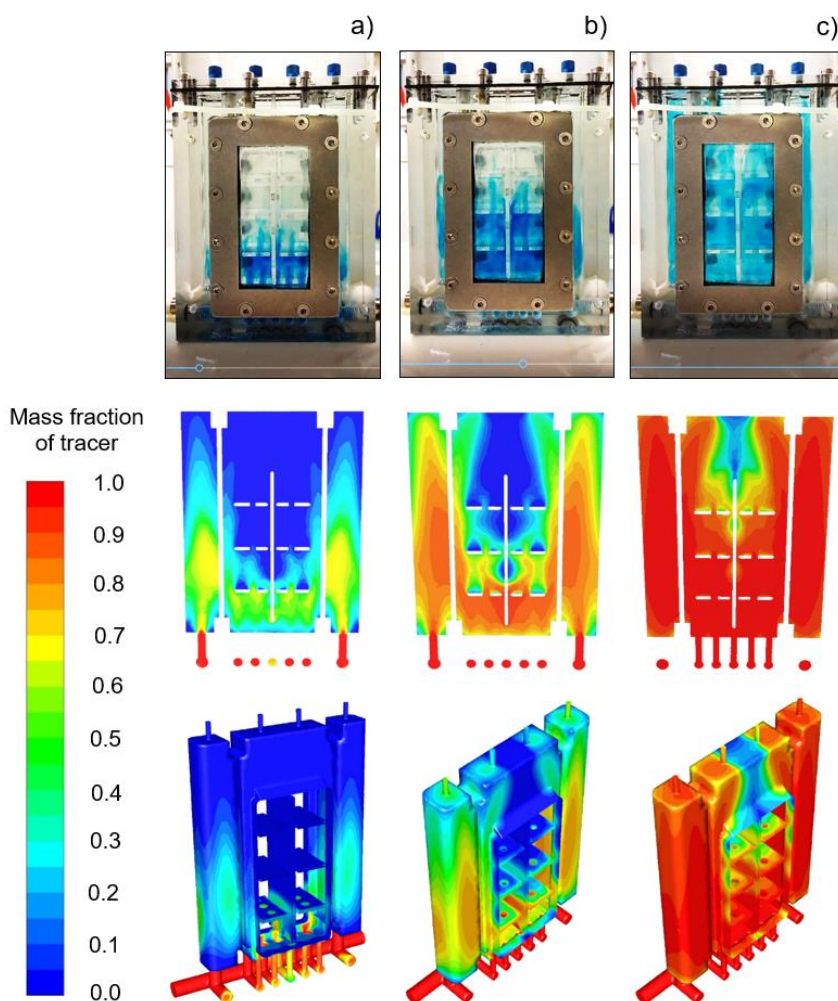


Figure 4.4. Tracer test performed with a blue dye and distilled water with a feeding flow rate of $0.5 \text{ L} \cdot \text{min}^{-1}$ pictured at different instants after the injection of the dye, and CFD results for the contours of mass fraction of tracer for the same instants; a) 4 s; b) 8 s; c) 15 s.

Good agreement between experimental and simulated results was obtained. Moreover, no relevant stagnant areas are observed. This optimized electrolyte flow path is essential for assuring efficient heat dissipation when the CoolPEC cell is operated under concentrated sunlight. CFD simulations were performed to assess heat dissipation inside the electrolyte reservoir when the cell works under concentrated sunlight and assembled with the multi-PE window. The

obtained results are available in Appendix 4-i. Considering an incident solar radiation of 17-sun, a maximum temperature of 62 °C is reached inside the cell, detected only in a small area at the upper part of the multi-PE window; most of the electrolyte in contact with the PEs reached temperatures up to 47 °C. These results show that the strategically drilled acrylic plates do not compromise the self-cooling ability of the CoolPEC cell design.

In a second set of tests, water electrolysis was promoted in 1.0 M aqueous solution of KOH using two Ni foils and a bare FTO glass window (7 Ω square, 2.2 mm thick) as cathode and as anode, respectively. The experimental results are available in Appendix 4-j. The drilled acrylic separators did not cause accumulation of gas bubbles inside the CoolPEC cell and evolved H₂ and O₂ were efficiently collected at the top. This is crucial for avoiding losses in the performance of the PEs due to light trapping ³³. The tracer test and the electrolysis experiments were also performed with separators without holes (Appendix 4-k). Several stagnant flow zones are identified, and significant accumulation of evolved gas bubbles occurs shortly after the onset of the water electrolysis.

4.4.3 J-V MEASUREMENTS OF MULTIPLE PHOTOELECTRODES CONNECTED IN PARALLEL

J-V measurements were performed in the CoolPEC cell with the segmented support assembled at the back, replacing the original 50 cm² PE (back window). Eight α -Fe₂O₃ PEs were assembled in the segmented support; α -Fe₂O₃ prepared by spray pyrolysis was the selected semiconductor material due to its high stability and reproducible performance ^{23, 34}. Two nickel foils were used as counter-electrodes, placed perpendicular, in both sides, to the segmented PE (back window) – Appendix 4-h and Appendix 4-l. Despite the *J-V* measurements were performed with in-house PEs, the developed segmented window can be assembled with any type of PE.

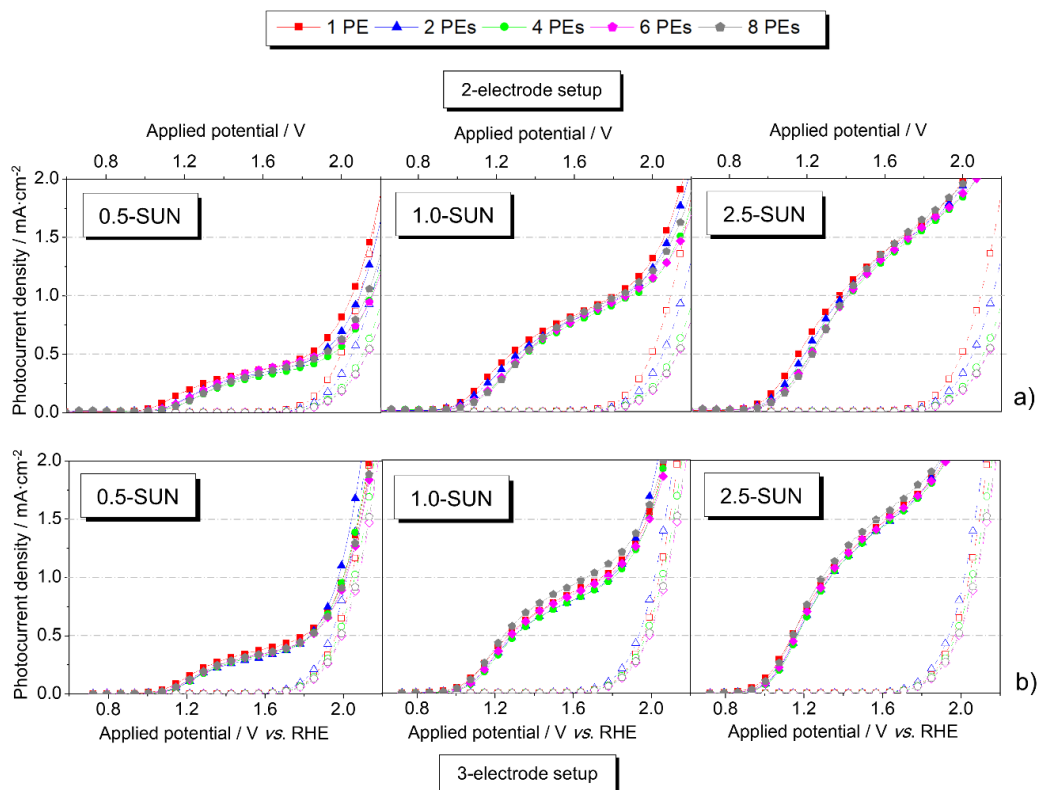


Figure 4.5. *J-V* characteristics of $\alpha\text{-Fe}_2\text{O}_3$ PEs assembled in the segmented support obtained under dark conditions (open symbols, dashed lines) and under simulated sunlight (500, 1000 and 2500 $\text{W}\cdot\text{m}^{-2}$, full symbols, solid lines) in 1.0 M KOH; a) 2-electrode measurements; b) 3-electrode measurements.

First, $\alpha\text{-Fe}_2\text{O}_3$ PEs were connected in parallel and *J-V* curves were obtained under dark conditions and under simulated sunlight (500 – 2500 $\text{W}\cdot\text{m}^{-2}$). A schematic representation of the arrangement of PEs is shown also in Appendix 4-g and Appendix 4-l. The number of PEs connected in parallel was stepwise increased for assessing any detrimental interaction – Appendix 4-m. The obtained results are presented in Figure 4.5. Each PE assembled in the segmented support was characterized individually with *J-V* curves (Appendix 4-n and Appendix 4-o).

As evidenced in Figure 4.5, the developed support allows connecting multiple PEs in parallel without any decrease in the photocurrent density or in the

photovoltage when compared to the performance of a single PE. After connecting the eight PEs in parallel, photocurrent densities of $0.29 \text{ mA}\cdot\text{cm}^{-2}$ and $0.65 \text{ mA}\cdot\text{cm}^{-2}$ were recorded under $1000 \text{ W}\cdot\text{m}^{-2}$ at 1.23 V and 1.45 V, respectively. The performance was significantly enhanced when the cell was operated under higher simulated sunlight ($2500 \text{ W}\cdot\text{m}^{-2}$), with photocurrent densities of $0.52 \text{ mA}\cdot\text{cm}^{-2}$ and $1.11 \text{ mA}\cdot\text{cm}^{-2}$ recorded at 1.23 V and 1.45 V, respectively. These results demonstrate for the first time the applicability of sub-cell modules for constructing large-area PEC panels, a concept that has been successfully applied in PV cell modules for many decades ³⁵. When compared with a single 50 cm^2 $\alpha\text{-Fe}_2\text{O}_3$ PE, having smaller PEs working in parallel is advantageous both in terms of photocurrent density and photovoltage, as depicted in Appendix 4-p. In large-area PEs the resistance imposed by the FTO substrate decreases the performance of the cell. Under concentrated sunlight, the electron flux through the substrate is increased and the limiting effect of the FTO resistance is amplified ³⁶, therefore evidencing the importance of using smaller PEs.

When small PEs are operated in parallel sharing common electrolyte, it is essential to have separators between them to avoid parasitic ionic paths and additional overpotential losses. The electric field generated by PEs with different performances can harmfully influence the overall performance of the cell (Figure 4.1). This was experimentally assessed based on the *I-V* characteristics using the segmented support with and without internal acrylic separators –Figure 4.6.

As depicted in Figure 4.6, without internal separators a noticeable decrease in the generated photocurrent is observed, particularly when more PEs are connected in parallel. Considering the eight PEs operated in parallel at 1.45 V under $2500 \text{ W}\cdot\text{m}^{-2}$, when the internal separators were removed the photocurrent density decreased from $1.11 \text{ mA}\cdot\text{cm}^{-2}$ to $0.967 \text{ mA}\cdot\text{cm}^{-2}$, corresponding to a decrease of 14.8 %.

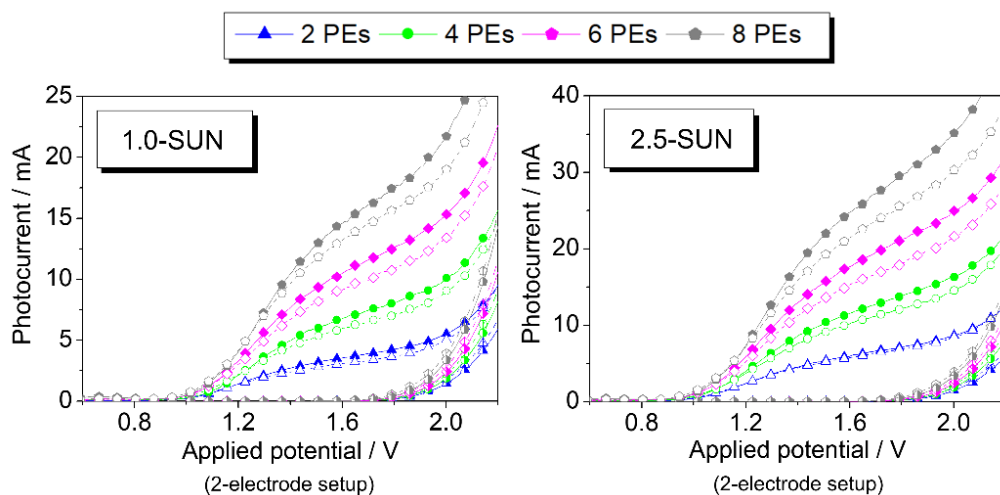


Figure 4.6. Comparison between I - V characteristics of α - Fe_2O_3 PEs assembled in the segmented support without the internal acrylic separators (open symbols, dashed lines) and in the original configuration with acrylic separators (full symbols, solid lines) obtained under dark conditions and under simulated sunlight (1000 and 2500 $\text{W}\cdot\text{m}^{-2}$) in 1.0 M KOH and in a 2-electrode configuration.

A key challenge for large-area PEC water splitting is the reproducibility of nanostructures along large substrates³⁷. Available lab techniques for producing highly efficient nanostructured semiconductor materials are usually optimized for small substrates^{8, 38}. However, assuring similar performances among these small PEs is also a major challenge^{39, 40}. The role of these non-homogeneities was assessed by applying a blocking mask in PE #5, now renamed as PE #5-B, and then increasing stepwise the number of healthy performing PEs connected to this PE. J - V measurements were performed for multiple arrangements of PEs connected in parallel to PE #5-B – Figure 4.7; Appendix 4-q illustrates this experiment. The J - V characteristics of PE #5-B are provided in Appendix 4-r.

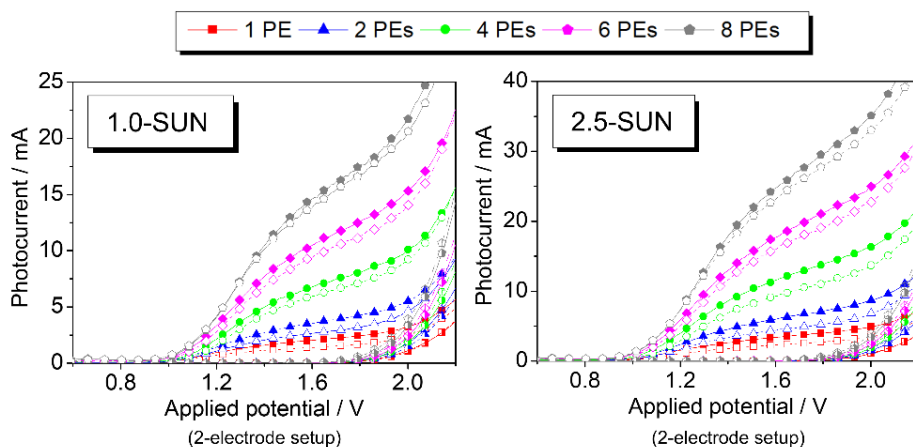


Figure 4.7. *I-V* characteristics of $\alpha\text{-Fe}_2\text{O}_3$ PEs assembled in the segmented support using a semi-transparent mask in front of PE #5 (open symbols, dashed lines) and using the original configuration (full symbols, solid lines) obtained under dark conditions and under simulated sunlight (1000 and $2500 \text{ W}\cdot\text{m}^{-2}$) in 1.0 M KOH and in a 2-electrode configuration.

After placing the blocking mask (a Scotch tape – Appendix 4-q) on PE #5, the photocurrent density at 1.45 V decreased from $0.699 \text{ mA}\cdot\text{cm}^{-2}$ to $0.483 \text{ mA}\cdot\text{cm}^{-2}$ under $1000 \text{ W}\cdot\text{m}^{-2}$ and from $1.14 \text{ mA}\cdot\text{cm}^{-2}$ to $0.777 \text{ mA}\cdot\text{cm}^{-2}$ under $2500 \text{ W}\cdot\text{m}^{-2}$, representing losses of 44.7% and 46.7% respectively. As depicted in Figure 4.7, when this underperforming PE is connected in parallel with healthy performing ones, the overall performance becomes affected. This is a well-known problem in the photovoltaic field, with several studies reporting that the overall current is limited by the sub-cell that delivers the lowest photocurrent⁴¹. When PE #2 was connected to PE #5-B, the photocurrent density at 1.45 V decreased from $0.659 \text{ mA}\cdot\text{cm}^{-2}$ to $0.498 \text{ mA}\cdot\text{cm}^{-2}$ under $1000 \text{ W}\cdot\text{m}^{-2}$ and from $1.12 \text{ mA}\cdot\text{cm}^{-2}$ to $0.807 \text{ mA}\cdot\text{cm}^{-2}$ under $2500 \text{ W}\cdot\text{m}^{-2}$, representing losses of 32.3% and 38.8% respectively. On the other hand, when the remaining seven healthy performing PEs were connected to PE #5-B, the photocurrent density at 1.45 V decreased from $0.648 \text{ mA}\cdot\text{cm}^{-2}$ to $0.626 \text{ mA}\cdot\text{cm}^{-2}$ under $1000 \text{ W}\cdot\text{m}^{-2}$ and from $1.11 \text{ mA}\cdot\text{cm}^{-2}$ to $1.04 \text{ mA}\cdot\text{cm}^{-2}$ under $2500 \text{ W}\cdot\text{m}^{-2}$, representing losses of only 3.5% and 6.7% , respectively. It can be concluded that the influence of the

underperforming PE gets diluted as the number of connected healthy PEs increases – Appendix 4-t. Appendix 4-s summarizes the photocurrent density at 1.45 V for the different sets of PEs connected in parallel with PE #5-B, and the corresponding losses. According to the obtained results, the influence of an underperforming PE decreases exponentially with the number of PEs operated in parallel, as it should be expected. The relation between the photocurrent losses (η) and the number of PEs connected in parallel (N) can be written in the following generic form:

$$\eta = ke^{-\alpha N} \quad (7)$$

where k is related to the solar irradiance and α is related to the underperformance level of the underperforming PE.

Taking advantage of the open path for the sunlight provided by the CoolPEC cell design, a 50 cm² α -Fe₂O₃ PE was assembled at the front, thus replacing the original glass, in a stack arrangement. Pictures of the cell and a schematic representation of this arrangement are available in SM (Appendix 4-u). J - V measurements were performed with the 50 cm² α -Fe₂O₃ PE connected in parallel with the segmented window having the eight smaller α -Fe₂O₃ PEs already connected in parallel. The obtained results are presented in Figure 4.8.

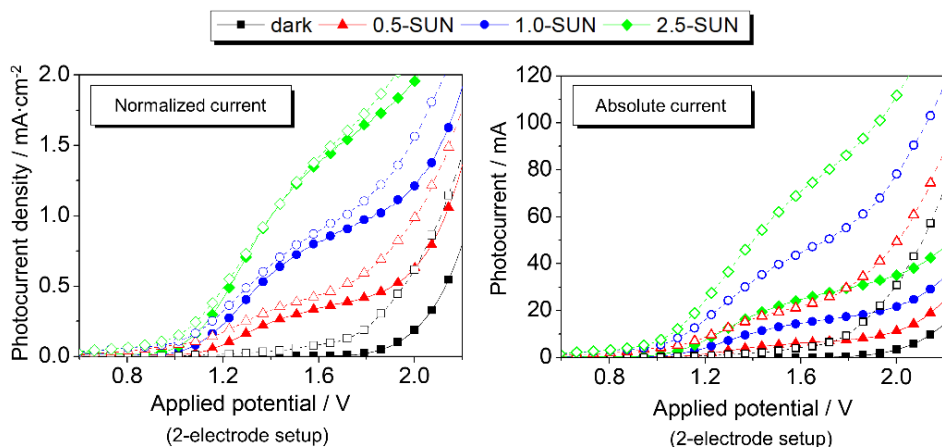


Figure 4.8. Comparison between 8 small $\alpha\text{-Fe}_2\text{O}_3$ PEs operated in parallel (full symbols, solid lines) and this multi-electrode connected in parallel with a 50 cm^2 $\alpha\text{-Fe}_2\text{O}_3$ PE (open symbols, dashed lines). The generated current was normalized by the illuminated area (50 cm^2). J - V and I - V measurements were performed under dark conditions and under simulated sunlight in 1.0 M KOH in a 2-electrode configuration.

In the stack configuration, a decrease in the generated current density is expected due to the radiation that is absorbed at the first PE (single PE of 50 cm^2) and transmitted to the multi-electrode (effective area of 28 cm^2)⁴². In this work, the front PE had a transmittance of 0.30 and an absorbance of 0.31, both measured at 400 nm , which restricted the performance of the multi-electrode assembled on the back. Despite this, the total current produced by the cell was increased from 19.8 mA (multi-PE) to 55.4 mA (stack PE cell). In terms of H_2 production, and assuming operation at 1.45 V under $2500\text{ W}\cdot\text{m}^{-2}$ of concentrated solar power, the stack cell would produce $2.37\text{ g}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$.

4.5 CONCLUSIONS

The main objective of this chapter was to develop and test a segmented window for holding up to eight PEs connected in parallel. The multi-PE was assembled and characterized in the CoolPEC cell. CFD results showed the importance of having internal separators between PEs that are immersed in a common electrolyte to avoid undesired ionic paths and additional overpotential losses. A

CFD-driven optimization of the holder was performed to minimize the retention of evolving gases and electrolyte stagnant volumes. A tracer test and an experiment with forced gas evolution (water electrolysis) allowed validating the results obtained in the simulator. No stagnant flow zones or accumulation of gas bubbles were observed in the optimized design.

When the eight PEs were connected in parallel, photocurrent densities of $0.52 \text{ mA}\cdot\text{cm}^{-2}$ and $1.11 \text{ mA}\cdot\text{cm}^{-2}$ were recorded at 1.23 V and 1.45 V under $2500 \text{ W}\cdot\text{m}^{-2}$, respectively. When compared with a single 50 cm^2 $\alpha\text{-Fe}_2\text{O}_3$ PE, eight PEs working in parallel produced a slightly higher photocurrent density, showing also a higher photovoltage. Without the internal separators, a photocurrent loss of 14.8 % was observed under the same experimental conditions.

The influence of an underperforming PE in the overall performance of the cell was also assessed. The overall performance of the cell decreases when the underperforming PE is connected in parallel, but its influence decreases exponentially with the number of connected PEs.

Finally, when the cell was operated in a stack configuration with a 50 cm^2 $\alpha\text{-Fe}_2\text{O}_3$ PE assembled as front window, the generated current increased from 19.8 mA to 55.4 mA; this current corresponds to an estimated H_2 production of $2.37 \text{ g}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$, assuming operation at 1.45 V under $2500 \text{ W}\cdot\text{m}^{-2}$ of concentrated solar power.

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CHAPTER 5

SOLAR WATER SPLITTING UNDER NATURAL CONCENTRATED SUNLIGHT USING A 200 CM² PHOTOELECTROCHEMICAL-PHOTOVOLTAIC DEVICE

“I couldn't find the sports car of my dreams, so I built it myself”.

Ferdinand Porsche



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5 SOLAR WATER SPLITTING UNDER NATURAL CONCENTRATED SUNLIGHT USING A 200 cm² PHOTOELECTROCHEMICAL-PHOTOVOLTAIC DEVICE

This work reports a 200 cm² PEC-PV device that comprises four 50 cm² PEC cells coupled in a modular array and optimized for continuous operation under concentrated sunlight. The developed module is the second largest PEC-PV device ever reported and the first tested under natural concentrated sunlight (up to 12.8 kW·m⁻²). Demonstration tests were conducted outdoor in a continuous operation mode, over four days and using highly stable α -Fe₂O₃ PEs. When assembled with four multi-PE windows, each comprising eight small nanostructured PEs connected in parallel, the module generated a stable current density of ca. 2.0 mA·cm⁻² at 1.45 V, resulting in an average H₂ production rate of 5.6×10^{-5} g_{H2}·h⁻¹·cm⁻² (based on the net active area). A maximum current density of ca. 4.0 mA·cm⁻² was reached during *J-V* measurements (before the dark current onset potential). It was observed that when α -Fe₂O₃ PEs are subjected to gradually higher solar irradiances the generated photocurrent follows a logarithmic saturation behaviour. This work provides important insights for demonstrating the viability of solar-driven water electrolysis by presenting a PEC-PV device that answers to the main challenges of large-scale PEC-H₂ production.

5.1 INTRODUCTION

Materials and devices have received different attention by the researchers; few studies address the optimization of PEs for large-areas or, at least, scalable PEC device architectures.^{1, 2} However, numerous studies mention that the design of the device is as important as the efficiency of the PEs if low-cost PEC-H₂ production is ambited.^{3, 4} Indeed, over the past few years, nanomaterials for solar water splitting have been notably optimized, mostly thanks to the implementation of pioneering preparation techniques and surface treatments that brought highly efficient, stable, and morphologically controlled PEs to the field.^{5, 6} Up to now, the best performing metal-oxide PE is cuprous oxide (Cu₂O), producing 10.0 mA·cm⁻² at 0 V versus the reversible hydrogen electrode (V_{RHE}), though it is photo-unstable.⁷ On the other hand, hematite (α-Fe₂O₃) is the most stable metal-oxide PE reported to date, with a demonstrated stable photoresponse over 1000 h under PEC operating conditions^{8, 9}. In a work by Jeon *et al.*, α-Fe₂O₃ PEs have reached 6 mA·cm⁻² at 1.23 V_{RHE}, corresponding to 50 % of its theoretical limit.¹⁰

Although remarkable achievements have been accomplished in the field of nanomaterials for solar water splitting, state-of-the-art PEs still require an external bias to carry out the water splitting.¹¹ Montoya *et al.*¹² demonstrated that STH efficiencies of single absorber devices are in the range of 10–15 % for semiconductors with bandgaps of approximately 1.7–2.2 eV, whereas dual absorber PEC devices should be able to achieve STH efficiencies higher than 25 %, assuming semiconductors with bandgaps of approximately 1.6–2.0 eV and 0.8–1.4 eV.^{13, 14} Similar to dual absorber cells, PEC-PV tandem cells are also a reliable approach, combining wider-bandgap PEs (1.8–2.4 eV) with smaller-bandgap PV-cells (1.0–1.4 eV) for producing unbiased hydrogen.¹⁵ Additionally, the use of power management systems in PEC-PV tandem devices allow increasing the STH efficiency up to 21 %.¹⁶ Nevertheless, the efficiency of both dual absorber and tandem cells is highly restricted by the performance of the PEs.

The integration of solar concentrating technologies in PEC devices is a simple and effective approach to overcome this limitation and further increase the photoresponse of semiconductor materials.¹⁷ This technological synergy is deeply studied and optimized for CPV (concentrator photovoltaic) devices, which are a mature technology. In these systems, several studies show that the PCE (power conversion efficiency) increases linearly with the solar flux, if the generated heat and related performance losses are concurrently reduced.^{18, 19} Increasing the photon flux in PEC devices allows increasing the generated photocurrent and reducing the onset potential.^{20, 21} However, CIPEC (concentrator integrated PEC) systems have been poorly explored.^{22, 23} In the pioneer work by Segev *et al.*²⁴ the photocurrent generated by a 0.28 cm² PEC cell increased linearly with the solar input, while the photovoltage scaled logarithmically with the light intensity. Haussener *et al.*²⁵ showed that optical concentrations of 10 times can be used in PEC devices without any decrease in the performance; however, since the operating temperature is expected to increase, cooling solutions may be required for keeping the stability of the PE. Nevertheless, CIPEC systems should reach higher energy yield ratios – the ratio between the energy produced during the lifetime of the equipment and the energy that this equipment incorporates – compared to devices that do not use concentrated sunlight.²⁶ Additionally, LCA (life cycle assessment) demonstrated that these systems allow decreasing the atmospheric impact, given by the GYR (greenhouse gas yield ratio, kg_{CO2-eq}·kg_{H2}⁻¹), by more than half, compared to PEC systems operated without concentrated sunlight.²⁷

To become a commercial alternative, lab-scale PEC devices need to be engineered into a competitive large-scale technology. Device architectures with an illuminated area of at least 50 cm² are considered a viable first approach for large-scale applications; higher scalability can be achieved by coupling module units. An ongoing change in paradigm is perceptible in the literature, with increasing relevance being given to the design and construction of large-area, or at least scalable, devices. As already mentioned in the introduction, over the last 5 years the number of publications demonstrating large-area PEC devices

almost doubled the total of the previous five years (2010 - 2015). For better contextualizing the results presented in this chapter, Table 5.1 comprises a brief overview of relevant works that demonstrated upscaled PEs for PEC water splitting.

Table 5.1. Overview of demonstrated photoelectrodes for PEC water splitting with an active area $\geq 25 \text{ cm}^2$.

Top absorber [bottom or side absorber]	Electrolyte / pH	Area / cm^2	Current density / $\text{mA}\cdot\text{cm}^{-2}$	Stability / h	Year	Reference
FTO / WO_3 / Mo- BiVO_4 / Co-Pi	0.5 M Na_2SO_4 0.1 M KH_2PO_4 / pH 7	25	2.2 @ 1.23 V	1	2018	Yao <i>et al.</i> ²⁸
FTO / Fe_2O_3	1.0 M KOH / pH 13.6	26	1.11 @ 1.45 V	-	2018	Vilanova <i>et al.</i> ²⁹
W / WO_3	3 M MSA acid / pH 0.14	49	0.9 @ 1.45 V	-	2014	Lopes <i>et al.</i> ³⁰
FTO / Fe_2O_3 [2 x SHJ Si]	1.0 M KOH / pH 13.6	50	0.25 @ 1.45 V	1008	2017	Vilanova <i>et al.</i> ⁹
FTO / Ag-Pt / W: BiVO_4 / CoPi [2 x SHJ Si]	0.1 M KPi buffer / pH 7	50	1.5 @ 1.23 V	-	2019	Ahmet <i>et al.</i> ³¹
FTO / Fe_2O_3	1.0 M KOH / pH 13.6	51	0.47 @ 1.45 V	-	2014	Lopes <i>et al.</i> ³⁰
2 series-connected a-Si:H / $\mu\text{c-Si:H}$ tandem PV cells	1.0 M KOH / pH 13.6	64	-	40	2016	Turan <i>et al.</i> ³²
FTO / WO_3 [2 x SHJ Si]	0.5 M H_2SO_4 / pH 0.3	131	1.18 @ 1.23 V	-	2011	Lee <i>et al.</i> ³³
FTO / Ti-Fe_2O_3	1.0 M KOH / pH 13.6	200	2.0 @ 1.45 V	48	2019	This work
Mo- BiVO_4 / CoPi [Si PV]	0.1 M KPi buffer / pH 7	16 000	-	-	2017	Tolod <i>et al.</i> ³⁴

The first large-scale demonstration of PEC water splitting was made by Lee *et al.* ³³ This work reports a 130 cm^2 WO_3 PE with an embedded Ag grid; however, the current density measured at 1.23 V decreased 75 % when compared with a similar PE with 4.8 cm^2 (from $2.63 \text{ mA}\cdot\text{cm}^{-2}$ to $1.18 \text{ mA}\cdot\text{cm}^{-2}$). More recently, within EU Project PECDEMO, it was reported a 50 cm^2 PEC-PV device

optimized for continuous operation under concentrated sunlight, the CoolPEC cell⁹. This α -Fe₂O₃/silicon cell tandem device generated ca. 0.45 mA·cm⁻² at 1.6 V, under 1 kW·m⁻² of simulated sunlight, over 42 days (1008 h), with the electrolyte recirculating at 45 °C. The largest PEC-PV device demonstrated to date is a 1.6 m² module developed within EU Project Artiphyction, which comprised 100 BiVO₄-based (8 × 8 cm²) PEC cells, and Si-PV cells placed on the frames of the panel.³⁴ However, this system cannot be used with concentrated solar radiation and showed poor stability. These three works are considered the most relevant contributions for demonstrating the viability of solar-H₂ production using upscaled PEs and devices.⁵

This chapter describes the development of a 200 cm² PEC module that was optimized for continuous operation under concentrated sunlight. This modular device, comprising four 50 cm² PEC cells, was tested outdoor using two types of α -Fe₂O₃ PEs. In a first testing campaign, the module was assembled with four 50 cm² α -Fe₂O₃ PEs, each one coupled to a HIT (heterojunction with intrinsic thin layer) silicon cell (two junctions) in a tandem arrangement. In a second set of tests, the module was assembled with four 50 cm² multi-PE windows, each cell comprising eight nanostructured α -Fe₂O₃ PEs with 2.4 × 2.3 cm², connected in parallel. Both experimental campaigns were carried out over two days in a continuous mode, under natural concentrated sunlight (up to 12.8 kW·m⁻²) and with electrolyte recirculation. Therefore, the work developed within this chapter aims at combining the main results achieved throughout the complete PhD work, answering to the main challenges of PEC-H₂ production identified at the beginning, focusing the three main pillars for commercialization: efficiency, stability and scalability.

5.2 MATERIALS AND METHODS

5.2.1 PREPARATION OF HEMATITE PHOTOELECTRODES

The work developed within this chapter comprises two main types of α -Fe₂O₃ photoelectrodes: i) 50 cm² bare α -Fe₂O₃ PEs prepared by spray pyrolysis (SP) and ii) 2.4 × 2.3 cm² Ti-doped α -Fe₂O₃ PEs (used in the four multi-PE windows) prepared by a combined spray pyrolysis/hydrothermal method. Spray pyrolysis allows preparing highly reproducible, stable and compact thin films (ca. 30 nm), which guarantees the full coverage of the FTO glass substrate.^{35, 36} This type of morphology prevents the later appearance of hematite-free zones, which are starting points for the degradation of the semiconductor in long-term tests.³⁷ On the other hand, solution-based methods allow preparing nanostructures with a “worm-like” morphology, *i.e.* nanorods, which have a higher surface area in contact with the electrolyte, enhancing the performance of the PEs.³⁸

Due to equipment size restrictions, spray pyrolysis was the only technique available for producing PEs with an active area of 50 cm². Therefore, single-large PEs used as back window in the PEC module were prepared by this technique (Figure 5.1-a). Before the deposition step, the FTO glass substrates (Solaronix TCO 22-7, 2.2 mm thick, 7 Ω ·square⁻¹, 120 mm × 70 mm) were subjected to a multi-step cleaning procedure, described in Appendix 5-a. Each cleaned substrate was placed on a heated plate and a TEOS (tetraethyl orthosilicate) pre-treatment³⁹ was applied at 450 °C; ca. 20 mL of a diluted TEOS solution (99.9 %, Sigma-Aldrich; 10 % volume in EtOH) were hand-sprayed with a glass atomizer. Then, the hematite thin film was prepared by spray-pyrolysis, as described elsewhere.⁸ Briefly, the spray nozzle (Spraying Systems Co. model SU J4B-SS) was placed 30 cm over the TEOS pre-treated substrate. An automatic syringe pump (Cronus Sigma 2000 Dual Syringe Pump) was used to deliver 42 pulses, 35 s apart, of 1 mL of the precursor solution containing 10 mM of Fe(acac)₃ (99.9 %, Sigma-Aldrich) in EtOH (absolute, BDH Chemicals, VWR International) at a flowrate of 12 mL·min⁻¹. During the spray-

pyrolysis deposition, the temperature of the heated plate was set to 425 °C. Finally, the as-prepared PEs were subjected to an annealing treatment in air at 550 °C during 1 h; this type of PEs are hereafter labelled as SP-PEs.

Hematite PEs with an active area of $2.4 \times 2.3 \text{ cm}^2$, used in multi-PE windows, were prepared following a multi-step procedure, which allowed producing eight PEs per batch. In the first step, a planar $\alpha\text{-Fe}_2\text{O}_3$ thin film was prepared by spray pyrolysis, as previously described (Figure 5.1-1). Again, before the hematite deposition, the FTO glass substrates (Solaronix TCO 10-10, 1.0 mm thick, $10 \Omega\text{-square}^{-1}$, 30 mm $\times$ 20 mm) were subjected to the same multi-step cleaning procedure and TEOS pre-treatment.

In a second stage (Figure 5.1-2), a solution-based method (hydrothermal synthesis)^{40, 41} was used to promote the growth of $\beta\text{-FeOOH}$ nanorods over the thin $\alpha\text{-Fe}_2\text{O}_3$ film. In short, the eight SP-PEs were placed tilted (ca. 80°) in a home-designed PEEK support and then immersed in an aqueous solution of 0.15 M $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ($\geq 99 \%$, Sigma-Aldrich) and Ti 0.2 % (w/w) (TiF_4 crystalline 98 %, Alfa Aesar). The hydrothermal treatment was conducted at 100 °C during 7 h in a home-designed PEEK-coated stainless-steel autoclave (Appendix 5-b and Appendix 5-c). After this period, the SP-PEs with $\beta\text{-FeOOH}$ nanorods were rinsed with distilled water and then subjected to a two-step annealing in air (Figure 5.1-3): i) 550 °C during 1 h ($5 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$); ii) 800 °C during 20 min ($10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$). These thermal treatments allowed obtaining “worm-like” nanostructured Ti-doped $\alpha\text{-Fe}_2\text{O}_3$ PEs.

In a final stage (Figure 5.1-4), the eight nanostructured PEs were subjected to a surface acid treatment⁴², which consisted of immersing the as-prepared PEs in an aqueous solution of 2.0 M HCl (36 % w/w, Alfa Aesar) during 90 min, followed by drying with pure nitrogen. After the acid treatment, the PEs were named as SPHA-PEs.

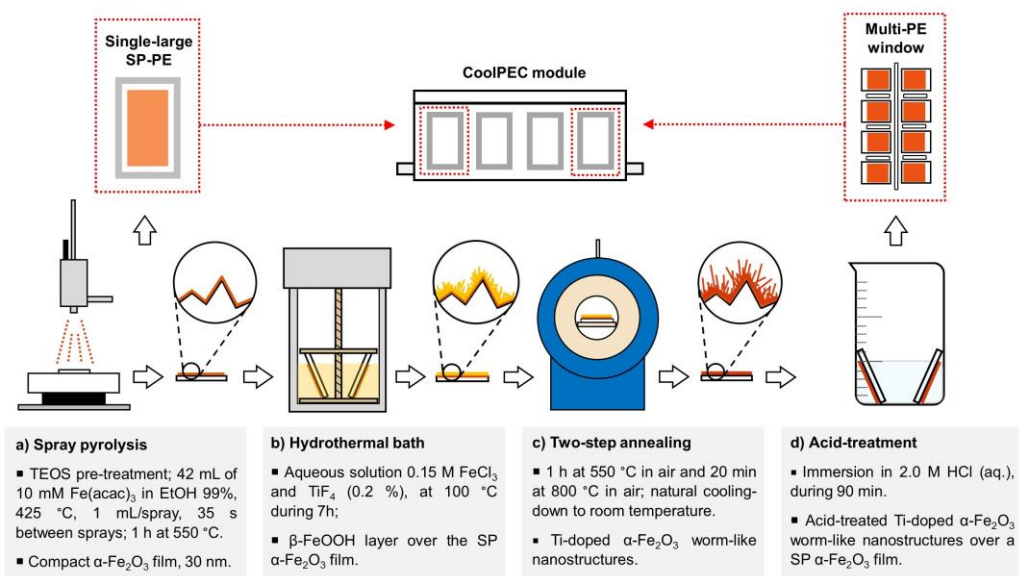


Figure 5.1. Experimental procedure used to prepare $\alpha\text{-Fe}_2\text{O}_3$ PEs assembled in the developed PEC-PV modular device.

5.2.2 COOLPEC MODULE

The CoolPEC module is a PEC device comprising four optimized PEC cells based on the CoolPEC cell design⁹, totalling an active area of 200 cm² (Figure 5.2). The embodiment was manufactured in acrylic (Perspex®, from Lucite®), which assures good resistance to the electrolytes normally used in experiments for solar water splitting, and to a wide range of operating temperatures – from 0 °C to 65 °C.⁴³ Each cell can be assembled with a single-large 50 cm² PE, working as front and/or back window (Figure 5.2-a), or with a multi-PE window, replacing the back window/PE (Figure 5.2-b).

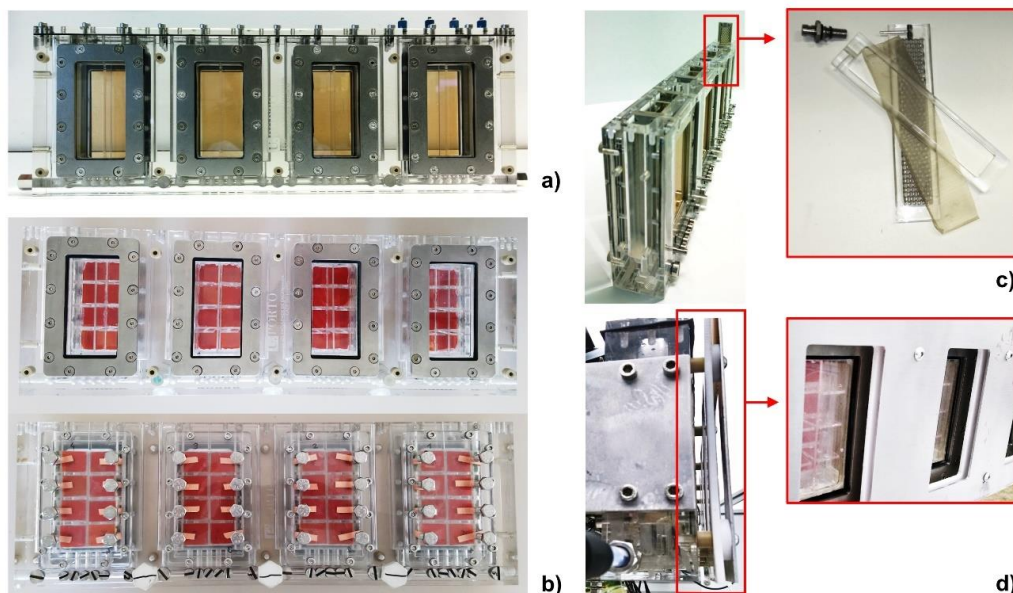


Figure 5.2. CoolPEC module: a) front view of the module assembled with four single-large $\alpha\text{-Fe}_2\text{O}_3$ SP-PEs; b) front view (top) and back view (bottom) of the module assembled with four multi-PE windows, each one comprising eight nanostructured $\alpha\text{-Fe}_2\text{O}_3$ PEs (SPHA-PEs); c) detailed view of the counter-electrode support; d) detailed view of the double-layer reflective shield (PTFE-aluminium).

When the module is operated with multi-PE windows, the total active area decreases to ca. 180 cm^2 due to the use of internal separators, as illustrated in Appendix 5-d. The module has two main electrolyte inlets, located at the bottom on both sides ($\varnothing = 10\text{ mm}$), and comprises sixteen electrolyte outlets located at the top ($\varnothing = 4\text{ mm}$). Each cell has two electrolyte outlets for the PE compartment and one for each counter-electrode (CE) compartment. This arrangement of inlets and outlets generates an optimized electrolyte flow path, assuring good heat dissipation and efficient collection of evolved gases, both crucial for operation under concentrated sunlight.⁴⁴ The CEs and the PE are positioned side-by-side, making a total of eight, two per cell. Acrylic parts hold the ionic exchange membrane (Fumatech Fumasep® FAA-3-PK-100) against the platinized-Ti meshes (CEs), in a near zero-gap configuration Figure 5.2-c), which avoids gas mixing inside the cell. On/off valves placed at the entrance of each

cell allow operating with a single cell or with any combination of the four cells. A double-layer (aluminium-PTFE) reflective shield can be screwed on the front side in specific housing areas made of PEEK (Figure 5.2-d) for operation under concentrated sunlight. Additional images of the CoolPEC module are available in Appendix 5-e and Appendix 5-f.

5.2.3 TEST FACILITY SoCRATUS

Outdoor experiments conducted under concentrated sunlight were performed in the SoCRatus testing facility at DLR in Köln, Germany. The SoCRatus is a solar concentrator equipped with 22 linear mirrors and with a two-axis tracking system that provides homogeneous and concentrated radiation in a rectangular focal plane of $250 \times 10 \text{ cm}^2$, with a geometric concentration factor up to 20.2.⁴⁵⁻⁴⁷ The CoolPEC module was installed in the testing facility, comprising two electrolyte cycle loops, heat exchangers and micro gas chromatograph (GC) equipment, as illustrated in Appendix 5-g. Each PE and CE compartment of the four PEC cells was individually connected to the two main electrolyte outlet streams. This way, evolved hydrogen (H_2) and oxygen (O_2) were collected separately, leaving the PEC cells together with the corresponding electrolyte stream, which flows into the respective electrolyte tank. Upstream the two tanks, defined nitrogen (N_2) streams are introduced to the electrolyte loops in order to carry the evolved O_2 or H_2 to the corresponding GC, allowing their accurate quantification. Temperature, pressure, flow rate, pH and O_2 and H_2 concentrations were continuously monitored and processed by the data acquisition and control systems. The electric wiring made in the testing facility is schematically represented in Appendix 5-h.

5.2.4 PHOTOELECTROCHEMICAL CHARACTERIZATION

Small-size SPHA-PEs used in multi-PE windows were individually characterized in a cappuccino PEC cell⁴⁸ using a three-electrode configuration where the $\alpha\text{-Fe}_2\text{O}_3$ PE was the WE (working-electrode), 99.9 % pure platinum wire (Alfa

Aesar®, Germany) was used as CE, and a Metrohm Ag/AgCl sat. KCl was used as reference electrode. The cell was filled with 1.0 M KOH electrolyte solution. For obtaining the current-density voltage (J - V) characteristic curves, an external potential bias was applied to the cell and the generated photocurrent was measured with a ZENNIUM workstation (Zahner Elektrik, Germany) controlled by Thales software package (Thales Z 2.0). J - V measurements were performed in the dark and under simulated sunlight provided by a class B solar simulator equipped with a 150 W Xe lamp (Oriel, Newport, USA) and an AM 1.5 G filter ($1 \text{ kW}\cdot\text{m}^{-2}$, 25°C ; Newport, USA) calibrated with a c-Si photodiode (Newport, USA), between 0.8 and $2.0 \text{ V}_{\text{RHE}}$ at a scan rate of $10 \text{ mV}\cdot\text{s}^{-1}$.

When the CoolPEC module was assembled in the solar concentrator, J - V measurements were performed using an Aim TTI QL 355 P Power Supply, controlled by LabVIEW software, between 0.8 and 2.2 V, at a scan rate of $10 \text{ mV}\cdot\text{s}^{-1}$. J - t curves were also performed to evaluate the behaviour of the current density over time under different conditions, such as natural concentrated sunlight, with or without bias potential. A two-electrode configuration was used, where the WEs and CEs were individually connected to the power supply unit. The connection to the data acquisition system allowed making measurements with a single cell or with any combination of the four cells. J - V measurements were performed in the dark and under natural sunlight, with an incident irradiance up to ca. $13 \text{ kW}\cdot\text{m}^{-2}$ (13-sun). Both single-large SP-PEs and multi-PE windows (with SPHA-PEs) were used in the experiments conducted outdoor.

5.2.5 STRUCTURAL CHARACTERIZATION OF α - Fe_2O_3 PES

The morphology, surface topography and thickness of α - Fe_2O_3 films were studied using a high-resolution scanning electron microscope (SEM) (Quanta 400 FEG, FEI Company, USA); these analyses were made at CEMUP (Centro de Materiais da Universidade do Porto). SEM top-view images were obtained by

applying an acceleration voltage of 15 keV while an in-lens detector was employed with a working distance of ca. 10 mm.

The thickness of nanostructured SPHA-PEs was determined from SEM cross-section images. This methodology cannot be used for truthfully determining the thickness of planar $\alpha\text{-Fe}_2\text{O}_3$ thin films, since it is not possible to rigorously distinguish the $\alpha\text{-Fe}_2\text{O}_3$ layer (with only ca. 30 nm) from the FTO layer (ca. 500 nm), even with high magnifications (Appendix 5-i). Therefore, the thickness of spray-pyrolysis $\alpha\text{-Fe}_2\text{O}_3$ films was estimated assuming a Lambertian absorption behaviour, as described elsewhere.⁴⁹ An UV-vis-NIR spectrophotometer (Shimadzu Scientific Instruments Inc., model UV-3600, Kyoto) was used to determine the reflectance and transmittance data. The absorbance was determined by subtracting the reflectance and transmittance to the incident radiation, which was later corrected by subtracting the absorbance of the FTO glass (control).

5.2.6 THEORY/CALCULATION

Solar irradiance

The solar irradiance, E_e , reaching the surface of the photoelectrodes was calculated using the following expression:

$$E_e = I_N \cdot R_m \cdot R_w \cdot C_{g,eff} \quad (1)$$

where I_N is the direct normal irradiance, measured and processed by the testing facility equipment, R_m is the solar weighted hemispheric reflectance of the mirrors, R_w is the solar weighted transmittance of the front quartz window (air-quartz-electrolyte) and $C_{g,eff}$ is the effective geometric concentration ratio on the surface of the PEs (see Appendix 5-j). The latter was calculated based on the geometric concentration ratio in the focal plane of the SoCRatus and depends on specific constraints of the installed PEC device: i) part of the sunlight towards the inner mirrors was blocked by the radiation shield of the installed PEC module

and ii) part of the radiation reflected by the mirrors that reached the PEs (through the front window and the electrolyte) was blocked by some components of the CoolPEC module (*i.e.* by the front metal frame and the acrylic body); this blocked fraction depended on the considered mirrors and associated incident angles.

Hydrogen production rate

The produced hydrogen flow rate, Q_{H_2} , was calculated by:

$$Q_{H_2} = \frac{\left[V_{S,N_2} \times \left(\frac{X_{H_2}}{1 - X_{H_2}} \right) \right] \times P_S}{R \times T_S \times \eta} \quad (2)$$

where V_{S,N_2} is the volumetric standard flow rate of N_2 and X_{H_2} is the molar fraction of H_2 in the gas sample, both measured and processed by the testing facility equipment, P_S is the standard pressure, R is the gas constant, T_S is the standard temperature and η is the hydrogen recovery factor of the test facility, referring to the losses of hydrogen between the PEC reactor and the GC (predominantly diffusion through tubing and the tank), which was experimentally assessed before.

The expected H_2 flowrate (Q_{H_2}) was estimated from the generated current assuming a faradaic efficiency of 100 %:

$$I = \frac{n \times F \times Q_{H_2}}{A} \quad (3)$$

where I is the generated photocurrent, n is the stoichiometric coefficient of the H_2 generation reaction, F is the Faraday constant and A is the active area. The expected H_2 production was calculated based on the values of generated current, measured by the sourcemeter (installed in the SoCRatus testing facility) and recorded every second. Then, the corresponding moles of hydrogen produced in each second were calculated using Equation (3). Finally, the total expected hydrogen production was calculated by the sum of moles produced

during the period of interest, later converted to grams of hydrogen per hour and per cm² of net active area.

Solar-to-Hydrogen (STH) efficiency

The STH efficiency was estimated considering a system where the energy input is the sunlight and the energy output is the current density generated by the PEs (then converted to H₂ derived from solar-driven water splitting) ⁵⁰⁻⁵², as follows:

$$STH = \frac{\left(\frac{J_{PE} \times A}{2 \times F}\right) \times \Delta G_{H_2}}{E_e \times A} \quad (4)$$

where J_{PE} is the photocurrent density generated by the PE at zero bias, ΔG_{H_2} is the Gibbs free energy of water electrolysis (237 kJ·mol⁻¹) and E_e is the incident illumination power density. The active area of the PEs assembled in the module with four multi-PE windows was accurately measured by using ImageJ® software; the unusable surface area, e.g. covered by the silicone sealing paste, was methodically quantified and then subtracted to the total housing area.

5.3 RESULTS AND DISCUSSION

5.3.1 COOLPEC MODULE ASSEMBLED WITH 50 CM² PLANAR α -Fe₂O₃ PEs

In the first set of tests the CoolPEC module was operated with four single-large α -Fe₂O₃ SP-PEs, assembled as back windows and front-illuminated. Four HIT Si cells (each one with an active area of 50 cm²) were placed at the back of the module, thus receiving the solar radiation transmitted through the PEs. This PEC-PV tandem arrangement corresponds to the original configuration of the CoolPEC cell ⁹, represented schematically in Appendix 5-j. The temperature of the recirculated electrolyte, the total solar irradiance, the current density and the molar flow of generated H₂ were continuously recorded over two days –Figure 5.3-a and Figure 5.3-b. Individual *J-V* characteristics of the SP-PEs and the HIT

Si cells are shown in Appendix 5-k and Appendix 5-h, respectively. The intersection of the J - V characteristics of each single-large PE and the corresponding HIT Si cell is presented in Appendix 5-m.

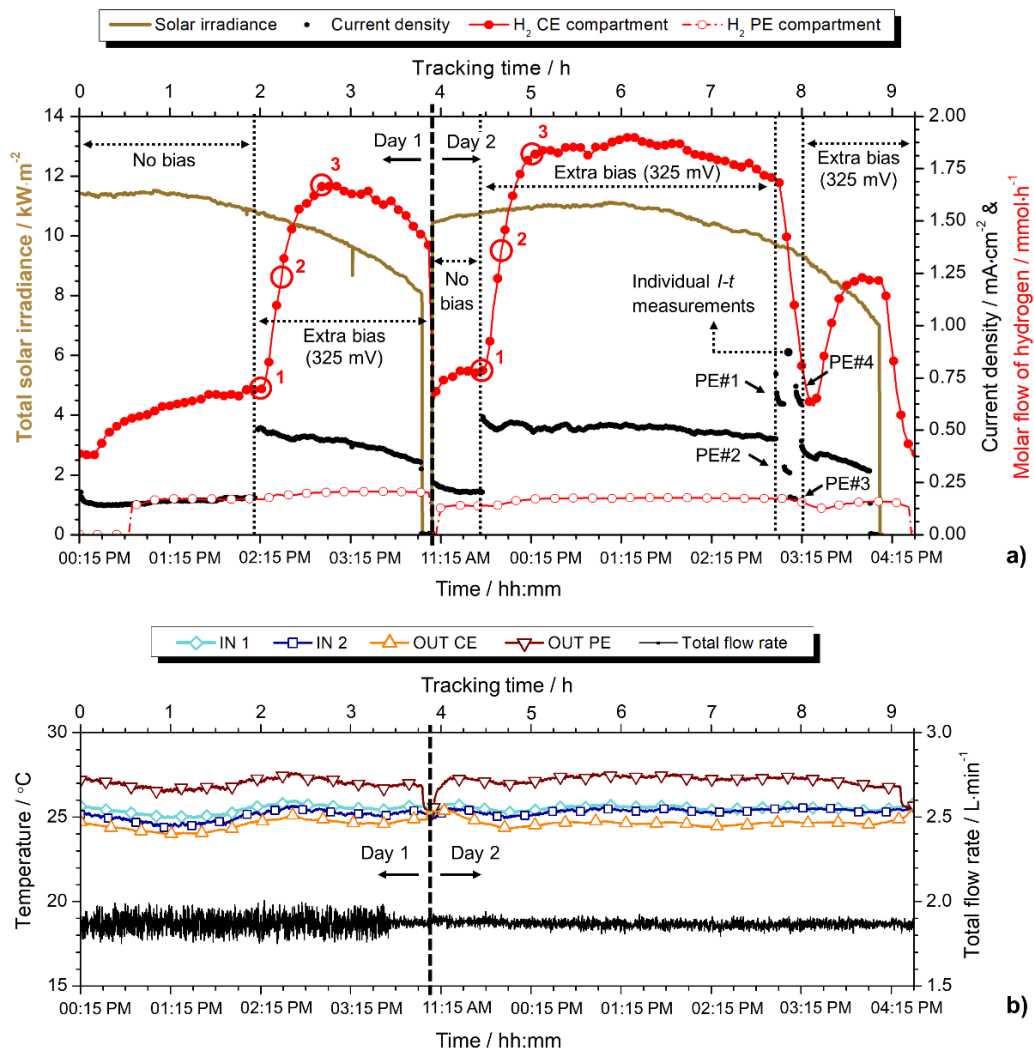


Figure 5.3. History of (a) current density generated by single-large α - Fe_2O_3 SP-PEs (●), molar flow of H_2 measured in fluid cycles 1 and 2 (● - fluid cycle 1, CE compartments, ○ - fluid cycle 2, PE compartments) and (b) history of electrolyte temperature and flow rate, measured at inlets 1 (◇) and 2 (□), at the outlets of the CE compartments (△) and at the outlets of the PE compartments (▽). The total electrolyte flow rate is represented by a solid black line. Instants 1, 2 and 3 (highlighted in red), are explained in Appendix 5-n.

In the first day of field tests, the CoolPEC module was operated for almost 4 h in two different configurations: i) without any external bias, for half the time; and ii) with an additional bias of 325 mV provided by the power supply unit. The current density generated without bias steadily rose from ca. $0.15 \text{ mA}\cdot\text{cm}^{-2}$ to $0.18 \text{ mA}\cdot\text{cm}^{-2}$ (ca. 17 % increase) and the H_2 production stabilized at ca. $0.7 \text{ mmol}\cdot\text{h}^{-1}$. The solar irradiance was almost constant at about $11 \text{ kW}\cdot\text{m}^{-2}$ (11-sun) during this period of the day. In the second part of the tests, between 2:10 PM and 4:10 PM, the incident solar radiation decreased from ca. $11 \text{ kW}\cdot\text{m}^{-2}$ to $8 \text{ kW}\cdot\text{m}^{-2}$, due to the expected variation of sunlight during the daytime; the maximum recorded irradiance was ca. $11.5 \text{ kW}\cdot\text{m}^{-2}$.

To have a constant operating potential of 1.6 V, reproducing the experimental conditions used in the long-term test with the CoolPEC cell ⁹, a bias potential of 325 mV was provided by the power supply unit during the second testing period of day 1. The molar flow of H_2 in the exiting stream from the CE compartments reached the steady state after ca. 30 min due to mixing and saturation along the fluid circuit, corresponding to instants 1, 2 and 3 (highlighted in red, and explained in detail in Appendix 5-n). With the extra bias, the current density increased to ca. $0.5 \text{ mA}\cdot\text{cm}^{-2}$, and then decreased continuously, agreeing with the solar input. The H_2 flow also increased rapidly to ca. $1.7 \text{ mmol}\cdot\text{h}^{-1}$, which corresponds to an increase > 140 % compared to the first part of the tests (without the extra 325 mV). This amount of H_2 is in accordance with the expected values for undoped $\alpha\text{-Fe}_2\text{O}_3$ PEs.⁵³ A small amount of H_2 was measured in the recirculating stream of the photoelectrode due to gas leakage through the CE acrylic holders; the maximum recorded value of H_2 in the recirculating stream of the PE compartments was ca. $0.21 \text{ mmol}\cdot\text{h}^{-1}$ (ca. 10 % of the total H_2 production rate). The molar flow of H_2 measured in this recirculating stream is not visible in some periods of Figure 5.3-a, corresponding to values lower than the limit of detection.

On day 2 a similar set of two experiments was performed. Between instants 11:10 AM and 11:45 AM, the module was operated without bias from the power

supply. The current density slowly decreased and levelled-off at ca. $0.2 \text{ mA}\cdot\text{cm}^{-2}$, replicating the results obtained in the previous day. The H_2 flow measured in the recirculating stream of the CEs reached a stable value of ca. $0.8 \text{ mmol}\cdot\text{h}^{-1}$, also agreeing with the values recorded in day 1. After applying the extra bias of 325 mV at instant 11:45 AM (total potential of PV cell + bias of ca. 1.6 V) the current density increased to ca. $0.5 \text{ mA}\cdot\text{cm}^{-2}$ and remained stable until 2:55 PM. During this period, the H_2 measured at the CE exiting stream rose to ca. $1.9 \text{ mmol}\cdot\text{h}^{-1}$ and the H_2 measured in the PE exiting stream reached a maximum of ca. $0.18 \text{ mmol}\cdot\text{h}^{-1}$, representing less than 10 % of the total H_2 production. Individual J - t measurements were performed for each PE assembled in the CoolPEC module between instants 2:54 PM and 3:15 PM. The obtained results show that PE#1 and PE#4 performed better than PE#2 and PE#3. The combined performance of the PEs resulted in a mean photocurrent density that agrees with the values recorded between instants 11:45 AM and 2:55 PM.

Under concentrated solar radiation, the maximum temperature, 27.7°C , was recorded at the electrolyte outlets of the PE compartments – cf. Figure 5.3-b. This value represents a maximum temperature difference of 3°C compared to the mean electrolyte temperature of 24.7°C at the inlets. Hence, the developed PEC module was able to maintain the temperature of the electrolyte efficiently dissipating the heat under up to ca. 11.5-sun of concentrated solar radiation. The increase in the electrolyte temperature at the PE compartments was expected since these are the areas of the module that are not covered by the protective shield (Figure 5.2-d) and are directly exposed to concentrated sunlight.

5.3.2 COOLPEC MODULE ASSEMBLED WITH FOUR MULTI-PE WINDOWS

The resistance imposed by the FTO substrate in single-large $\alpha\text{-Fe}_2\text{O}_3$ SP-PEs muffled the beneficial effect brought by the concentrated solar radiation –Figure 5.3; the expected linear increase in the generated photocurrent was not observed. Nanostructured PEs prepared on small FTO substrates, displaying then a lower electrical resistance, should allow observing an increase in the

generated photocurrent and a decrease in the onset potential under concentrated sunlight. A new set of experiments was performed, where each cell was equipped with a multi-PE window, comprising eight $\alpha\text{-Fe}_2\text{O}_3$ SPHA-PEs with an active area of $2.4 \times 2.3 \text{ cm}^2$ each. To have four multi-PE cells with very similar performances, the SPHA-PEs were distributed by the acrylic supports according to their performance (Appendix 5-o and Appendix 5-p). As so, before being installed in the corresponding multi-PE window, the $\alpha\text{-Fe}_2\text{O}_3$ SPHA-PEs were characterized individually with J-V measurements performed in a cappuccino PEC cell assembled with a 3-electrode configuration; values of the recorded photocurrent at $1.23 \text{ V}_{\text{RHE}}$ and $1.45 \text{ V}_{\text{RHE}}$ are available in Appendix 5-o. During this testing campaign, the CoolPEC module was operated at 1.45 V provided by the power supply unit. Due to the design of the multi-PE windows, described elsewhere ²⁹, it was not possible to install PV cells at the back in a tandem arrangement due to the configuration of the back contacts. The current density history, generated hydrogen and electrolyte temperature recorded over the two days of continuous operation is depicted in Figure 5.4. In the final set-up, part of the active area was covered by silicone, which inhibits the contact with the electrolyte. The net active area that effectively participated in photoelectrochemical reactions equalled 93.28 cm^2 .

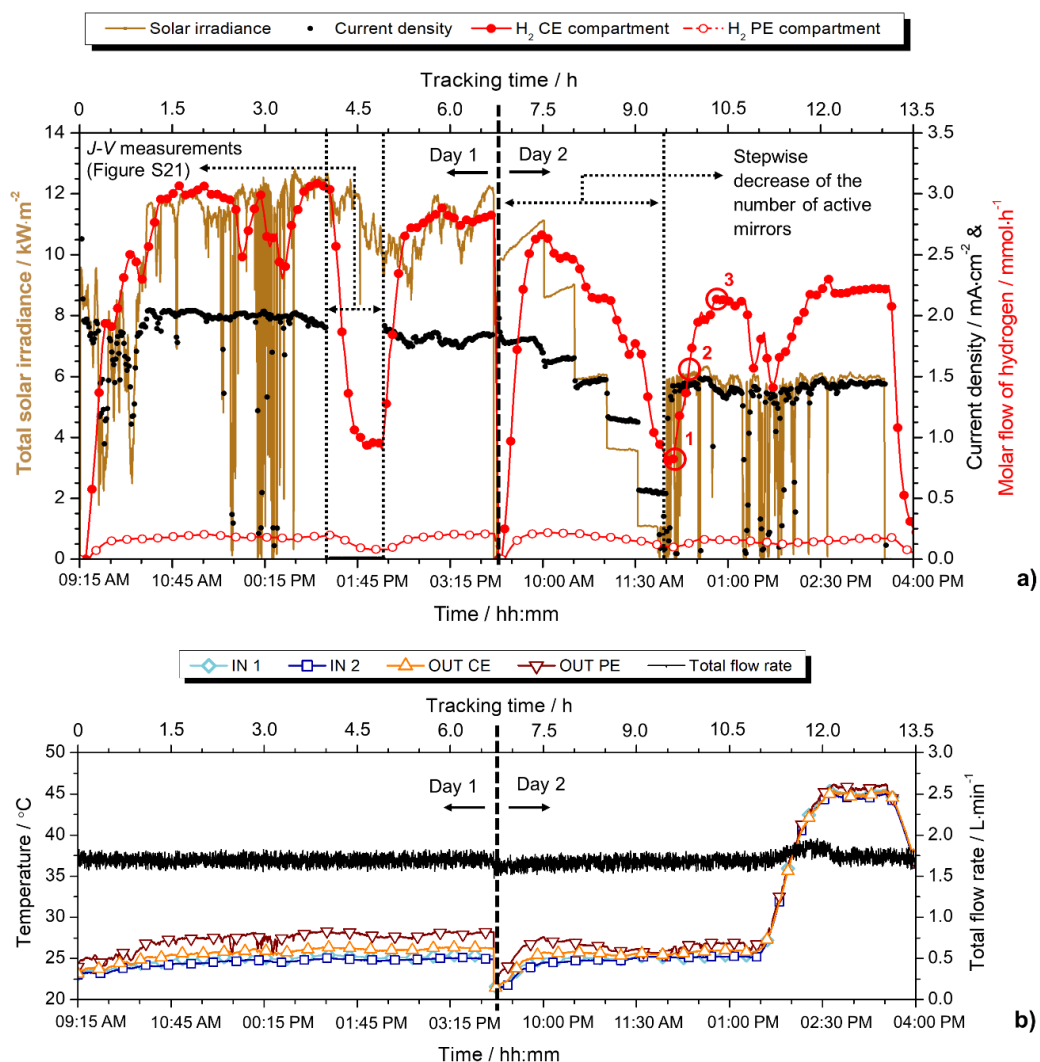


Figure 5.4. History of (a) current density generated by $\alpha\text{-Fe}_2\text{O}_3$ multi-PE cells ($\bullet$), molar flow of H_2 measured in fluid cycles 1 and 2 ($\bullet$ - fluid cycle 1, CE compartments; $\circ$ - fluid cycle 2, PE compartments) and (b) history of electrolyte temperature and flow rate, measured at inlets 1 ($\diamond$) and 2 ($\square$), at the outlets of the CE compartments ($\triangle$) and at the outlets of the PE compartments (∇). The electrolyte flow rate is represented by a solid black line. Instants 1, 2 and 3 (highlighted in red), are explained in Appendix 5-n.

On the first day of field tests, the CoolPEC module was operated with a constant feeding flow rate of ca. $2.0 \text{ L}\cdot\text{min}^{-1}$ ($0.5 \text{ L}\cdot\text{min}^{-1}$ per cell) and with an average concentrated solar irradiance of $10.3 \text{ kW}\cdot\text{m}^{-2}$; the maximum recorded solar

irradiance was $12.8 \text{ kW}\cdot\text{m}^{-2}$. During this period, the module produced a stable current density of ca. $2 \text{ mA}\cdot\text{cm}^{-2}$ at 1.45 V, which represents a considerable improvement compared to the previous campaign; the fluctuations in the recorded current density agree with the variation in the recorded solar irradiance. These results allow concluding that in CIPEC systems smaller PEs connected in parallel generate higher photocurrent densities than larger PEs.

According to Figure 5.4-a, a mean H_2 flow of $2.50 \text{ mmol}\cdot\text{h}^{-1}$ was measured in the recirculating stream of the CE compartment whereas $0.17 \text{ mmol}\cdot\text{h}^{-1}$ were measured in the recirculating stream of the PEs. The latter represents ca. 6.7 % of the total H_2 flow rate, indicating minor gas mixing inside the module. Also, the fluctuations in the H_2 flow agree with the variation in the recorded current density. When multi-PE windows with perforated separators are used, the upward electrolyte flow near the membrane is reduced, which decreases the gas leakage through the CE parts – Appendix 5-q. During day 1, the total H_2 production was ca. $3.5 \times 10^{-2} \text{ g}$ (total tracking time of 6.7 h), corresponding to $5.6 \times 10^{-5} \text{ g}_{\text{H}_2}\cdot\text{h}^{-1}\cdot\text{cm}^{-2}$ based on the net active area, corresponding to a faradaic efficiency of 81.4 %. The obtained hydrogen production rate, based on the micro-GC analyses, agree well with the expected value of $6.9 \times 10^{-5} \text{ g}_{\text{H}_2}\cdot\text{h}^{-1}\cdot\text{cm}^{-2}$ (Equation (3)). Also, these results represent the first continuous quantification of evolved hydrogen produced by a large-area PE and correspond to the largest amount of H_2 ever reported for an upscaled PEC-PV device. The only fair comparison that can be made with the literature is with the work by Lee *et al.*³³ The reported $131 \text{ cm}^2 \text{ WO}_3$ photoelectrode allowed obtaining a flowrate of $3 \text{ mL}_{\text{H}_2}\cdot\text{min}^{-1}$, corresponding to $1.2 \times 10^{-4} \text{ g}_{\text{H}_2}\cdot\text{h}^{-1}\cdot\text{cm}^{-2}$. However, this result is based on a punctual measurement, over 20 s, and therefore cannot be considered a true quantification of continuous and stable hydrogen production.

On day 2 of this testing campaign, the effect of concentrated sunlight in the performance of nanostructured $\alpha\text{-Fe}_2\text{O}_3$ PEs was assessed. Between instant 9:10 AM (6.42 h of tracking time) and instant 11:58 AM (9.4 h of tracking time) the number of active linear mirrors was gradually reduced from 22 to 2, after

periods of 30 min, creating a stepwise decrease in the effective geometric concentration ratio. During this period, it was clearly observed a stepwise decrease in the generated current density at 1.45 V, from ca. $1.8 \text{ mA}\cdot\text{cm}^{-2}$ (with 22 active mirrors) to ca. $0.5 \text{ mA}\cdot\text{cm}^{-2}$ (with 2 active mirrors). The molar flow of H_2 measured at the electrolyte stream of the CEs decreased accordingly, from ca. $2.5 \text{ mmol}\cdot\text{h}^{-1}$ to ca. $1.0 \text{ mmol}\cdot\text{h}^{-1}$.

After this experiment, the CoolPEC module was operated with 10 linear mirrors, receiving a mean solar irradiance of $5.2 \text{ kW}\cdot\text{m}^{-2}$. During this period, the module generated a stable current density of ca. $1.4 \text{ mA}\cdot\text{cm}^{-2}$, corresponding to a mean H_2 flow of $2.0 \text{ mmol}\cdot\text{h}^{-1}$ measured in fluid stream of the CEs. Between instants 12:00 AM and 3:30 PM, the total H_2 production was $1.5 \times 10^{-2} \text{ g}$, which corresponds to $4.4 \times 10^{-5} \text{ g}_{\text{H}_2}\cdot\text{h}^{-1}\cdot\text{cm}^{-2}$ of net active area. Again, these results based on micro-GC analyses are in line with the expected value of $4.8 \times 10^{-5} \text{ g}_{\text{H}_2}\cdot\text{h}^{-1}\cdot\text{cm}^{-2}$ of H_2 , computed using Equation (3), corresponding to a faradaic efficiency of 92.4 %, which agrees with the literature.^{54, 55}

A maximum temperature of $28.4 \text{ }^\circ\text{C}$ was recorded at the electrolyte outlets of the PE compartments, for a mean inlet electrolyte temperature of $25.3 \text{ }^\circ\text{C}$ (Figure 5.4-b, from instants 0 h to 11 h of tracking time), representing a maximum increase of $3.1 \text{ }^\circ\text{C}$. When the inlet electrolyte temperature was set to $45 \text{ }^\circ\text{C}$, the temperature difference between the inlets and outlets was even smaller. These results confirm that the CoolPEC module can efficiently dissipate heat and maintain a targeted electrolyte temperature under concentrated sunlight when assembled with multi-PE windows. Therefore, Figure 5.3-b and Figure 5.4-b confirm that the design features included in the CoolPEC module allow having an efficient thermal management.²⁰ As concluded by the PECDEMO consortium, lowering the costs related to active cool systems (piping, heat exchangers, pumps, etc.) allows reducing the hydrogen cost up to $5 \text{ €}\cdot\text{kg}_{\text{H}_2}^{-1}$, making this the most critical issue for lowering the levelized price of hydrogen produced in an industrial plant.⁵⁶

5.3.3 STRUCTURAL CHARACTERIZATION OF α -Fe₂O₃ PES

Hematite PES prepared by spray pyrolysis have a long-term demonstrated stability (at least 1000 h) when immersed in 1.0 M KOH and under 1.0 kW·m⁻² of simulated sunlight.^{8, 9} On the other hand, the stability of α -Fe₂O₃ PES morphologically structured with nanowires, nanorods or worm-like structures is poorly addressed in the literature. Even so, these types of α -Fe₂O₃ PES are known for being less stable than planar films.^{57, 58} Figure 5.3 and Figure 5.4 plot the current density history of α -Fe₂O₃ SPHA-PES during two days of operation under severe testing conditions, including sudden changes in the (effective) geometric concentration ratio and in the electrolyte temperature (*i.e.* from 25 °C to 45 °C). During this period, under concentrated solar radiation provided by up to 22 active mirrors, the PES produced a stable photocurrent density, which is a preliminary indicator of morphological stability. The structural integrity of both types of α -Fe₂O₃ PES was assessed by SEM and EDS (energy-dispersive X-ray spectroscopy) after the testing campaign – Figure 5.5. These analyses were made on fresh samples and on samples taken from PES used in field tests (categorized as “aged” samples). PE#4 was selected as aged large SP-PE, whereas PE#16 (removed from the central zone of window 1, Appendix 5-p) was selected as aged SPHA-PE; the latter was compared to PE#33, selected as fresh sample (Appendix 5-o).

SEM images presented in Figure 5.5-a and Figure 5.5-b show that both samples presented a uniform α -Fe₂O₃ layer fully covering the underneath FTO structure. Figure 5.5-c and d show that both the thin α -Fe₂O₃ nonporous film and the α -Fe₂O₃ worm-like nanostructures, respectively, were resistant to the operation under natural concentrated sunlight. Also, according to Figure 5.5-d, worm-like α -Fe₂O₃ nanostructures presented a morphology that agrees with other PES reported in the literature that were prepared following a similar procedure.^{41, 59, 60} EDS results presented in Figure 5.5-e and 5-f show no significant differences between fresh and tested samples, which supports the hypothesis of non-degradation.

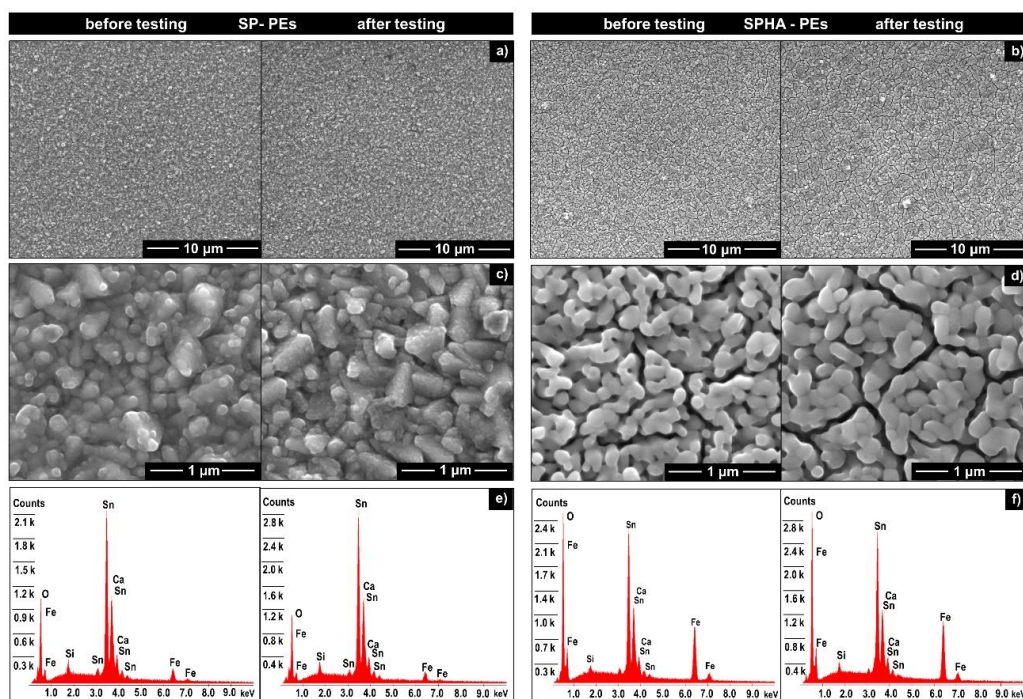


Figure 5.5. Top-view SEM images and EDS analyses of $\alpha\text{-Fe}_2\text{O}_3$ PEs before and after the field tests under concentrated sunlight with continuous electrolyte recirculation; a) and b) mag. 10 000 $\times$; c) and d) mag. 100 000 $\times$; e) and f) EDS analyses.

SEM and EDS analyses were also performed on different areas of the samples to ensure a representative analysis; no exposed FTO areas were identified. Complementary to these results, cross-section images were obtained for fresh and aged SPHA-PEs (Appendix 5-r); no differences were observed in the thickness of the $\alpha\text{-Fe}_2\text{O}_3$ layer – ca. 400 nm – before and after the testing period. SEM and EDS analyses were also made to other SPHA-PEs (fresh and aged) and very similar results were obtained – Appendix 5-s. Finally, no visible differences were identified in J-V curves obtained under dark conditions before and after the testing period (Appendix 5-t), which gives additional support to the hypothesis of non-degradation.

5.3.4 EFFECT OF CONCENTRATED SUNLIGHT IN THE PERFORMANCE OF α -Fe₂O₃ PES

One of the main goals of the present work was to provide new insights regarding the effect of concentrated sunlight on the performance of α -Fe₂O₃ PES. As evidenced in Figure 5.4-a, between instants 6.42 h and 9.4 h of tracking time, the generated current density did not follow a linear increase with the solar irradiance. Between instants 1:15 PM and 2:10 PM of day 1, *J-V* characteristics were obtained for each multi-PE window and for the module (Appendix 5-u and Appendix 5-v) for different solar irradiances – Figure 5.6. Table 5.2 summarizes the obtained results.

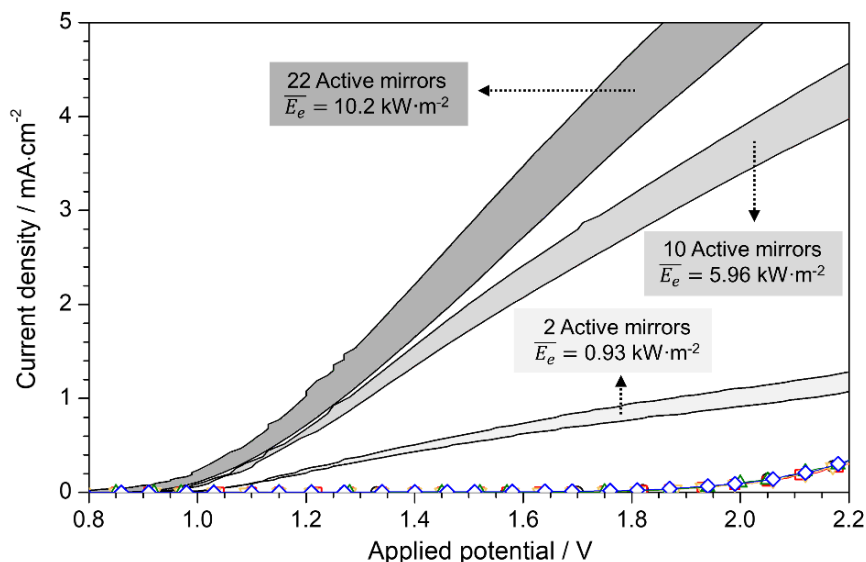


Figure 5.6. *J-V* characteristics of multi-PE windows obtained under different solar irradiances with electrolyte recirculation (1.0 M KOH, 25 °C, 0.5 L·min⁻¹ per cell). Each shadowed band corresponds to a specific concentration factor, given by 2, 10 and 22 active mirrors, and includes the *J-V* curves depicted in Appendix 5-u and Appendix 5-v. *J-V* curves with open symbols correspond to measurements performed under dark conditions for each window and the complete module. For better readability, *J-V* measurements performed with 6 and 16 active mirrors were not included in this figure but are available in Appendix 5-w.

Table 5.2. Values of current density (J , in $\text{mA}\cdot\text{cm}^{-2}$) recorded at applied potentials of 1.23 V, 1.45 V, 1.6 V and 1.8 V and extracted from the J-V curves depicted in Appendix 5-u and Appendix 5-v, performed for each window (W) and to the complete module (M), under concentrated sunlight provided by 2, 10 and 22 active mirrors (m). The STH efficiency (in %) and the mean solar irradiance ($\overline{E_e}$, in $\text{kW}\cdot\text{m}^{-2}$) are presented accordingly. For better readability, the values recorded with 6 and 16 active mirrors are not included in this table but are available in Appendix 5-x.

		W1				W2			W3			W4			M		
m	V	J	STH	$\overline{E_e}$	J	STH	$\overline{E_e}$	J	STH	$\overline{E_e}$	J	STH	$\overline{E_e}$	J	STH	$\overline{E_e}$	
2	1.23	0.29			0.25			0.28			0.26			0.22			
	1.45	0.57	0.41	1.02	0.48	0.36	1.03	0.55	0.41	1.01	0.50	0.41	0.95	0.47	0.36	0.93	
	1.60	0.74			0.63			0.70			0.64			0.61			
	1.80	0.95			0.77			0.90			0.81			0.77			
10	1.23	0.80			0.69			0.72			0.79			0.65			
	1.45	1.79	0.20	5.80	1.54	0.17	6.03	1.71	0.18	5.85	1.72	0.20	5.88	1.51	0.16	5.96	
	1.60	2.41			2.07			2.35			2.32			2.08			
	1.80	3.17			2.74			3.13			3.06			2.78			
22	1.23	1.11			0.97			1.00			1.22			0.84			
	1.45	2.41	0.14	11.5	2.17	0.12	12.1	2.26	0.13	11.9	2.53	0.15	12.0	1.91	0.12	10.2	
	1.60	3.33			3.00			3.17			3.47			2.72			
	1.80	4.57			4.09			4.41			4.68			3.80			

As evidenced in Figure 5.6, the current density generated by each window and by the complete module increases with the solar irradiance, though not linearly. This is also confirmed by the STH efficiency values shown in Table 5.2, which slowly decrease with the solar irradiance. In fact, the photocurrent generated by the module displays a saturation behaviour as the solar irradiance increases – Figure 5.7.

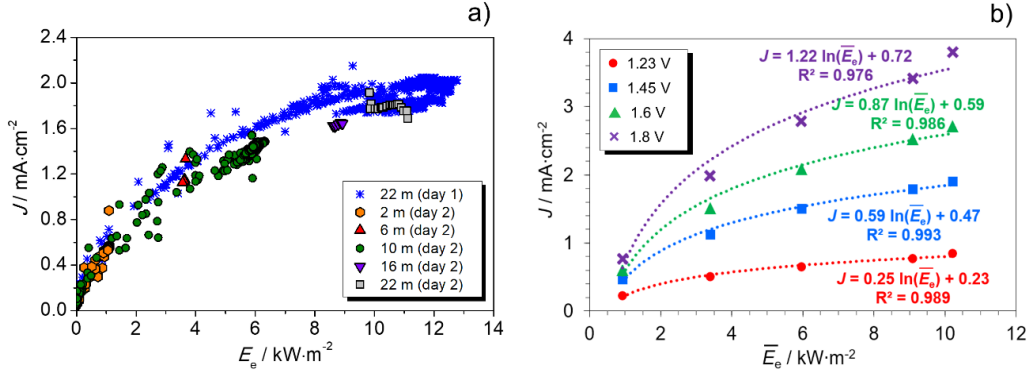


Figure 5.7. Relation between the photocurrent generated by multi-PEs and the solar irradiance: a) current density (J) measured at 1.45 V as a function of the solar irradiance (E_e), the latter related to the number of active mirrors (m); these values correspond to the recorded data during the two days of continuous operation (see Figure 5.4-a); b) current density (J) generated at different applied potentials as a function of the mean solar irradiance reaching the surface of the PEs ($\bar{E}_e$); these values were extracted from J - V measurements (depicted in Appendix 5-u and Appendix 5-v).

Field tests performed under natural concentrated sunlight show that the photocurrent density (J) generated by α -Fe₂O₃ PEs connected in parallel, subjected to a linear increase in the solar irradiance (E_e), *i.e.* due to a linear increase in the number of active mirrors (n_m), exhibits a logarithmic saturation behaviour, which can be written as:

$$J = k \ln E_e + b \quad (5)$$

where k is related to the applied potential. The appearance of a saturating current is related to recombination phenomena in the semiconductor material.⁴⁸

Surface recombination typically is the type of recombination responsible for most of the photocurrent losses in α -Fe₂O₃ PEs, since the water oxidation reaction is the limiting reaction.⁶¹ Slow hole transfer kinetics across the hematite/water interface has been considered a key reason for the low photovoltages displayed by α -Fe₂O₃ PEs⁶²; during the field tests it was not affected, since the CoolPEC module was operated at an almost constant electrolyte temperature of 25 °C.

Nevertheless, surface recombination strongly affects the photogenerated charge carriers, as the short-lived carriers do not have enough time to drive the water oxidation.⁶³ In a *n*-type semiconductor, the variation of surface-accumulated holes depends on the incoming hole flux and on two consuming processes: hole transfer to the electrolyte and surface hole recombination.⁶⁴ Also, the hole current is promoted by light absorption and by charge separation in the space charge layer. Under concentrated sunlight, the hole transfer in α -Fe₂O₃ PEs has been shown to promote only the water oxidation.⁶⁵ Electrolyte recirculation provides a constant supply of OH⁻ ions and the so-called “long-lived holes”, referring to the holes that have reached the surface of the semiconductor in contact with the electrolyte, are not likely to recombine with generated electrons, thus avoiding surface recombination that competes with the water oxidation reaction.⁶⁶ Nanostructured SPHA-PEs have a high surface area, which assures that generated holes can freely react with OH⁻ ions. Combining all these assumptions, surface recombination was not considered the main cause of the behaviour plotted in Figure 5.7.

Bulk recombination reduces the flux of photogenerated holes to the surface, generating back recombination that competes with the forward charge transfer reaction.⁶⁷ This type of recombination is enhanced by the thickness of the material⁶⁸ and by localized recombination sites, such as grain boundaries.⁶⁹ In the work made by Segev *et al.*²⁴ the current density generated by a 0.28 cm² α -Fe₂O₃ photoanode with ca. 500 nm thickness, responded linearly to the solar-simulated input, ranging from 1 to 25 kW·m⁻². As shown in Appendix 5-r, the PEs used in this work had a nanostructured α -Fe₂O₃ layer with ca. 400 nm thickness. As so, the lack of internal charge mobility due to the thickness of the α -Fe₂O₃ nanostructures should not be responsible for the limiting saturation current.⁷⁰ However, bulk recombination related to localized recombination sites, namely grain boundaries, could be induced by the transition between the planar α -Fe₂O₃ thin film and the worm-like nanostructures in SPHA-PEs.

The size of the PE is the major differentiating element between the present work and others reporting the use of concentrated sunlight to promote the water electrolysis. Although the arrangement in multi-PE windows allows dividing the 50 cm² active area into eight smaller parts, the resulting PEs still have an active area larger than the PEs used in other studies.^{24, 71} The increased flow of generated charge carriers still needs to surpass the resistance imposed by the FTO substrate, which delays their injection into the external circuit, thus increasing the probability of interfacial carrier trapping and recombination.⁷² It was then concluded that the electronic path between the semiconductor and the current collection point, as well as the conductivity of the current collector, are the main causes for the observed saturation behaviour.

5.4 CONCLUSIONS

In this chapter, the performance of a 200 cm² PEC-PV modular device, comprising four 50 cm² PEC cells, under concentrated sunlight was assessed. The module was first tested with four 50 cm² single-large α -Fe₂O₃ PEs prepared by spray pyrolysis (SP), coupled to four HIT Si cells in a tandem arrangement. In a second set of tests, the module was assembled with four 50 cm² multi-PE windows, each comprising eight α -Fe₂O₃ PEs with 2.4 × 2.3 cm², prepared via combined spray pyrolysis/hydrothermal method (SPHA). The objective of using multi-PE windows was to reach higher STH conversion efficiencies under concentrated sunlight and to better understand which phenomena – charge transfer, charge separation or collection efficiency – had the most significant influence in the overall performance of the module under such operating conditions.

During continuous operation under concentrated sunlight provided by with 22 active mirrors (max. 12.8 kW·m⁻² reaching the surface of the PEs), single-large SP-PEs generated current densities within the range of 0.2 to 0.5 mA·cm⁻² at 1.6 V, whereas multi-PE windows generated a stable current density of ca. 2.0 mA·cm⁻² at 1.45 V (*J-t* measurements) and reached a photocurrent density

of ca. $4.0 \text{ mA}\cdot\text{cm}^{-2}$ (J - V measurements, before the dark current onset potential). The total hydrogen production was 72 mg during 13.5 h of tracking time. When the number of active mirrors was increased, the photocurrent generated by the module assembled with $\alpha\text{-Fe}_2\text{O}_3$ SPHA-PEs followed a logarithmic saturation behaviour. This phenomenon was attributed to: i) recombination losses imposed by the grain boundaries between the planar film and the worm-like nanostructures and ii) to non-efficient current collection, mainly caused by the resistance between the semiconductor and the current collector.

Temperature measurements allowed concluding that the CoolPEC module dissipates heat efficiently under concentrated sunlight, avoiding the degradation of both PEC and PV components. A maximum temperature of 28.4°C was recorded in the electrolyte near the PE outlets, when the module was assembled with multi-PE windows, for an inlet electrolyte temperature of 25°C . SEM and EDS analyses showed no morphological differences between non-used and used samples in field tests, confirming the stability of both types of $\alpha\text{-Fe}_2\text{O}_3$ PEs.

Though the performance of the developed modular device was assessed with in-house prepared $\alpha\text{-Fe}_2\text{O}_3$ PEs, it can be assembled with other semiconductor materials, allowing achieving higher STH efficiencies. Even so, this work reports the largest amount of hydrogen produced by a large-scale PEC-PV device operated in a continuous mode under natural concentrated sunlight. Further upscaling can be easily made by stacking more modules.

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CHAPTER 6

GENERAL CONCLUSION AND OUTLOOK

“Why does the eye see a thing more clearly in dreams than the
imagination when awake?”

Leonardo da Vinci

6 GENERAL CONCLUSION AND OUTLOOK

6.1 MAIN CONCLUSIONS

At present, it is unambiguously established that green-H₂ will play a central role in the energy market over the upcoming decades, given its advantages as energy carrier and as industrial feedstock.¹ Several studies agree that green-H₂ will be vital for replacing fossil fuel combustion processes in the transportation, building, and industry sectors.² Still, to be considered a fully green alternative to the currently available technologies, H₂ must be produced from renewable sources in a cost-competitive, emission-free, and efficient way.³

Based on the broad comparative analysis of LCA studies made on H₂ production processes made in chapter 1, it was possible to conclude that PEC water splitting is the production method with the lowest environmental impact. Still, alkaline electrolysis (AEC) and steam-methane reforming remain the more financially appealing options to investors and H₂ consumers, due to their maturity within the energy market.⁴ Given thermodynamics and kinetic constraints, the best PEC-H₂ systems can only hope to match the best PV-electrolysers.⁵ For this reason, the differentiating competitive factor of PEC water splitting will reside on its environmental and functional advantages, which are strongly linked to the design of the operating device, to the intrinsic properties of the photoactive materials and to their successful upscaling.

Within the field of PEC-H₂ production, materials engineering has been mainly focused on optimizing photoabsorber materials, *i.e.* the PEs, since they materialize the photon-to-H₂ conversion, having a major influence on the efficiency of the device. Indeed, the PE is the main distinguishing element

between PEC and PV-EC systems, enabling to combine light absorption, charge generation and separation, hole, electron, ionic and molecular transport in a single device.⁶ Additionally, PEC systems can be operated at a lower current density, exhibiting lower overpotentials, and ultimately incorporating earth-abundant and cheap materials, instead of the expensive and scarce materials typically used in commercial electrolyzers.⁷ Among them, hematite ($\alpha\text{-Fe}_2\text{O}_3$) is one of the most promising semiconductors for achieving commercially viable PEC- H_2 production.⁸ This metal oxide is inexpensive, abundant, non-toxic and presents notable chemical stability under standard PEC operating conditions.⁹ Unfortunately, research efforts have been focused primarily on meeting efficiency targets, and the field still lacks a $\alpha\text{-Fe}_2\text{O}_3$ -PE that is simultaneously highly efficient and stable.¹⁰

Hematite PEs can achieve a maximum theoretical STH efficiency of ca. 16% (corresponding to $12.6 \text{ mA}\cdot\text{cm}^{-2}$ at $1.23 \text{ V}_{\text{RHE}}$).¹¹ Still, $\alpha\text{-Fe}_2\text{O}_3$ PEs comprise some important drawbacks: i) short diffusion length, mainly due to slow mobility of holes; ii) low water oxidation kinetics; iii) fast charge carrier recombination in the bulk; iv) low absorption coefficient; and v) the need of an external bias due to the low conduction band position.^{8, 12} Materials engineering allows overcoming most of these limitations, especially if including: i) morphology control, ii) addition of dopants, and iii) surface control.^{8, 13} The ideal $\alpha\text{-Fe}_2\text{O}_3$ PE should meet the three-pillar criteria required for commercialization – efficiency, stability, and scalability, *i.e.*, it should be prepared with low-cost and scalable techniques, should achieve a STH efficiency of 10 %, and should present a stable performance over ca. 3000 hours (ca. 8 working hours over 365 days). The state-of-the-art $\alpha\text{-Fe}_2\text{O}_3$ PE generated $6 \text{ mA}\cdot\text{cm}^{-2}$ at $1.23 \text{ V}_{\text{RHE}}$ (ca. 7% STH efficiency), but demonstrated a stable performance only over 100 h, which remains far from commercial ambitions.¹⁴ Stability-related problems are still considered the main drawback of nanostructured $\alpha\text{-Fe}_2\text{O}_3$ PEs.

The work developed within chapter 2 focused on optimizing a low-cost and scalable hydrothermal method for preparing highly efficient and stable nanostructured $\alpha\text{-Fe}_2\text{O}_3$ PEs. The stepwise optimization process implemented in

this work allowed obtaining ca. 500 nm thick highly porous α -Fe₂O₃ nanocubes with a sponge-like morphology, presenting feature sizes of ca. 20-40 nm. This α -Fe₂O₃ PE, decorated with a Co-Pi co-catalyst, generated 2.01 mA·cm⁻² at 1.23 V_{RHE} and reached 2.6 mA·cm⁻² before the dark current onset. More important, this PE presented a record-breaking stable performance over 2014 h, under standard PEC operating conditions, continuously generating ca. 2.0 mA·cm⁻² at 1.23 V_{RHE}, without catalyst regeneration. The linear fit made to the stability data allowed concluding that a 10 % decrease on the photocurrent would be achieved after 3516 hours, which meets the stability target for commercialization, *i.e.* 2920 h.

The optimization process described in chapter 2 allowed identifying the experimental parameters that have a greater influence on the performance of the PE, being: i) the concentration of fluoride ions in the precursor solution; ii) the duration and temperature of the hydrothermal synthesis; and iii) the type of annealing. Accordingly, the optimal preparation conditions were found to be: i) a F⁻ concentration in the precursor solution between 0.05 and 0.075 M; ii) a hydrothermal synthesis performed at a constant temperature of 100 °C, over 6 h; iii) separate morphological and functional annealing, conducted at 550 °C for 2 h, and at 800 °C for 20 min, respectively, allowing the PE to cool down in between. It was also found that performing an encapsulation with SiO₂ or TiO₂ between the annealing steps is crucial for preserving the porosity of the semiconductor.

Once the ideal PE is obtained, it becomes mandatory to design a device comprising structural features that not only do not limit the performance of the PE, but that can, somehow, boost its performance, for example, through the incorporation of components that enable the operation under concentrated sunlight.¹⁵ According to the configuration of electrodes and strategies adopted for gas separation, chapter 1 includes a possible categorization of PEC devices, divided into four main types: wired back-to-back (Type I), wireless back-to-back (Type II), wired side-by-side (Type III) and wired, separate electrode membrane-free (Type IV). Independently from the device architecture, using concentrated

sunlight is a key strategy for achieving the efficiency targets. This approach implies a symbiotic optimization process, requiring both the development of solar concentrators compatible with the restrictions of PEC devices, and the complementary development of PEC devices compatible with the technical specifications of solar concentrators. On the other hand, due to the voltage needed to drive water splitting (typically > 1.5 V), a dual-absorber tandem configuration, in which the bottom and top photoactive materials absorb complementary parts of the solar spectrum, is envisaged as the most feasible, surpassing the efficiency of PV-electrolysis systems, when considering the same PV for both cases.¹⁶

A PEC device that can host a tandem PE/PV cell needs to display an open path from the front to the back window, allowing sunlight to reach the PV cell installed at the back. Therefore, in chapter 3, a 50 cm² type III PEC cell was designed, built, and optimized for that purpose. This device, named CoolPEC cell, comprises three key design features: i) an open path for sunlight; ii) an innovative PE that is simultaneously one window of the cell; and iii) an optimized electrolyte feeding system arranged in a manifold configuration. CFD simulations were performed to optimize the fluid flow inside the cell, assuring good heat dissipation and efficient collection of evolved gases.

The design of the CoolPEC cell was assessed with field tests conducted outdoor, performed in a continuous operation mode under concentrated sunlight. This testing campaign allowed concluding that: i) evolved H₂ can be collected separately from O₂; ii) the developed device can be safely operated under concentrated sunlight; iii) the electrolyte temperature can be kept at the desired value, independently from the tilt position and the feeding flow rate. In a second set of tests, focusing efficiency and stability, the CoolPEC cell was assessed under non-concentrated sunlight (1000 W·m⁻²) in a long-term stability test, using a 50 cm² planar α -Fe₂O₃ PE prepared by spray pyrolysis. It is important to mention that by the time the work comprised in chapter 3 was performed, the optimization of the experimental procedure for fabricating nanostructured

α -Fe₂O₃ PEs, included in chapter 2, was at its early stage. As so, despite presenting a lower efficiency, α -Fe₂O₃ prepared by spray pyrolysis was the selected semiconductor for the long-term test, since it had already demonstrated reasonable efficiency and stability. The 50 cm² α -Fe₂O₃ PE remained stable over 42 days (1008 hours) delivering a photocurrent density of ca. 0.45 mA·cm⁻² at 1.6 V, provided by two SHJ solar cells.

Transparent conducting oxides (TCOs) are commonly employed as substrates for preparing PEs used in PEC water splitting, especially because they present good resistance to corrosive electrolytes and are suitable for tandem PEC/PV arrangements. However, in large-area PEs (≥ 50 cm²), the ohmic losses imposed by these substrates strongly limit the performance of the photoactive semiconductor. The results presented in chapter 3 clearly show that more than 50 % of the photocurrent density generated by α -Fe₂O₃ prepared by spray pyrolysis is lost when the PE is enlarged by one order of magnitude. Hence, overcoming this issue is a key requirement to bring upscaled PEC devices to a commercial level. Conductive lines can be applied across the substrate to reduce the electronic path until the current collection point; however, despite this approach can be easily implemented in solar cells, its implementation in PEs for PEC systems is more complex, given that the PE is immersed in a corrosive electrolyte. Therefore, metal lines need to be protected, which is a complex task and leads to significant losses of active area.¹⁷

The work developed within chapter 4 allowed developing a disruptive approach for overcoming the high electronic resistance imposed by large FTO-glass substrates: a segmented window for holding up to eight PEs connected in parallel. This multi-PE window was assembled and characterized in the CoolPEC cell, previously developed within chapter 3. A CFD-driven optimization was performed to minimize the retention of evolving gases and electrolyte stagnant volumes. CFD results also showed the importance of having internal separators between PEs immersed in a common electrolyte volume to avoid undesired ionic paths and additional overpotential losses. When eight α -Fe₂O₃

PEs were connected in parallel, photocurrent densities of $0.52 \text{ mA}\cdot\text{cm}^{-2}$ and $1.11 \text{ mA}\cdot\text{cm}^{-2}$ were recorded at 1.23 V and 1.45 V, respectively, under $2500 \text{ W}\cdot\text{m}^{-2}$ of simulated sunlight. When compared with a single 50 cm^2 $\alpha\text{-Fe}_2\text{O}_3$ PE, eight PEs working in parallel produced a higher photocurrent density and showed a higher photovoltage. It was also found that the influence of an underperforming PE in the overall performance of the cell decreases exponentially with the number of connected PEs.

Finally, the main achievements obtained within chapters 2, 3 and 4 were gathered to develop the first large PEC modular device assembled with multi-PE windows, capable of being operated under concentrated sunlight, and including an optimized electrolyte flow path. This 200 cm^2 PEC-PV module, comprising four 50 cm^2 PEC cells, was tested under concentrated sunlight, first using four 50 cm^2 $\alpha\text{-Fe}_2\text{O}_3$ PEs prepared by spray pyrolysis (SP-PEs), coupled to four HIT Si cells in a tandem arrangement, and then using four 50 cm^2 multi-PE windows, each containing eight nanostructured $\alpha\text{-Fe}_2\text{O}_3$ PEs with $2.4 \times 2.3 \text{ cm}^2$.

During continuous operation under concentrated sunlight, provided by a linear Fresnel reflector with 22 active mirrors (max. $12.8 \text{ kW}\cdot\text{m}^{-2}$ reaching the surface of the PEs), 50 cm^2 $\alpha\text{-Fe}_2\text{O}_3$ PEs generated current densities within the range of 0.2 to $0.5 \text{ mA}\cdot\text{cm}^{-2}$ at 1.6 V, whereas multi-PEs reached a photocurrent density of ca. $4.0 \text{ mA}\cdot\text{cm}^{-2}$. During *J-t* measurements carried out over 2 days, multi-PEs generated a stable current density of ca. $2.0 \text{ mA}\cdot\text{cm}^{-2}$ at 1.45 V.

One of the main objectives of using multi-PE windows was to achieve higher STH conversion efficiencies under concentrated sunlight and to better understand which phenomena – charge transfer, charge separation or collection efficiency – had the most significant influence on the overall performance of the 200 cm^2 module. When the number of active mirrors was increased, the generated photocurrent followed a logarithmic saturation behaviour, which was attributed to: i) recombination losses imposed by the grain boundaries between the planar film and the $\alpha\text{-Fe}_2\text{O}_3$ nanostructures and ii) non-efficient current

collection, mainly caused by the resistance between the semiconductor and the current collector.

Finally, the work developed within chapter 5 also aimed at demonstrating the feasibility of PEC-H₂ production under concentrated sunlight in real outdoor conditions. It was observed that the developed PEC module dissipates heat efficiently, preventing the degradation of both PEC and PV components; a maximum temperature of 28.4 °C was recorded in the electrolyte near the PE outlets, considering an electrolyte temperature of 25 °C at the inlet. This achievement reinforces the importance of incorporating smart design features in the architecture of a PEC device; in this particular case, having an optimized electrolyte flow path, generated by a feeding manifold designed with CFD tools, avoided additional cooling solutions.

6.2 RECOMMENDATIONS FOR FUTURE WORK

The experimental work developed within chapter 2 should be complemented with material analyses, aiming at investigating changes in the semiconductor promoted by the harsh operating conditions over the long-term test. Such material analyses should include: i) top-view and cross-section SEM analyses for investigating morphological changes in the PE that can indicate degradation over time; ii) XPS analyses on fresh and aged samples, for investigating the presence of co-catalyst at the surface of the PE after the long-term test; iii) ICP spectroscopy for examining any material detachment from the PE, namely through the quantification of iron and cobalt concentrations in fresh electrolyte and in the electrolyte used in the stability test. Later, it would be interesting to subject a Co- α -Fe₂O₃-NC-T PE to a similar stability test, aiming at investigating which encapsulation technique (with TiO₂ or SiO₂) provides the PE with better protection against corrosion and mechanical erosion.

The hydrothermal method optimized in chapter 2 should be subject of a more targeted optimization process, namely with the use of DoE software tools. Given the promising results already published for α -Fe₂O₃ PEs prepared via hydrothermal methods, one can infer that there is still plenty of room for

improving the results reported in chapter 2. Nevertheless, the results achieved in this work are already a solid contribution for future DoE studies performed on the topic. Indeed, the experimental parameters that have a greater influence on the performance of the α -Fe₂O₃ PEs were identified, and the lower and upper limits of each relevant experimental parameter were defined.

Another interesting approach for further improving the performance of nanostructured α -Fe₂O₃ PEs relies on using other co-catalysts, especially those that have already been studied in the hosting-lab, such as dual IrO₂/RuO₂ and NiFeOH co-catalysts. Future optimization studies focusing the preparation of α -Fe₂O₃ nanocubes should also include EIS and IMPS analyses for better identifying and understanding the key factors that limit the performance of these PEs. Finally, XPS analyses should be performed for assessing the diffusion of Ti⁴⁺ and Si⁴⁺ into the lattice of hematite (promoted by the functional annealing).

The development of the multi-PE window within chapter 4 was strongly limited by the lack of experience in working with the CoolPEC cell since the latter was a totally new PEC device developed within chapter 3. Ultimately, the design of the multi-PE window was conditioned by the dimensions of the already existing CoolPEC cell. As so, the multi-PE window should be redesigned, aiming at: i) reducing the spacing needed for the internal separators; ii) developing a new strategy for inserting and fixing the PEs in the segmented support, and especially one that does not require the use of a gluing paste; iii) simplifying the electrical contacts assembled at the back for reducing light-trapping; and iv) simplifying its assembly at the back of the CoolPEC cell, envisaging a thinner support that does not block so much light for a hypothetical PV cell.

Concerning the challenge of upscaling highly efficient PEs that was launched with this work, developing ETCO collectors¹⁸ resistant to the preparation and characterization procedures used on α -Fe₂O₃ PEs would be an appealing task, namely if those collectors could be resistant to: i) the hydrothermal synthesis, which is performed in an acidic media (ca. pH=1.5), at 100 °C, for at least 6 h; ii) the two-step annealing (550 °C over 2 h and 800 °C for 20 min); and iii) the

strong alkaline electrolyte (ca. pH=13.6). If such an approach could be materialized, it would be possible to obtain a 50 cm² PE with minimized resistance to the transport of electrons; more important, it would be possible to attain a PE that fulfils large-area requirements, but that is simpler to prepare and to assemble than the multi-PE. Even so, considering only the elements obtained with this PhD work, it would be interesting to assemble the 200 cm² CoolPEC module with the α -Fe₂O₃ PEs optimized in chapter 2 and repeat the field tests under concentrated sunlight. It is also essential to take full advantage of the versatility of the developed PEC module, namely by conducting tests with other materials available in the hosting-lab, including: i) other semiconductor materials, like Ta₃N₅; ii) an integrated PV cell; iii) dual photoabsorbers, assembled in a stack configuration, *i.e.*, back- and front-illuminated PEs, working as front and back windows, respectively; and iv) tubular CEs based on half-membrane electrode assemblies (H-MEA). Further upscaling can be easily made by stacking more modules.

Overall, the main objectives specified in the underlying work plan were fully addressed. As so, this work provides the field of PEC-H₂ production with solid contributions, since pioneering technical solutions were successfully integrated into upscaled PEC devices, tackling all the three-pillar – efficiency, stability, and scalability – criteria required to turn this technology competitive in the energy market.

6.3 CLOSING REMARKS ON GREEN-H₂ PRODUCTION

Green-H₂ already won the reputation of “key player” in future energy systems; still, a critical question remains: will PEC water splitting be able to compete with other green-H₂ production technologies?

Most studies on PEC-H₂ production agree that the major challenge for the near future is the scalability of PEC devices.^{3, 10, 19} To reach a similar H₂ output as PV-electrolysis, the active area of PEC devices has to be at least 50 times larger.³ Additionally, efficient devices will require serious advances in the chemical stability of photoactive materials, ideally for achieving 10000 h of reproducible

performance; also, materials engineering at the nanoscale must be optimized for achieving reproducible structures across such macroscopic areas. If these targets are not met in the next decade, long-term PEC-H₂ production technologies will tend to become a subset of PV-EC devices.²⁰

Viable PEC architectures must deliver H₂ at a cost equal to or lower than available PV-EC systems and cannot be based on components that are also used to fabricate PV-EC devices. Indeed, decoupling the light-absorption and water splitting functions in solar-H₂ devices has fundamental advantages, arising from increased flexibility in the design, since each component (*i.e.* the light-absorber and water-splitting units) can be independently engineered and optimized, leading to higher modularity and lower electrolyte-degradation issues.²¹ For example, in PEC devices, detailed and clever design features are required for minimizing shading, light scattering and occlusion of electrocatalytic sites due to evolved gas bubbles. Also, catalysts used in PEC water splitting can be integrated with the photoabsorber but, contrary to AEC, the catalyst must be transparent, chemically stable, compatible with the photoabsorber, and cost-competitive with the best available electrocatalysts. On the other hand, PEC devices benefit from the integration of light absorbers with electrolysis technologies, with no peripheral electronics, especially in tandem architectures, which have higher theoretical efficiencies than silicon PV-electrolysers.¹⁶ For these reasons, the competitiveness of PEC water splitting must focus its environmental and functional advantages.

The third decade of the 21st century started with a coronavirus pandemic and world-leading countries are looking at whether the resulting economic turmoil wrought by unprecedented restrictions have muffled the determination to implement key changes in the energy market. Fortunately, and surprisingly, some organizations have interpreted this situation as a great opportunity to carry out such changes. As an example, the European Commission proposed a recovery package with a distinctly green tinge of 1.8×10^{12} € (2.1×10^{12} US\$), running on 2021-27, alongside an estimated 1.0×10^{12} € of private sector investment, to make the green transition in the energy market.²² In a recent

report, the EU Commission states that green-H₂ is a key priority to achieve the European Green Deal, since H₂ ensures backup for seasonal variations and connects production locations to distant demand centers, while replacing fossil fuels in some carbon-intensive industrial processes, namely the steel and chemical industries.

The EU Commission clearly states that large-scale deployment of green-H₂ is mandatory for reducing GHG emissions towards 55 % by 2030, in a cost-effective way, which requires²²: i) further research and innovation efforts, in the range of GW, with mass manufacturing capabilities able to supply H₂ to large consumers; solutions at lower technology readiness level will also be encouraged, namely H₂ production from marine algae, from PEC water splitting, and from pyrolysis processes; ii) infrastructure to distribute, store and dispense H₂ at large volumes and over long distances, including the repurposing of existing gas infrastructure; iii) the optimization of large-scale end-use applications for the successful incorporation of H₂-based technologies, notably in heavy-duty road, rail, waterborne and aviation transportation; iv) the development of reliable methodologies for assessing the environmental impacts of H₂-technologies; and v) an increase in the share of hydrogen in EU's energy, from the current less than 2 % to 13-14 %.

At present, neither renewable- nor low-carbon-H₂ production technologies are cost-competitive against fossil-based-H₂; estimated costs for fossil-based-H₂ with carbon capture and storage are ca. 2 €/kg, and for renewable-H₂ are ca. 2.5-5.5 €/kg⁻¹, far from the 1.5 €/kg⁻¹ of fossil-fuel-based H₂. Still, green-H₂ projects at the MW scale are taking place all around the world at an exponential rate. For example, in Fukushima, Japan, a 10 MW electrolyser is being built to provide 900 ton H₂·year⁻¹ for transport applications, using a 20 MW solar-PV plant as the main energy supplier; in Australia, a 50 MW solar/wind electrolyser is being developed as part of a new Hydrogen Hub, to be built near Crystal Brook; in Victoria, Canada, 120 MW worth of renewable H₂ (primarily supplied by wind, augmented by hydropower) will be inserted into the main natural gas line, equivalent to reducing the natural gas consumed in Metro Vancouver by 10 %.²³

The field of renewable-H₂ production is experiencing an unparalleled economic stimulus, which will allow bridging lab-scale research with commercial interests. With the feet on the ground, the best way to move forward is to accept, at first, that PEC devices will need to operate very close to their fundamental thermodynamic limits, at large-scale.^{24, 25} This will imply a solid convergence between academics and the industry; self-centered ambitious goals involving the use of scarce and expensive materials, together with very complex techniques must be left aside.

During the remainder first half of the 21st century, research efforts within the PEC water splitting field should be directed to: i) build and demonstrate PEC prototypes incorporating innovative architectures, clever design features, and promising materials, such as centralized H₂ production via separate-electrode cells, noble metal-free CEs and catalysts, *etc.*; ii) prepare large PEs with an active area $\geq 1 \text{ m}^2$, displaying low electronic losses across the transparent substrates, namely by developing embedded current collectors or multi-PE windows; iii) develop preparation techniques that can be easily implemented at an industrial scale; iv) enhance the chemical stability of large-area PEs targeting tens of thousands hours of stable operation; v) develop modular PEC panels with optimized thermal and power management, comprising a low-cost, durable and eco-friendly embodiment; vi) investigate and develop new approaches for coupling solar concentrators with PEC devices, integrated into a single unit (*e.g.* in the window of a PEC cell) or associated in separate structures (*e.g.* with linear Fresnel reflectors); and vii) reach consensual standards for evaluating the performance of PEC devices, including environmental and techno-economic criteria. If these targets are not met in the next decade, the feasibility of PEC-H₂ production technologies will be seriously compromised and the topic will tend to become another promising subject studied by the scientific community, but without any practical application in society.²⁴ The incorporation of PEC-H₂ production in the energy market will be a gradual process and it should not aim at dethroning existing technologies but aspire instead to be part of a symbiotic integration, as envisioned in Figure 6.1.

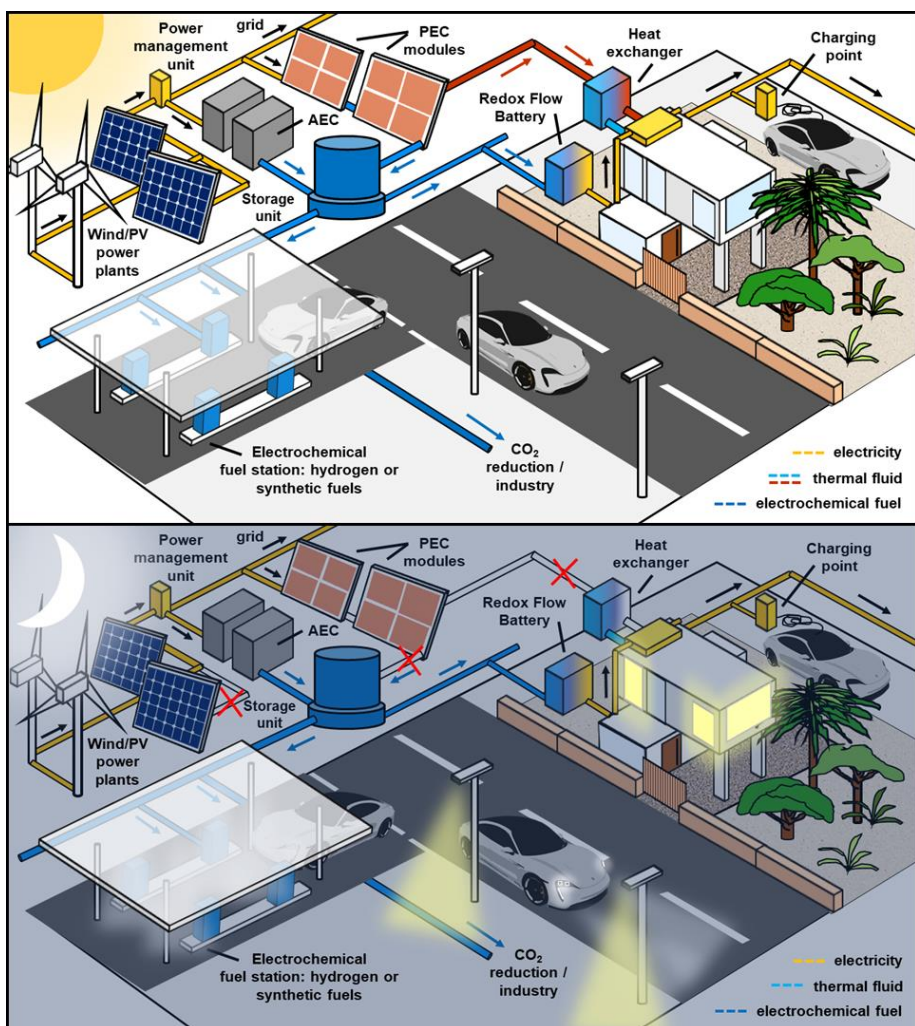


Figure 6.1. Hypothetical scenario of the integration of PEC-H₂ production in the energy market, comprising the electrical, thermal and fuel flows for day and night periods.

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ANNEX

1 APPENDIX 1

Number of publications of the most studied PE materials for PEC water splitting

Appendix 1-a. Number of publications of the most studied semiconductors for PEC water splitting devices including that include one of the keywords “water splitting”, “photoanode”, “photoanodes”, “photoelectrochemical”, “PEC”, and “solar hydrogen”, together with the semiconductor material, written using the chemical formula or the full name, obtained from the Google scholar database, and grouped into 4 specific periods; e.g. “Fe₂O₃ water splitting”, “hematite water splitting”.

Keyword → Material ↓	“chemical formula” + keyword						“full name of the material” + keyword						TOTAL
	water splitting	photoanode	photoanodes	photoelectrochemical	solar hydrogen	PEC	water splitting	photoanode	photoanodes	photoelectrochemical	solar hydrogen	PEC	
1972-1999													
WO ₃	0	1	2	8	0	0	0	2	0	10	0	1	24
Fe ₂ O ₃	2	0	2	13	0	0	0	0	0	5	0	0	22
BiVO ₄	0	0	0	0	0	0	0	0	0	0	0	0	0
Cu ₂ O	1	0	2	9	0	0	0	5	0	5	0	0	22
Ta ₃ N ₅	0	0	0	0	0	0	0	0	0	0	0	0	0
TiO ₂	7	11	23	177	3	1	3	1	5	54	3	0	288
MoS ₂	1	0	1	8	0	0	0	0	1	0	0	0	11
ZnFe ₂ O ₄	0	0	0	0	0	0	0	0	0	0	0	0	0

2000-2009													
WO ₃	5	1	1	4	1	2	5	0	4	6	0	1	30
Fe ₂ O ₃	21	2	7	27	2	3	6	3	3	14	1	1	90
BiVO ₄	4	0	1	6	0	3	0	0	0	0	0	0	14
Cu ₂ O	1	3	1	7	0	0	0	0	0	4	0	0	16
Ta ₃ N ₅	0	0	0	0	0	0	0	1	0	0	0	0	1
TiO ₂	93	26	28	301	15	13	5	2	1	52	10	0	546
MoS ₂	0	0	0	1	0	0	0	0	0	0	0	0	1
ZnFe ₂ O ₄	1	0	0	2	1	0	0	0	0	0	0	0	4
2010-2015													
WO ₃	23	11	20	46	3	0	11	4	5	20	0	0	143
Fe ₂ O ₃	70	23	34	102	4	1	192	44	66	163	5	7	711
BiVO ₄	49	15	25	52	1	0	18	6	11	19	1	0	197
Cu ₂ O	20	12	2	57	5	2	12	2	4	10	0	0	126
Ta ₃ N ₅	21	7	5	9	0	1	8	3	4	3	0	2	63
TiO ₂	337	251	223	703	55	7	12	26	15	56	9	0	1694
MoS ₂	8	1	0	17	3	2	3	0	0	2	2	0	38
ZnFe ₂ O ₄	4	0	1	6	1	0	0	0	0	1	0	0	13
2016-2020													
WO ₃	58	17	18	75	4	1	9	5	6	9	0	0	202
Fe ₂ O ₃	96	51	43	150	4	2	233	109	156	262	5	16	1127
BiVO ₄	226	172	155	295	5	10	44	22	33	42	3	3	1010
Cu ₂ O	64	36	143	11	5	13	6	5	27	4	1		315
Ta ₃ N ₅	29	12	15	13	2	1	11	2	3	6	2	0	96
TiO ₂	500	438	228	944	98	22	32	34	10	61	4	0	2371
MoS ₂	107	14	4	76	22	0	12	0	0	17	2	0	254
ZnFe ₂ O ₄	18	6	4	19	1	1	6	4	2	4	0	0	65

State-of-the-art PEs considering the so-called “classic” materials for solar water splitting

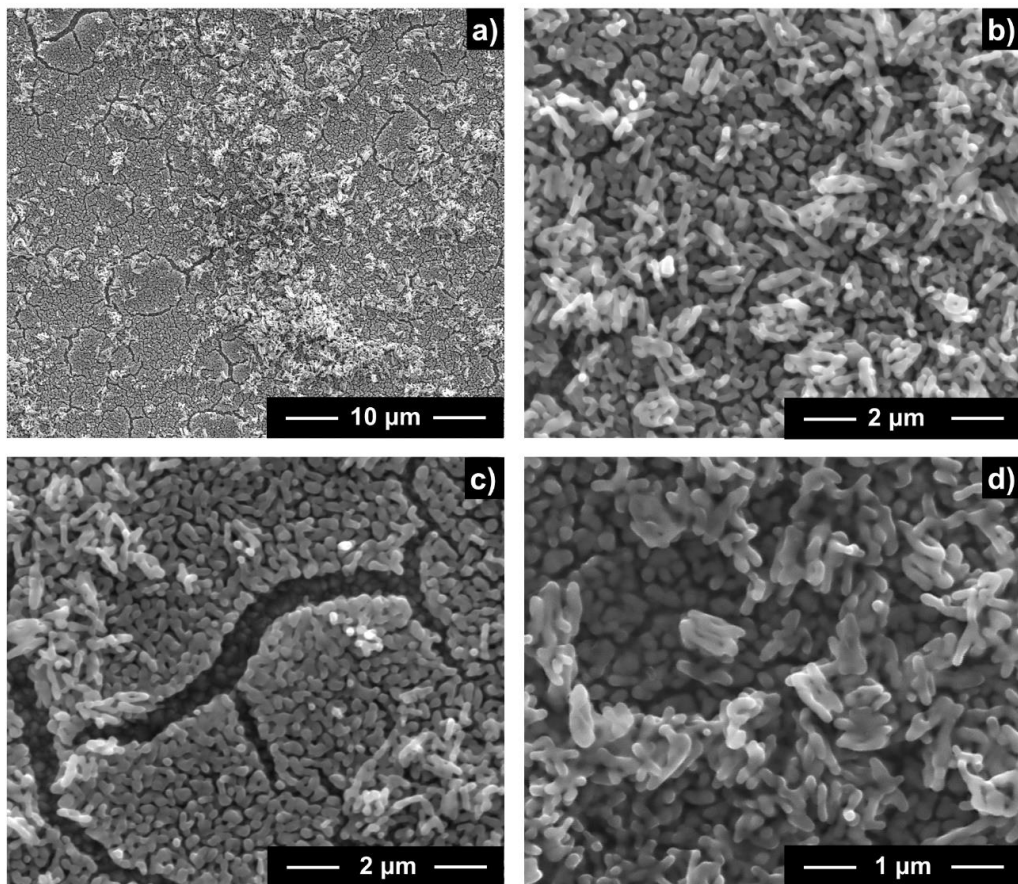
Appendix 1-b. Photoelectrodes of the so-called “classic” materials for solar water splitting (α -Fe₂O₃, BiVO₄, WO₃ and Cu₂O PEs) that established a state-of-the-art result (highlighted in red), with the corresponding performance ranking, based on the active area, stability and current density generated at a reference potential (1.23 V for α -Fe₂O₃, BiVO₄ and WO₃; 0 V for Cu₂O); normalization considered equal relevance for each criterion, delivering a total score out of 100, *i.e.* equal 33.3(3) % contribution for the active area, stability and current density; targets for each criterion were defined as follows: i) an active area of 100 cm²; ii) 2920 h of stable performance (8 hours over 365 days); iii) and a current density of 10 mA·cm⁻².

	PE with a state-of-the-art result	Active area		Stability		Photocurrent density	
		cm ²	1/3 · % (out of 100)	h	1/3 · % (out of 2920)	mA·cm ⁻²	1/3 · % out of 10
α -Fe ₂ O ₃	Vilanova <i>et al.</i> 2020 ¹	200	33.3	48	0.55	2	6.67
	Vilanova <i>et al.</i> 2018 ²	50	16.7	1008	11.5	0.25	0.83
	Jeon <i>et al.</i> 2017 ³	2	0.67	100	1.14	6	20.0
BiVO ₄	Ahmet <i>et al.</i> 2019 ⁴	50	16.7	0	0.00	1.5	5.00
	Kuang <i>et al.</i> 2016 ⁵	25	8.33	100	1.14	2.2	7.33
	Kosar <i>et al.</i> 2016 ⁶	0.16	0.05	1	0.01	6.72	22.4
WO ₃	Lee <i>et al.</i> 2011 ⁷	130.6	33.3	0	0.00	1.18	3.93
	Reinhard <i>et al.</i> 2016 ⁸	0.28	0.09	20	0.23	3.5	11.7
	Reinhard <i>et al.</i> 2016 ⁸	0.28	0.09	20	0.23	3.5	11.7
Cu ₂ O	PECDEMO report ⁹	50	16.7	0	0.00	3.7	12.3
	Luo <i>et al.</i> 2016 ¹⁰	0.5	0.17	57	0.65	10	33.3
	Luo <i>et al.</i> 2016 ¹⁰	0.5	0.17	57	0.65	10	33.3

1. A. Vilanova, P. Dias, J. Azevedo, M. Wullenkord, C. Spenke, *et al.*, *Journal of Power Sources*, 2020, **454**, 227890.
2. A. Vilanova, T. Lopes and A. Mendes, *Journal of Power Sources*, 2018, **398**, 224-32.
3. T. H. Jeon, G.-h. Moon, H. Park and W. Choi, *Nano Energy*, 2017, **39**, 211-8.
4. I. Y. Ahmet, Y. Ma, J.-W. Jang, T. Henschel, B. Stannowski, *et al.*, *Sustainable Energy & Fuels*, 2019.
5. Y. Kuang, Q. Jia, G. Ma, T. Hisatomi, T. Minegishi, *et al.*, *Nature Energy*, 2016, **2**, 1-9.
6. S. Kosar, Y. Pihosh, I. Turkevych, K. Mawatari, J. Uemura, *et al.*, *Japanese journal of applied physics*, 2016, **55**, 04ES1.
7. W. J. Lee, P. S. Shinde, G. H. Go and E. Ramasamy, *International journal of hydrogen energy*, 2011, **36**, 5262-70.
8. S. Reinhard, F. Rechberger and M. Niederberger, *ChemPlusChem*, 2016, **81**, 935.
9. Final Report Summary - PECDEMO, European Commission, 2017, vol. 2020.
10. J. Luo, L. Steier, M.-K. Son, M. Schreier, M. T. Mayer, *et al.*, *Nano letters*, 2016, **16**, 1848-57.

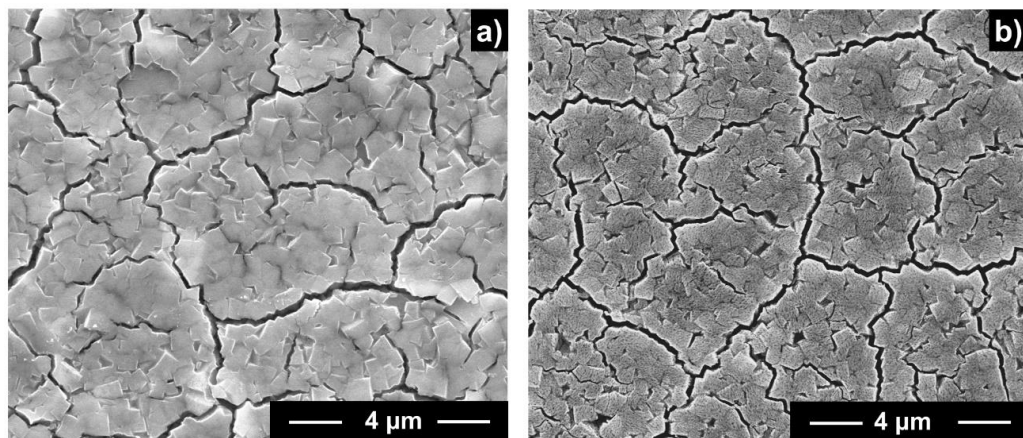
2 APPENDIX 2

Top-view SEM images of α -Fe₂O₃ nanoworms prepared with a hydrothermal method



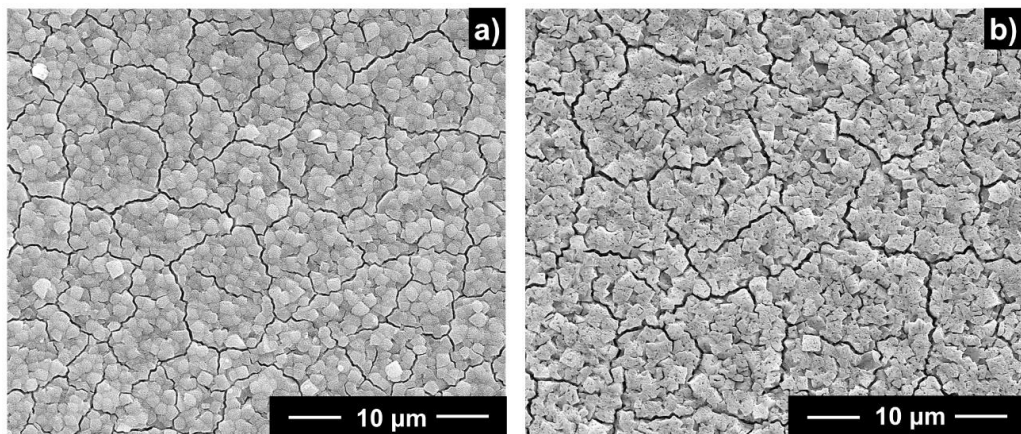
Appendix 2-a. Top-view SEM images of α -Fe₂O₃ nanoworms prepared with the same experimental conditions defined for the preparation of α -Fe₂O₃ nanocubes, but without the addition of fluoride to the precursor solution used in the hydrothermal synthesis; a) mag. 10 000 x; b) and c) mag. 50 000 x; d) mag. 75 000 x.

“Dry mud” appearance of α -Fe₂O₃ PEs



Appendix 2-b. Top-view SEM images of α -Fe₂O₃-NC-S PEs obtained with a magnification of 25 000 x; a) before removing the SiO₂ scaffold; b) after removing the SiO₂ scaffold.

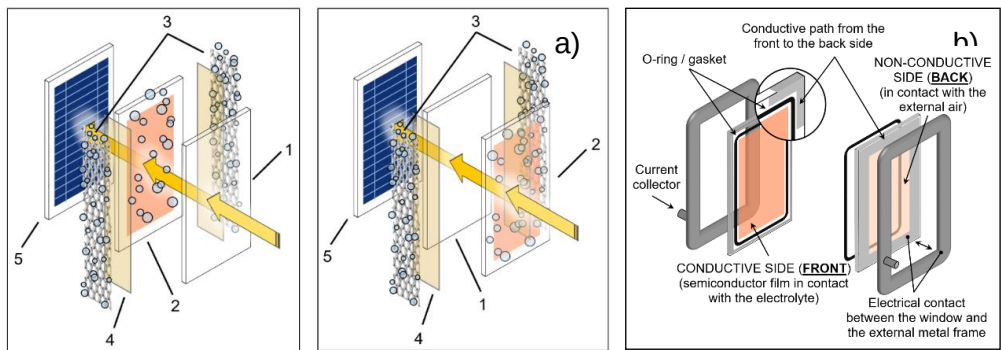
Uniformity of the α -Fe₂O₃ film



Appendix 2-c. Top-view SEM images of α -Fe₂O₃-NC-S PEs obtained with a magnification of 10 000 x; a) hydrothermal synthesis during 6:00 h at 95 °C with a precursor solution containing FeCl₃ 0.15 M, NH₄F 0.05 M, and TiF₄ 0.2 % Ti/Fe, followed by the morphological annealing (550 °C, for 2 h), TiO₂ encapsulation (TiCl₄·2THF 40 mM, at 70 °C for 30 min), and functional annealing (800 °C for 20 min); b) hydrothermal synthesis during 6:00 h at 95 °C with a precursor solution containing FeCl₃ 0.15 M, NH₄F 0.05 M, and TiF₄ 0.2 % Ti/Fe, followed by the morphological annealing (550 °C, for 2 h), SiO₂ encapsulation, and functional annealing (800 °C for 20 min).

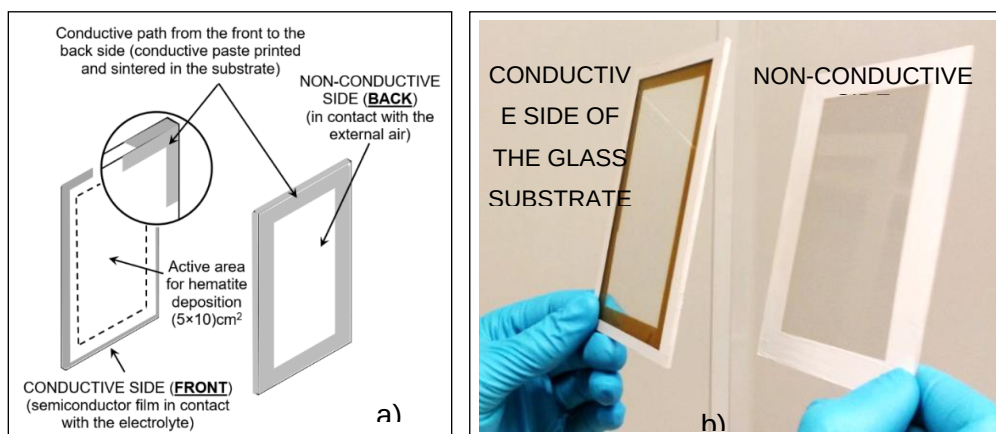
3 APPENDIX 3

Improved key features of the proposed PEC cell design



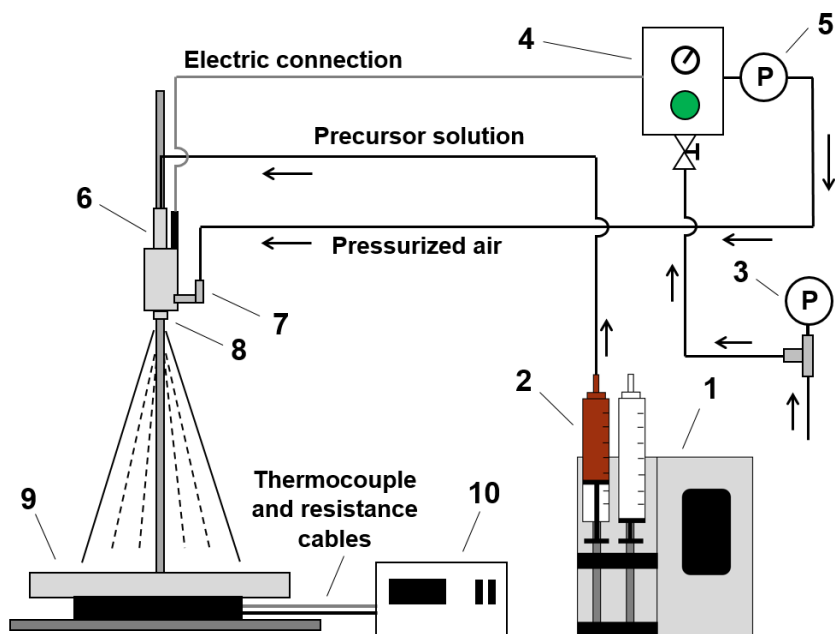
Appendix 3-a. Improved key features of the proposed PEC cell design: a) conceptual design of the envisioned arrangement of electrodes considering front [left-side] or back [right-side] illumination with the CEs placed side-by-side to the PE and physically separated by an ionic exchange membrane; 1 – glass window; 2 – photoelectrode (WE); 3 – CEs; 4 – ionic exchange membrane; 5 – PV cell; b) conceptual design of the envisioned strategy to have a PE that is simultaneously one of the windows of the cell.

FTO glass substrate with a conductive metal frame



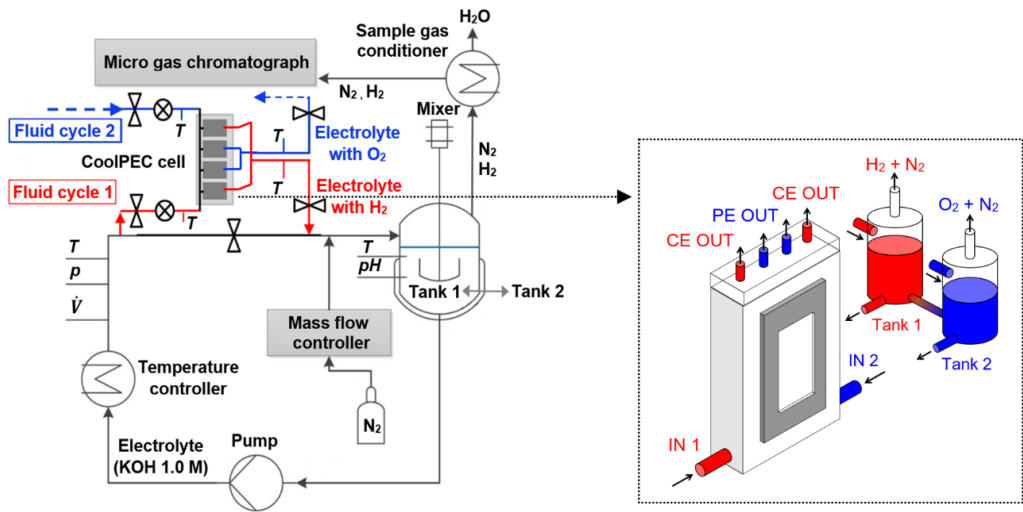
Appendix 3-b. Glass substrate with a conductive metal frame: (a) schematic representation of the printed metal frame on the FTO substrate; (b) photo of the in-house prepared substrate with the printed metal frame after sintering and annealing, ready for the $\alpha\text{-Fe}_2\text{O}_3$ film deposition.

Spray pyrolysis setup



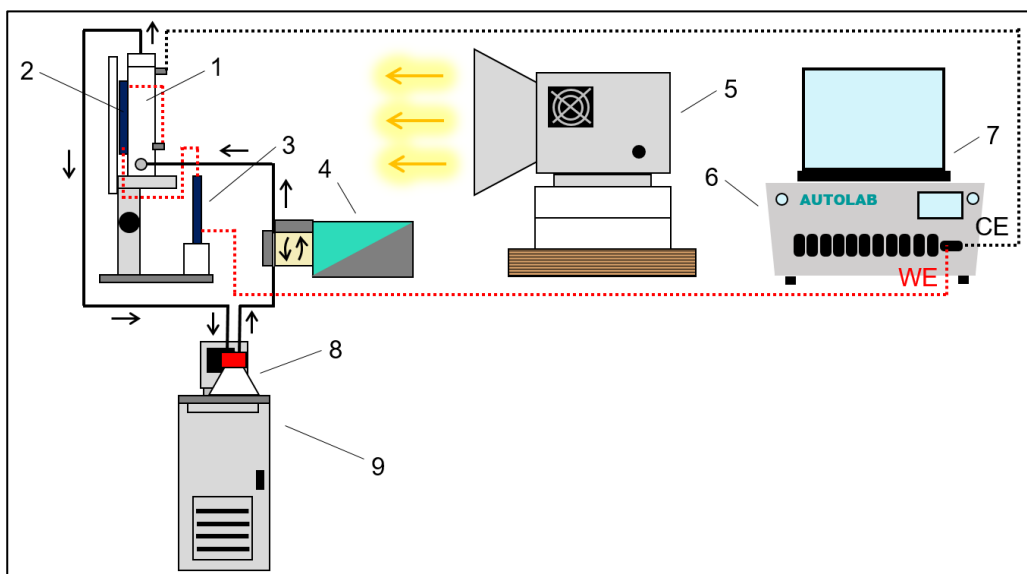
Appendix 3-c. Schematic representation of the spray pyrolysis setup used in the preparation of thin $\alpha\text{-Fe}_2\text{O}_3$ films: dual syringe pump (Cronus Sigma 2000 Dual Syringe Pump); 2 – plastic syringes; 3 – pressurized air inlet; 4 – control box for the air feeding to the spray nozzle; 5 – pressurized air outlet; 6 – Precursor solution inlet; 7 – pressurized air inlet; 8 – spray nozzle; 9 – heating plate; 10 – temperature control box.

Schematic representation of the CoolPEC cell, fluid cycles and auxiliary equipment in the SoCRatus test facility



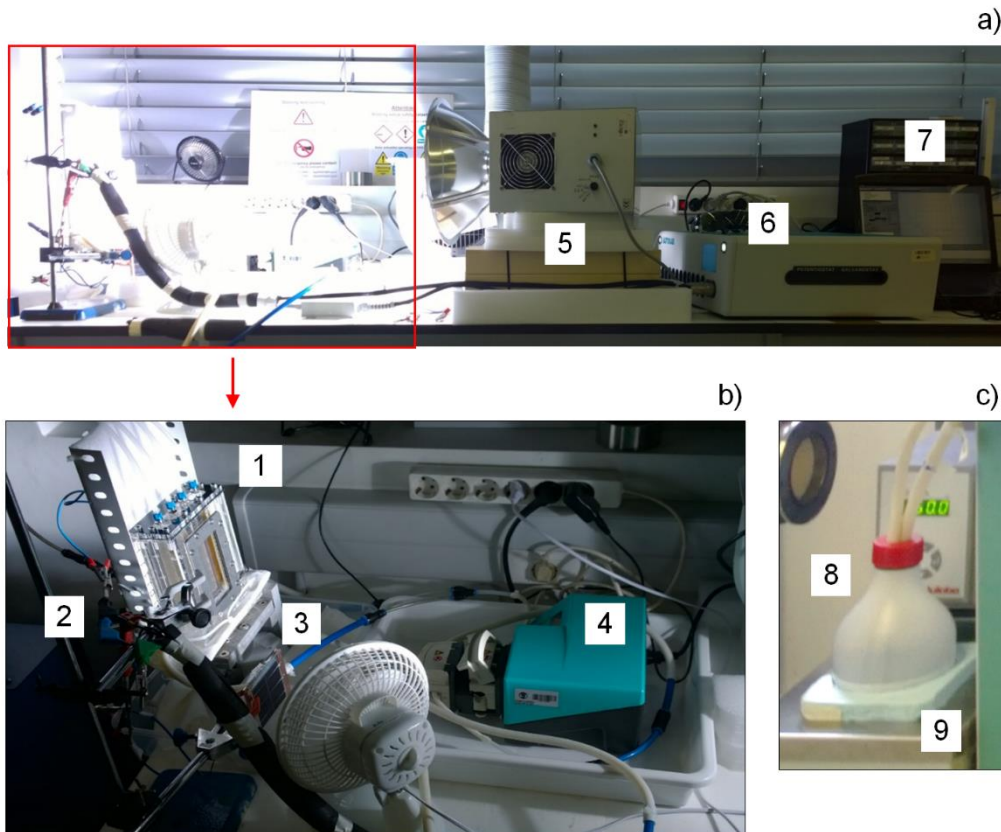
Appendix 3-d. CoolPEC cell, fluid cycles and auxiliary equipment in the SoCRatus unit; for readability, only Fluid cycle 1 (hydrogen) is illustrated.

Schematic representation of the test bench used in the long-term stability measurements



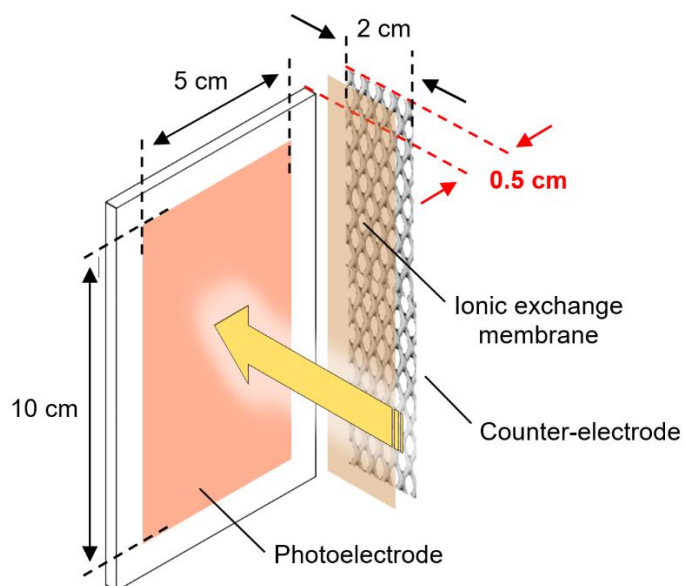
Appendix 3-e. Test bench assembled to perform the long-term stability test: 1 – CoolPEC cell; 2 – PV cell; 3 - auxiliary PV cell; 4 – peristaltic pump; 5 – Sulphur plasma lamp system AS 1300 V 2.0, Plasma International GmbH; 6 – Autolab/PGSTAT302N workstation; 7 – data acquisition software (Nova version 1.11); 8 – electrolyte container; 9 – water bath (Julabo F12 EH).

Test bench used in the long-term stability measurements



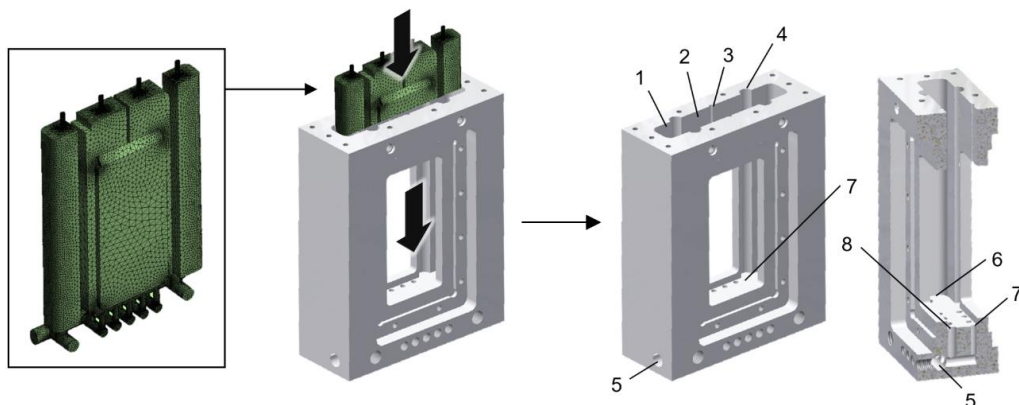
Appendix 3-f. Test bench assembled to perform the long-term stability test: a) general overview of the test bench; b) zoomed view of the equipment under illumination; c) zoomed view on the electrolyte container; 1 – CoolPEC cell; 2 – PV cell; 3 – auxiliary PV cell; 4 – peristaltic pump; 5 – Sulphur plasma lamp system AS 1300 V 2.0, Plasma International GmbH; 6 – Autolab/PGSTAT302N workstation; 7 – data acquisition software (Nova version 1.11); 8 – electrolyte container; 9 – water bath (Julabo F12 EH).

Low-overpotential arrangement of electrodes in the CoolPEC cell



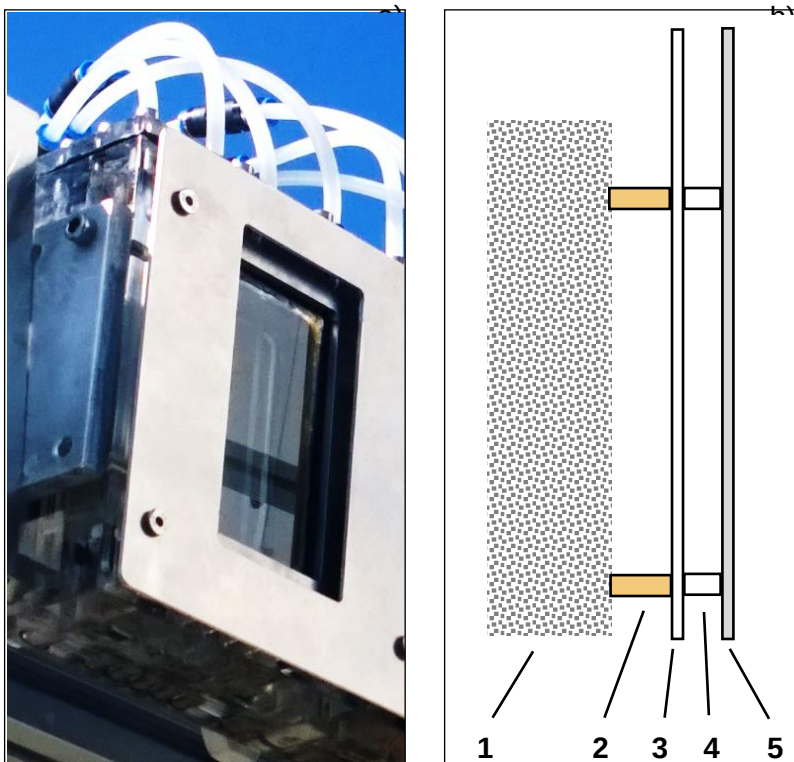
Appendix 3-g. Conceptual design of the optimal arrangement of electrodes in the developed PEC cell.

3-D Project of the CoolPEC cell



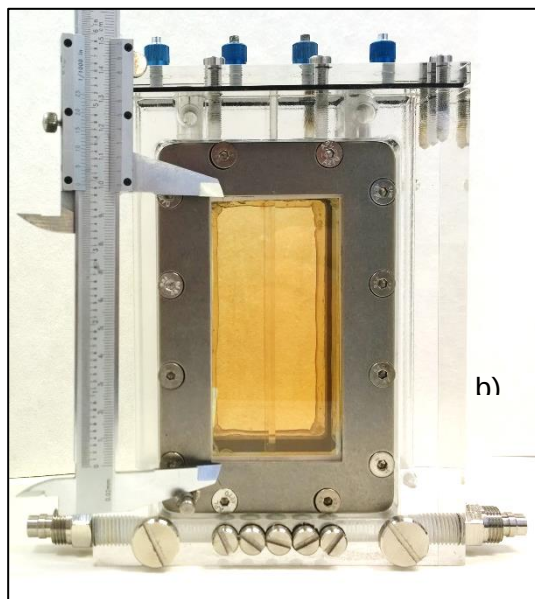
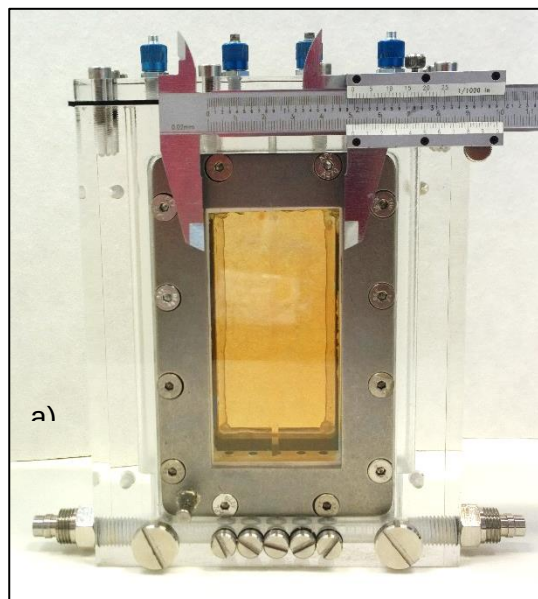
Appendix 3-h. 3-D project of the cell embodiment based on the optimized electrolyte design: 1 – CE compartment; 2 – working-electrode compartment; 3 – housing-area for the internal acrylic plate dividing the WE compartment; 4 - housing-area for the membrane holder; 5 – main electrolyte inlet ($\varnothing = 10$ mm); 6 – inlets of the CE compartments ($\varnothing = 8$ mm); 7 – inlets of the working-electrode compartment close to the front window ($\varnothing = 4$ mm); 8 – inlets of the working-electrode compartment close to the back window ($\varnothing = 6$ mm).

Protective aluminum shield for operation under concentrated sunlight



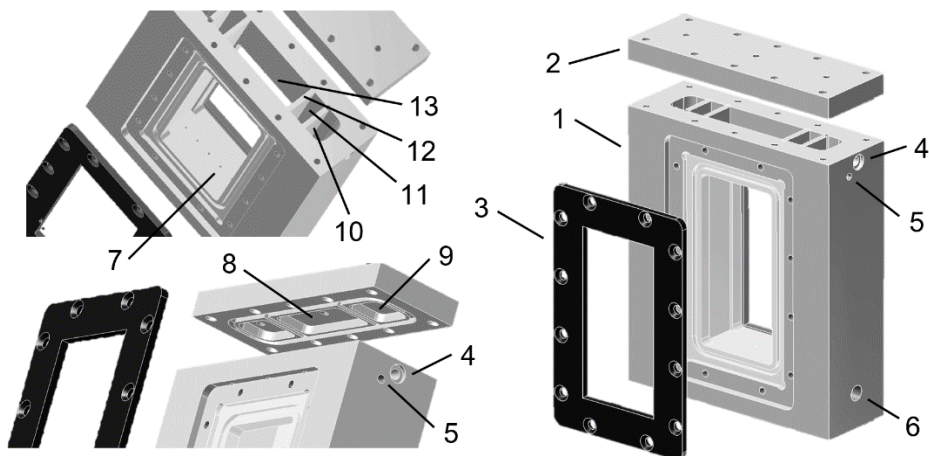
Appendix 3-i. Protective shield of the CoolPEC cell for operation under concentrated sunlight: a) CoolPEC cell assembled in the SoCRatus with the aluminium shield screwed in the front side; b) detail view of the multi-layered shield; 1 – acrylic embodiment; 2 – in-built PEEK elements to screw the PTFE shield; 3 – PTFE shield; 4 – PTFE rings to screw the aluminum shield; 5 – aluminum reflective shield.

CoolPEC cell with a scale bar



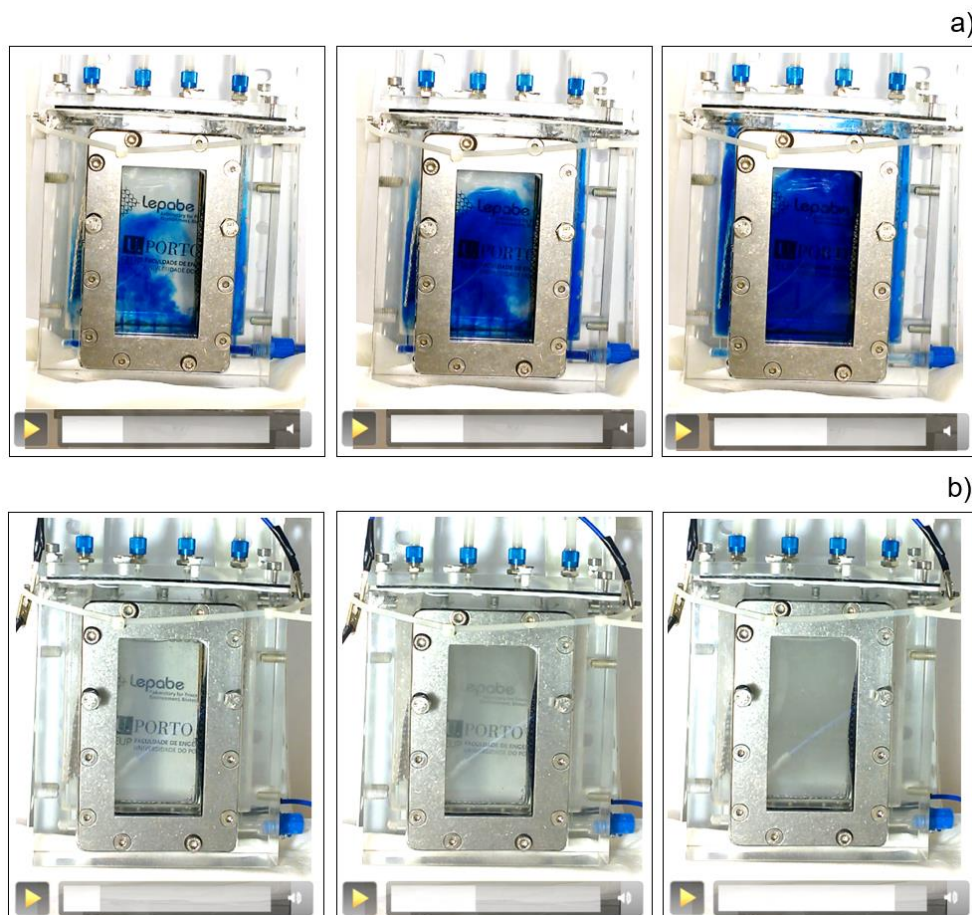
Appendix 3-j. CoolPEC cell with a scale bar, evidencing the dimensions of the 50 cm² PE.

PEC cell with continuous electrolyte feeding (non-optimized design)



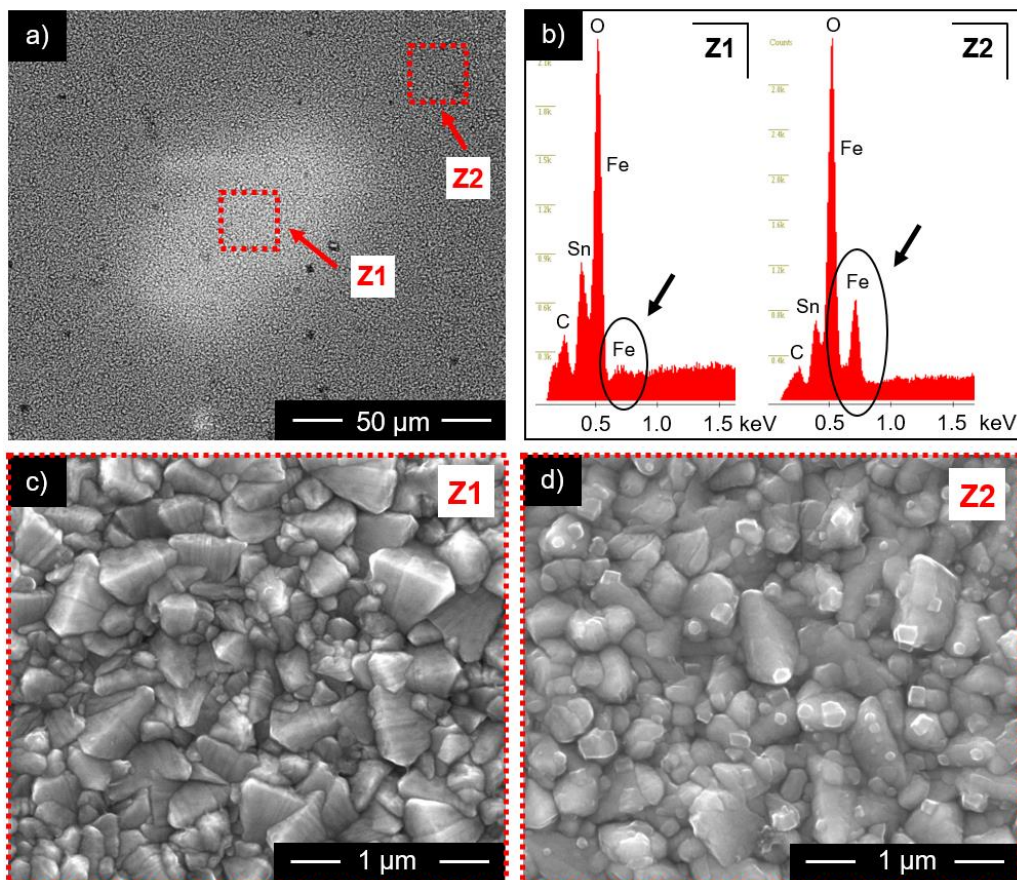
Appendix 3-k. 3-D project of a PEC cell developed previously to the CoolPEC cell, comprising a manifold electrolyte feeding system, not optimized with CFD simulations: 1 – acrylic embodiment; 2 – cover of the cell; 3 – front metallic frame; 4 – contact for the CE mesh; 5 – electrolyte outlet ($\varnothing = 3$ mm); 6 – electrolyte inlet ($\varnothing = 5$ mm); 7 – internal diffuser ($\varnothing = 1$ mm); 8 – oxygen collection chamber; 9 – hydrogen collection chamber; 10 – acrylic plate separating the hydrogen evolution zone from the electrolyte outlet; 11 – CE compartment; 12 – acrylic plate separating the hydrogen and oxygen evolution compartments; 13 – working-electrode compartment.

Tracer test and evolved gases collection in the non-optimized cell



Appendix 3-I. Experimental tests to assess the electrolyte flow path in a non-optimized cell: a) tracer test performed with a blue dye and distilled water with a feeding flow rate of $0.5 \text{ L} \cdot \text{min}^{-1}$ pictured at different instants after the injection of the dye (from left to right, 3 s, 6 s and 12 s); b) forced gas evolution at $5.4 \text{ mA} \cdot \text{cm}^{-2}$ with KOH 1.0 M and a feeding flow rate of $0.5 \text{ L} \cdot \text{min}^{-1}$ pictured at different instants after the water electrolysis was promoted (from left to right, 5 s, 20 s and 45 s).

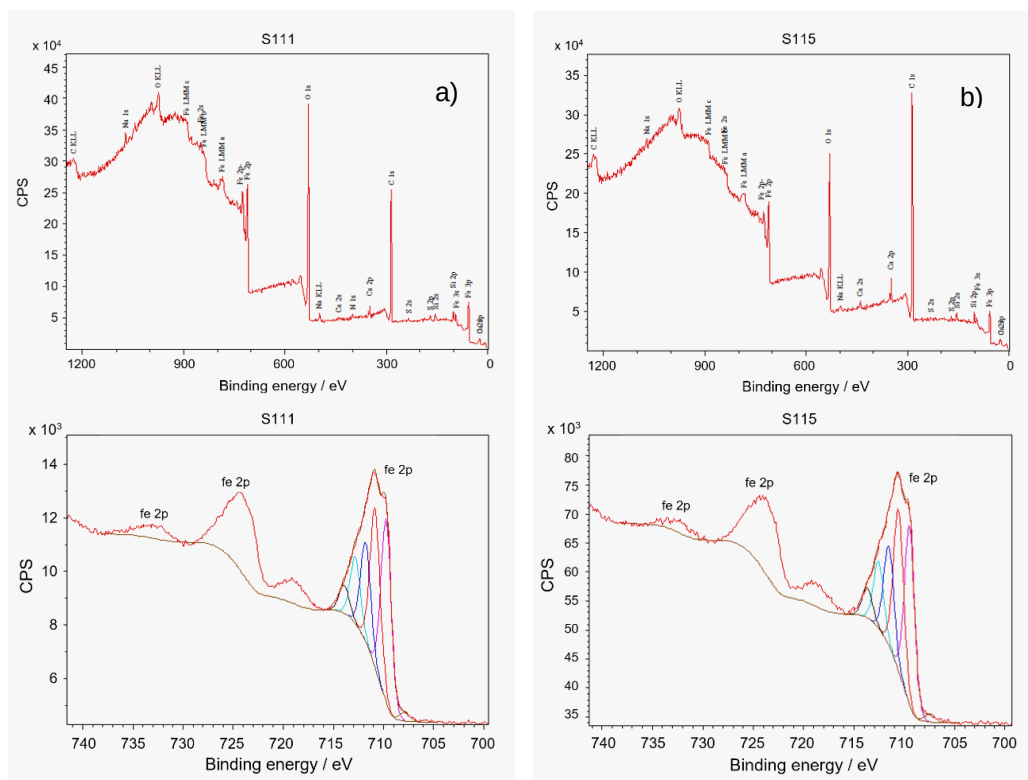
SEM and EDS analysis on a non-optimized α -Fe₂O₃ thin film submitted to a 168 h stability test



Appendix 3-m. Top-view SEM images of a non-optimized α -Fe₂O₃ thin film in-house prepared by spray pyrolysis over a FTO glass substrate aged during 168 h under 1000 W·m⁻² in 1.0 M NaOH: a) global view of the surface of the sample with the delimitation of an area where corrosion occurred (1) and an undamaged area (2); b) EDS analysis made on the two delimited zones with the identification of iron peaks; c) closer view on the area where the α -Fe₂O₃ film was corroded; d) closer view on the undamaged area.

XPS spectra of the α -Fe₂O₃ film before and after the stability test

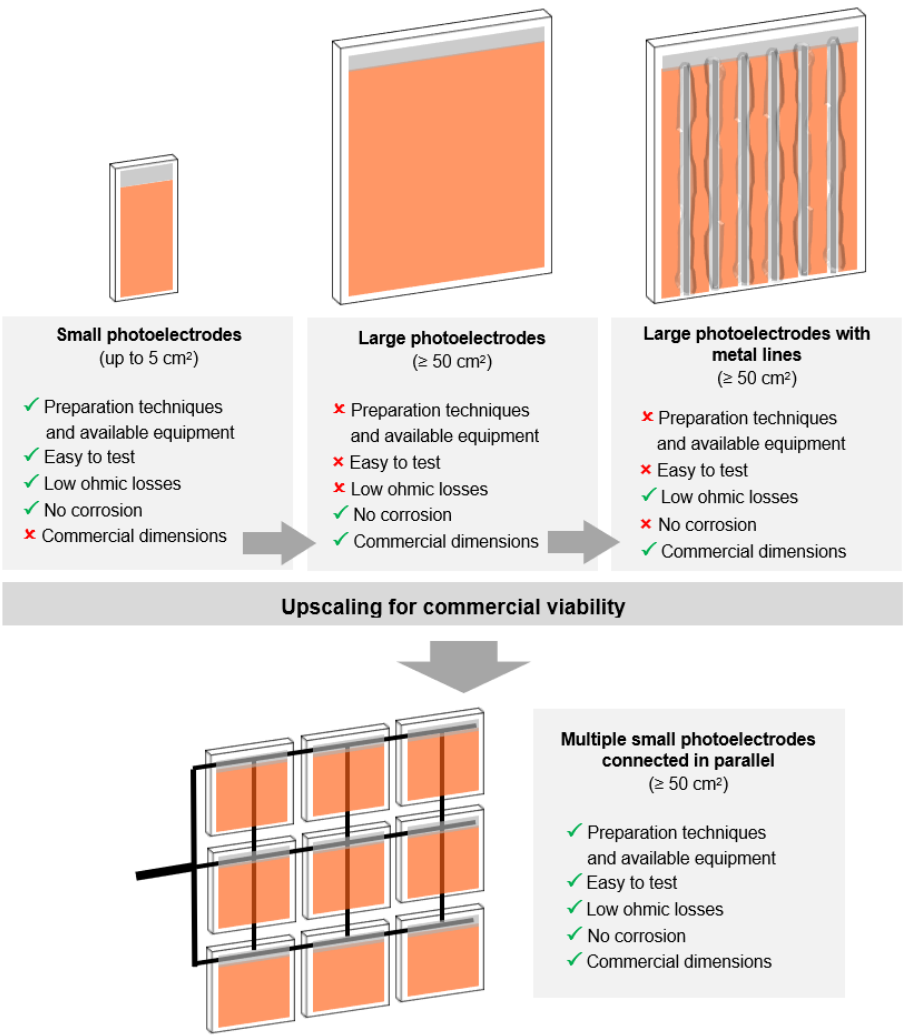
XPS spectra were acquired in an Ultra High Vacuum (UHV) system with a base pressure of 2×10^{-10} mbar located at TEMA, University of Aveiro. The system is equipped with a hemispherical electron energy analyzer (SPECS Phoibos 150), a delay-line detector and a monochromatic AlK α (1486.74 eV) X-ray source. High resolution spectra were recorded at normal emission take-off angle and with a pass-energy of 20 eV, providing an overall instrumental peak broadening of 0.5 eV. The XPS spectrum refers to the emission of photoelectrons in a material thickness between 5 and 10 nm, with an exponential weighting in the contribution of the different layers to the spectrum.



Appendix 3-n. XPS spectra of the iron oxide thin film on F:SnO₂ conducting glass prepared by spray pyrolysis; a) before [left - sample 111] and after [right – sample 115] performing the stability test over 1000 h. Global XPS spectrum is presented at the top and the Fe 2p peak spectrum is presented at the bottom.

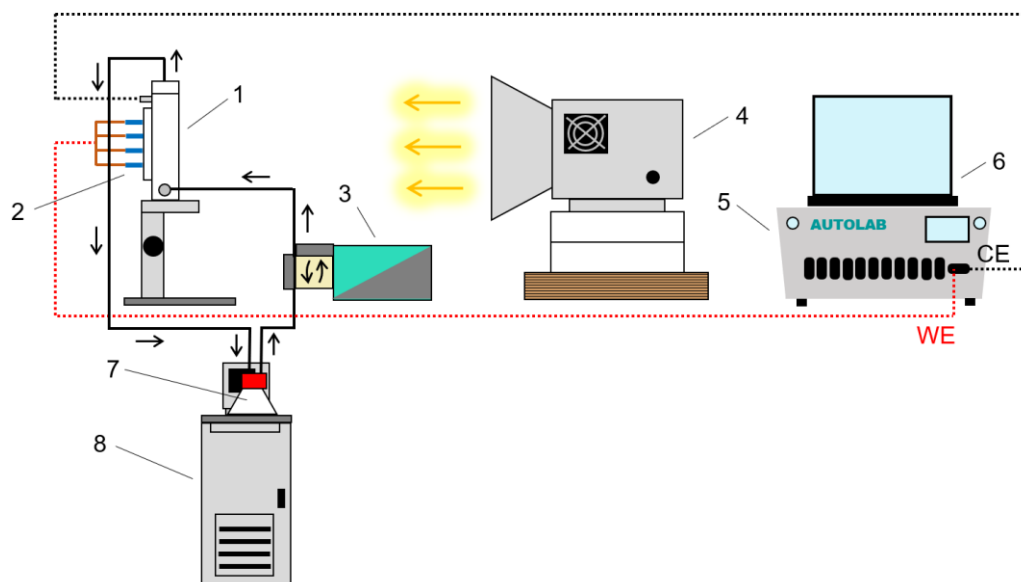
4 APPENDIX 4

Schematic representation of the multi-PE concept



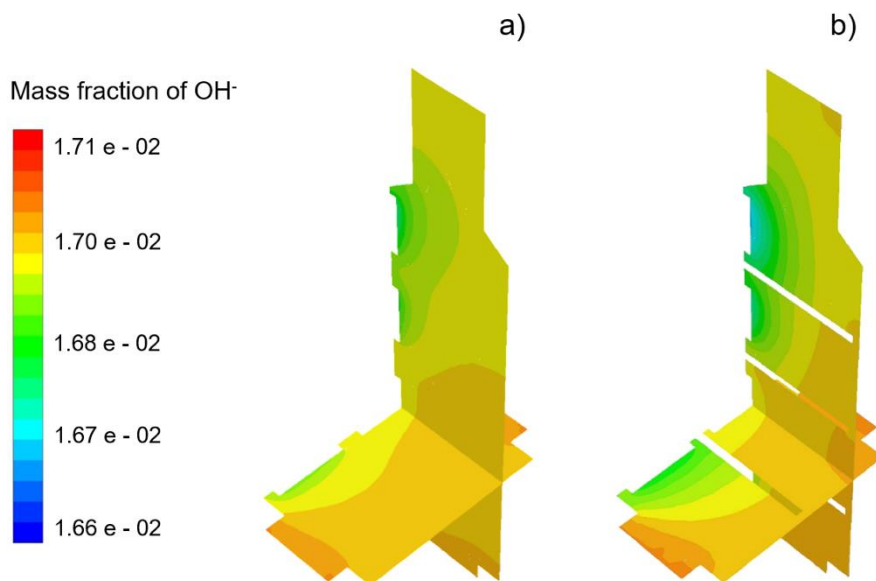
Appendix 4-a. Schematic representation of the proposed strategy for having PEC cells with a large photoactive area avoiding the common constraints that upscaling of PEs represents.

Test bench used to perform J - V measurements using the CoolPEC cell in continuous operation mode



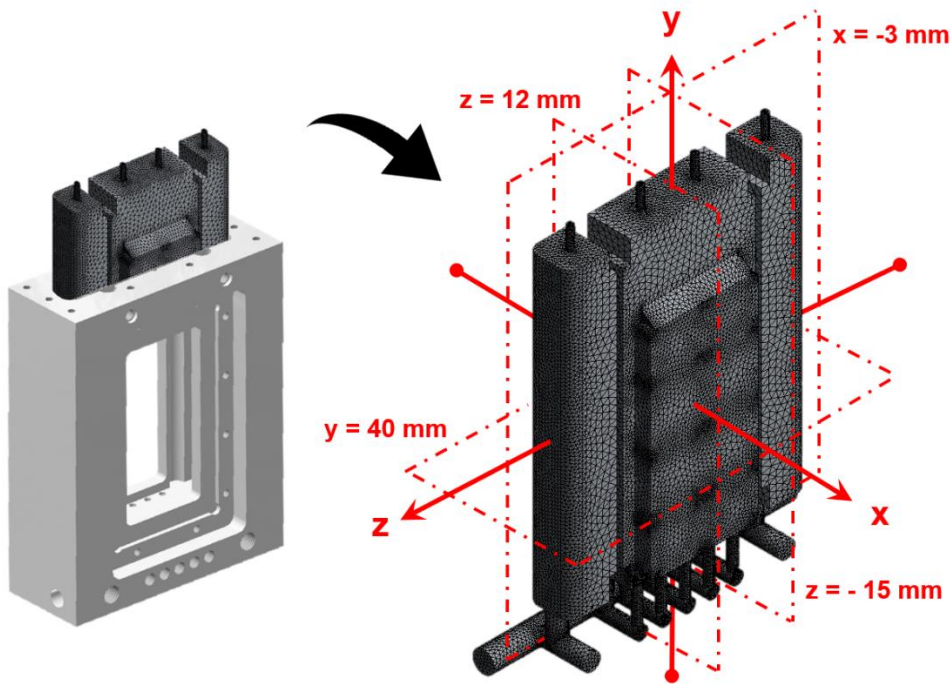
Appendix 4-b. Test bench assembled to perform J - V measurements using the CoolPEC cell in continuous operation mode: 1 – CoolPEC cell; 2 – segmented support with eight α -Fe₂O₃ PEs connected in parallel; 3 – peristaltic pump (Watson Marlow 323); 4 – Sulphur plasma lamp system AS 1300 V 2.0, Plasma International GmbH; 5 – Autolab/PGSTAT302N workstation; 6 – data acquisition software (Nova version 1.11); 7 – electrolyte container; 8 – water bath (Julabo F12 EH);

Contours of mass fraction of OH⁻ inside the CoolPEC cell



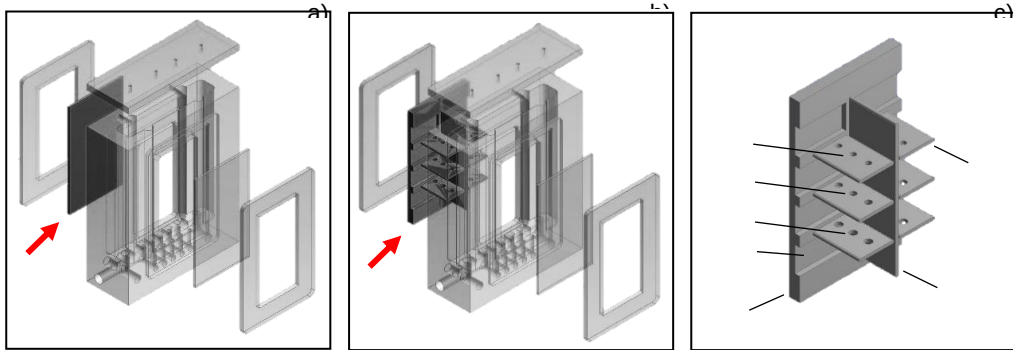
Appendix 4-c. Contours of mass fraction of OH⁻ inside the CoolPEC cell considering a feeding flow rate of 500 mL·min⁻¹ and an underperforming PE located at the crossing of represented planes; a) CoolPEC cell without internal separators; b) CoolPEC cell with internal separators. Current densities of 5 mA·cm⁻² and 1 mA·cm⁻² @ 1.45 V were assumed for healthy and underperforming PEs, respectively. Sectional planes $z = -15$ mm and $y = 40$ mm were used to visualize these results.

Sectional planes used to visualize the electrochemical reactions and the flow path inside the CoolPEC cell



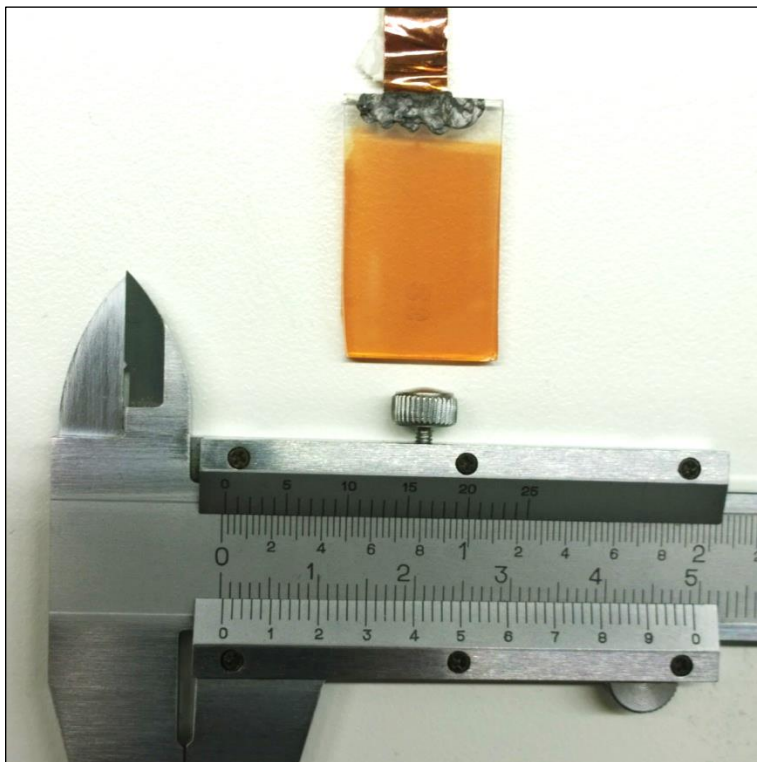
Appendix 4-d. Schematic representation of the sectional planes used to visualize the electrochemical reactions and the flow path generated by the simulator inside the electrolyte free volume of the CoolPEC cell.

3-D Project of the segmented support in the CoolPEC cell



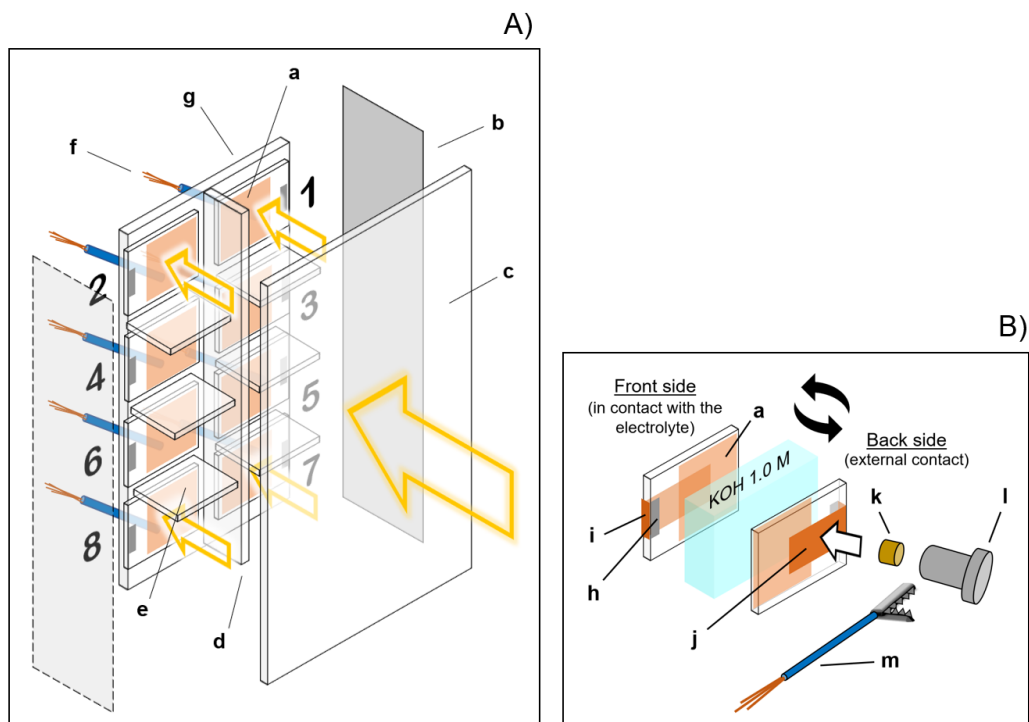
Appendix 4-e. 3-D project of the segmented support assembled in the CoolPEC cell: a) CoolPEC cell with a standard PE working as back window; b) CoolPEC cell with the segmented support replacing the standard back window; c) segmented support for holding up to 8 PEs connected in parallel: 1 – acrylic support; 2 – middle separator (acrylic); 3 – internal separator (acrylic); 4 – housing area of the PE; 5 – drills of the separators located at the bottom ($\varnothing = 4.6$ mm); 6 – drills of the separators located at the middle ($\varnothing = 4.0$ mm); 7 – drills of the separators located at the top ($\varnothing = 3.4$ mm).

Hematite PE used in the multi-PE window with a scale bar



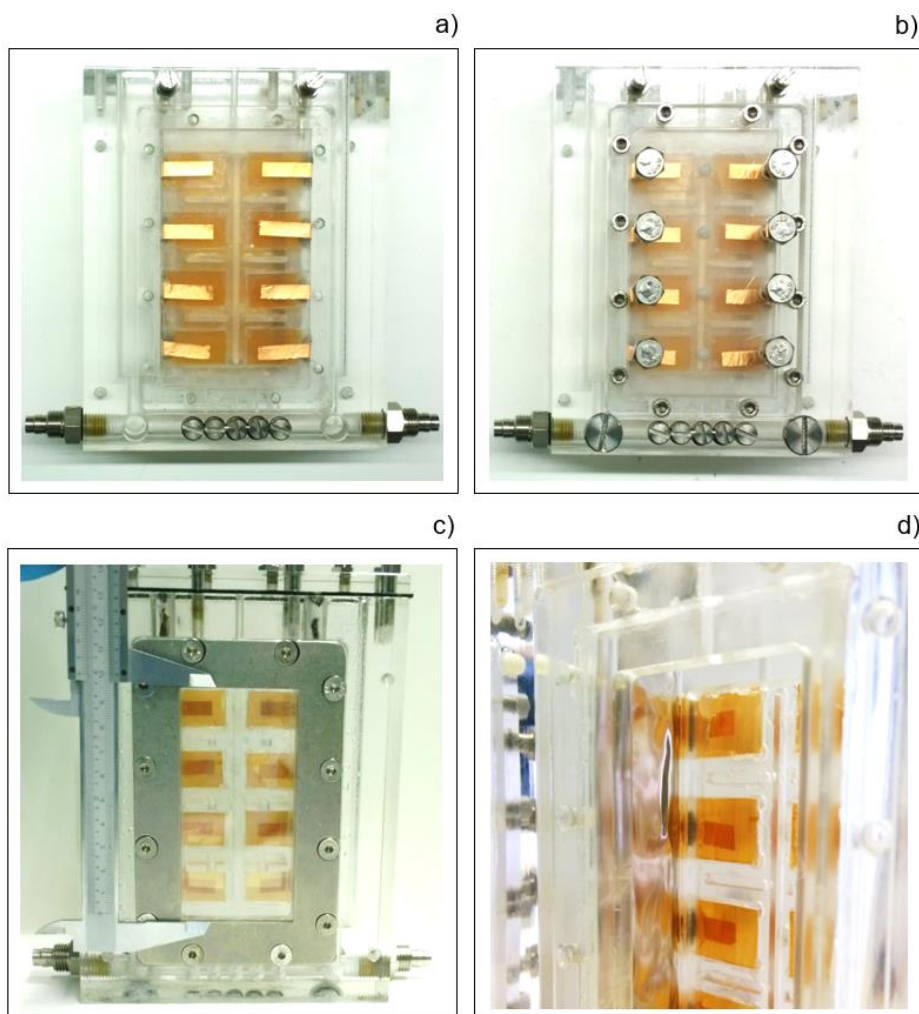
Appendix 4-f. Picture of one $\alpha\text{-Fe}_2\text{O}_3$ PE used in the segmented support aligned with a scale bar.

Segmented support with $\alpha\text{-Fe}_2\text{O}_3$ PEs – multi-PE window



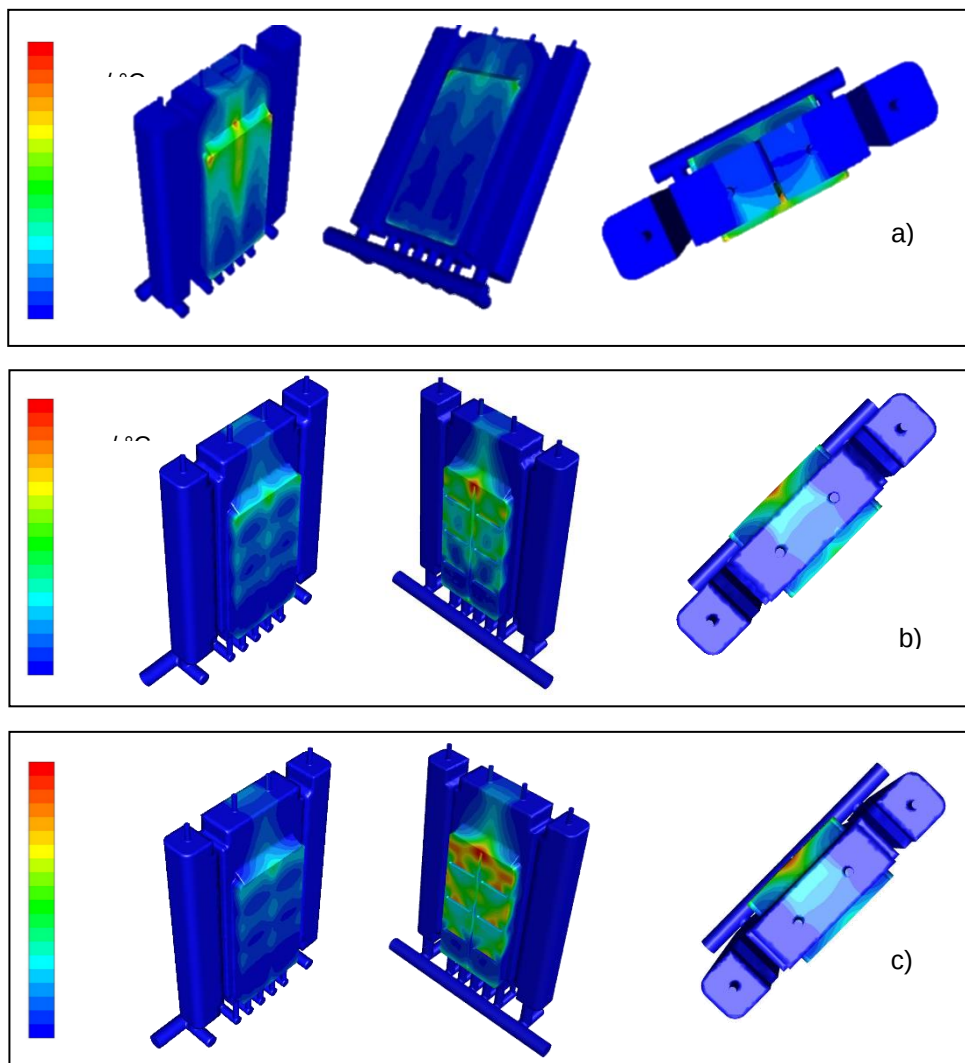
Appendix 4-g. Schematic representation of the multi-PE window: A) arrangement of PEs in the segmented support; B) assembly of a PE in the segmented support; a) $\alpha\text{-Fe}_2\text{O}_3$ thin film (working-electrode); b) nickel foil (counter-electrode); c) front glass window; d) middle separator (acrylic); e) internal separator (acrylic); f) low resistance cable; g) main acrylic support; h) welded contact; i) copper tape located at the side; j) copper tape located at the back; k) metal part to make the contact between the copper tape and the current collector; l) external screw used as current collector; m) low resistance cable with an alligator clip.

CoolPEC cell assembled with the multi-PE window



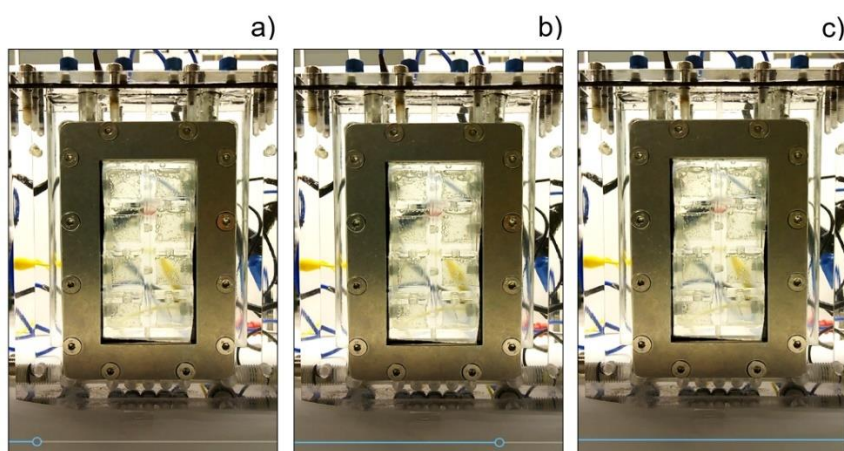
Appendix 4-h. Pictures of multi-PE window in the CoolPEC cell; a) back window before inserting the external screws for current collection; b) back window with the current collectors for each PE; c) front view of the CoolPEC cell assembled with the multi-PE window aligned with a scale bar; d) detailed view of the nickel foil placed side-by-side to the PEs.

Heat dissipation under concentrated sunlight



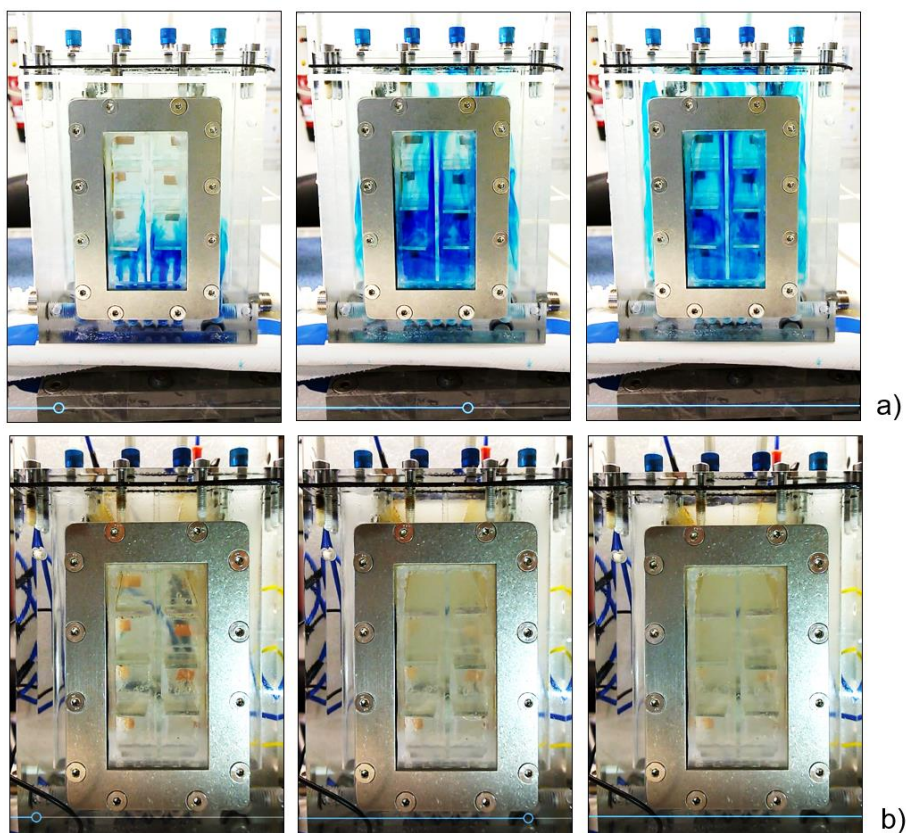
Appendix 4-i. CFD results of heat dissipation under concentrated sunlight: total temperature contours of the electrolyte inside the CoolPEC cell under $17 \text{ kW}\cdot\text{m}^{-2}$ considering an outside air temperature of 25°C and an electrolyte feeding of $0.5 \text{ L}\cdot\text{min}^{-1}$ at 25°C ; a) original CoolPEC cell design (adapted from Vilanova, A. *et al.* 2018); b) CoolPEC cell assembled with the multi-PE window including the strategically drilled acrylic plates (internal separators); c) CoolPEC cell assembled with the multi-PE window including the acrylic plates without drills.

Collection of evolved gases in the CoolPEC cell with the multi-electrode window and perforated acrylic separators



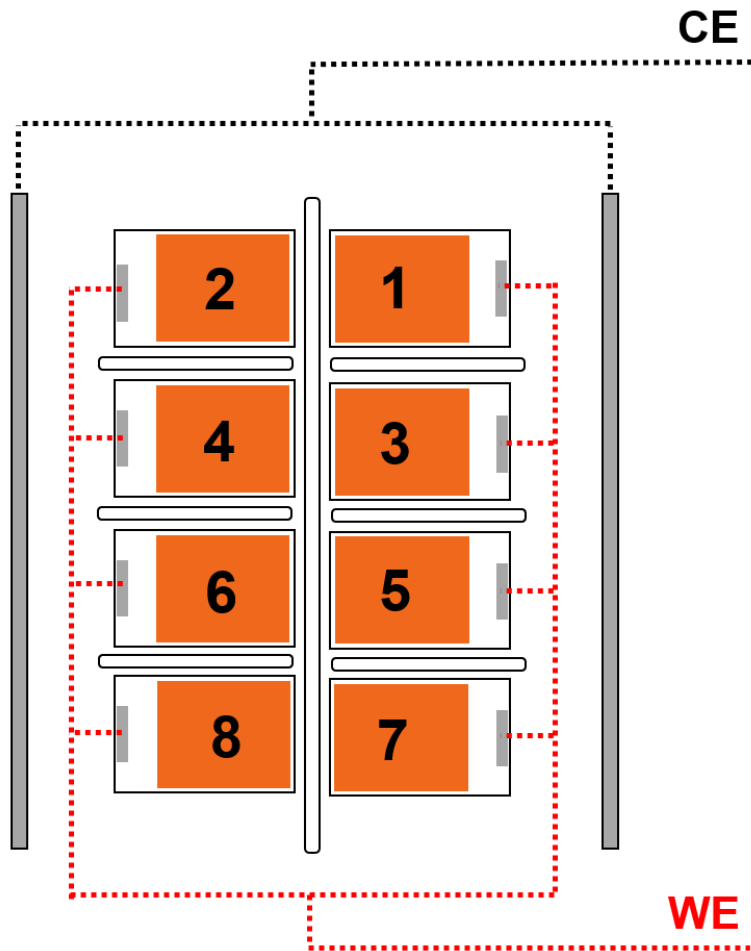
Appendix 4-j. Forced gas evolution at $5.4 \text{ mA} \cdot \text{cm}^{-2}$ with 1.0 M KOH and a feeding flow rate of $0.5 \text{ L} \cdot \text{min}^{-1}$ pictured at different instants after the water electrolysis was promoted; a) 5 s; b) 15 s; c) 25 s;

Tracer test and evolved gases collection in in the CoolPEC cell assembled with a non-drilled segmented support



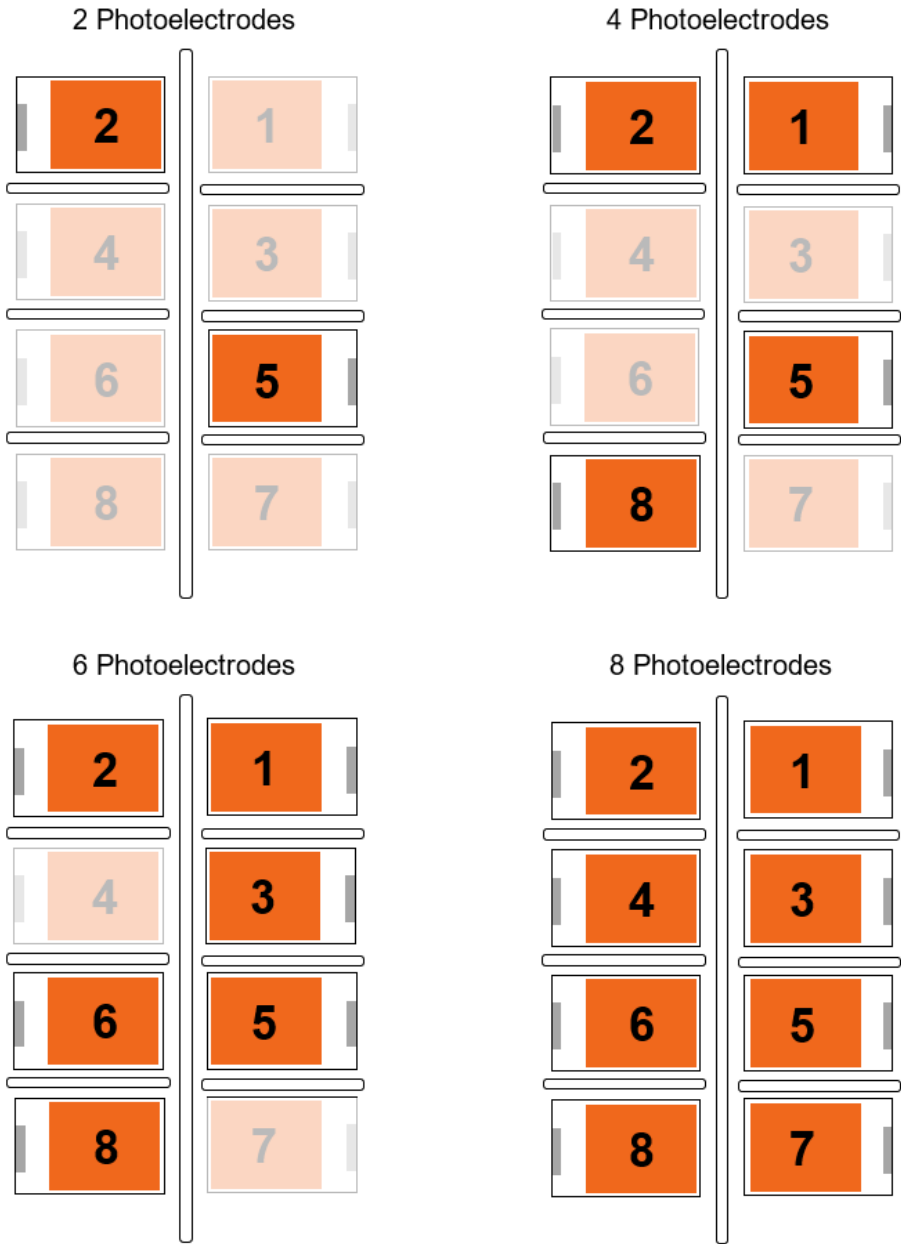
Appendix 4-k. Experimental tests to assess the electrolyte flow path in the CoolPEC cell assembled with a non-drilled segmented support: a) tracer test performed with a blue dye and distilled water with a feeding flow rate of $0.5 \text{ L} \cdot \text{min}^{-1}$ pictured at different instants after the injection of the dye (from left to right, 4 s, 8 s and 15 s); b) forced gas evolution at $5.4 \text{ mA} \cdot \text{cm}^{-2}$ with KOH 1.0 M and a feeding flow rate of $0.5 \text{ L} \cdot \text{min}^{-1}$ pictured at different instants after the water electrolysis was promoted (from left to right, 5 s, 15 s and 25 s).

Schematic representation of parallel connections in the CoolPEC cell



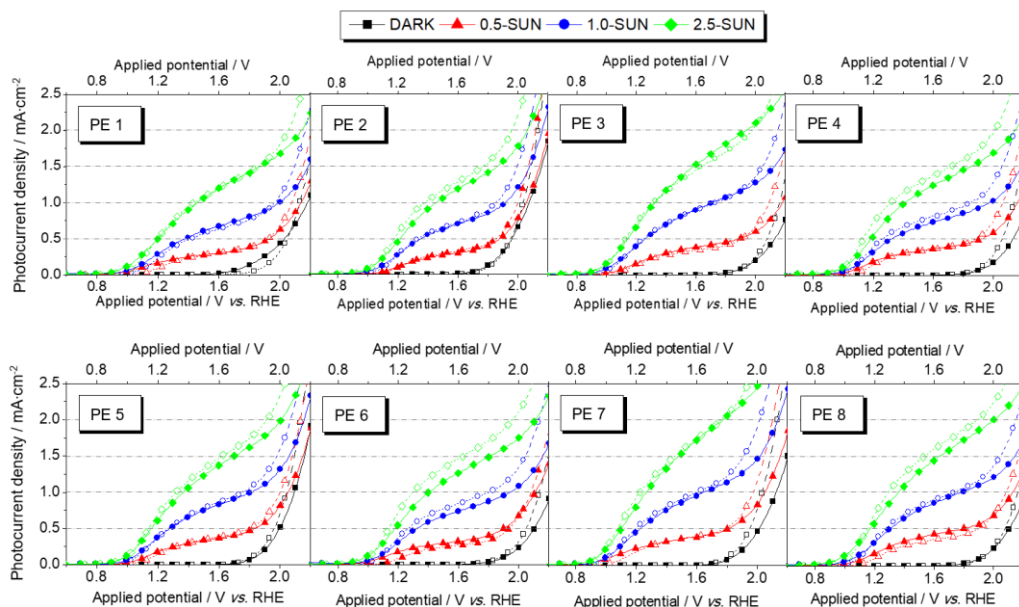
Appendix 4-l. Schematic representation of the parallel connections in the CoolPEC cell assembled with the multi-PE and the counter-electrodes placed perpendicular, in both sides.

Stepwise increase of PEs connected in parallel

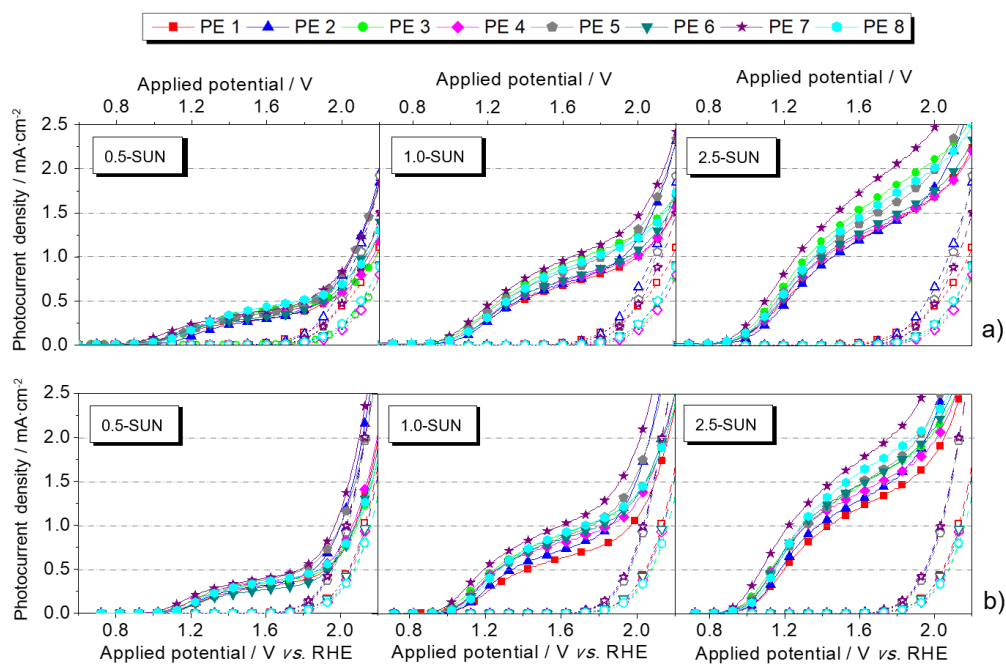


Appendix 4-m. Schematic representation of the stepwise increase of PEs connected in parallel.

J-V characteristics of each PE used in the multi-PE window

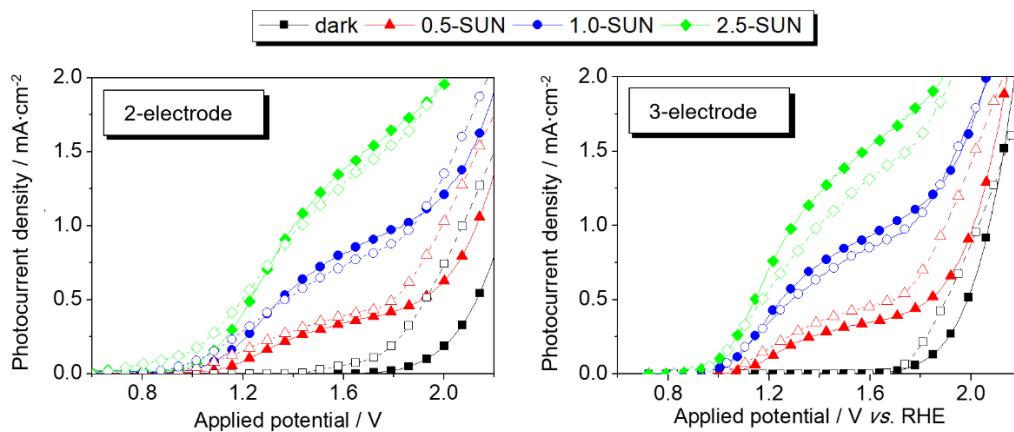


Appendix 4-n. J-V characteristics of each PE used in the multi-PE window obtained under dark conditions and under simulated sunlight (500, 1000 and 2500 W·m⁻², solid lines) in 1.0 M KOH, in a 2-electrode configuration (open symbols, dashed lines) and in a 3-electrode configuration (full symbols, solid lines).



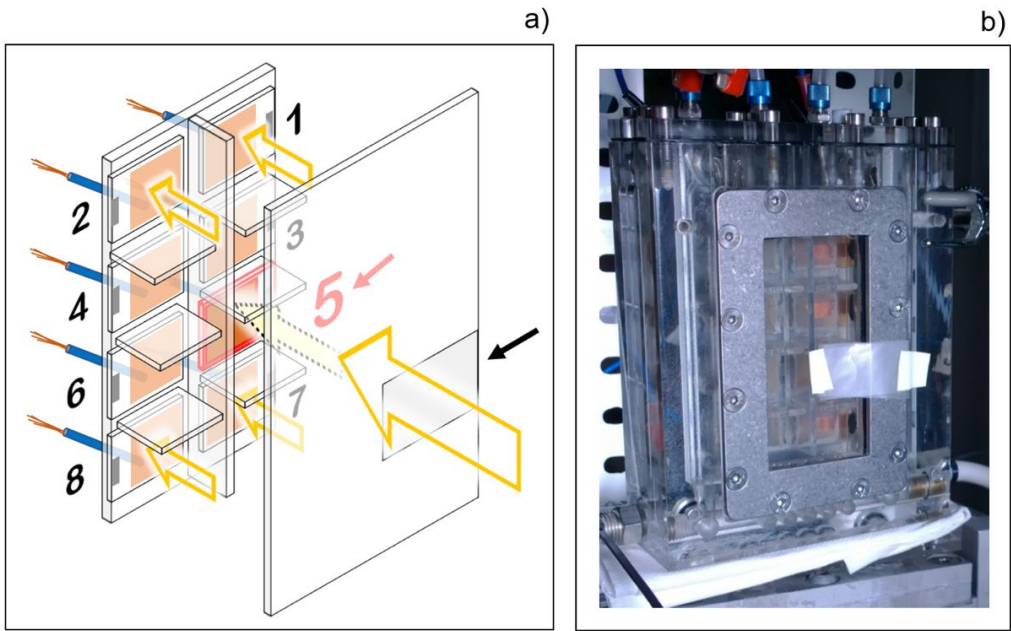
Appendix 4-o. Comparison between J - V characteristics of the PEs used in the multi-PE window obtained under dark conditions (open symbols, dashed lines) and under simulated sunlight (500, 1000 and 2500 $\text{W}\cdot\text{m}^{-2}$, full symbols, solid lines) in 1.0 M KOH; a) 2-electrode configuration; b) 3-electrode configuration.

Comparison between the multi-PE and a single 50 cm² PE



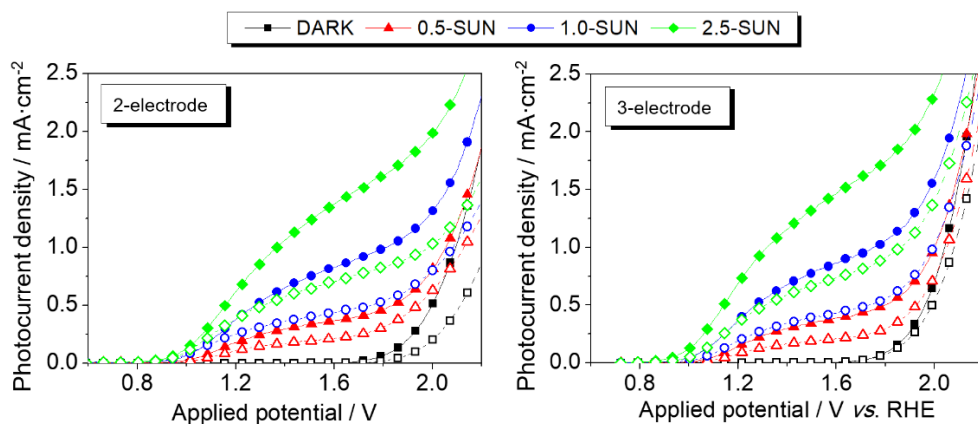
Appendix 4-p. Comparison between *J-V* characteristics obtained under dark conditions and under simulated sunlight (500, 1000 and 2500 W·m⁻²) in 1.0 M KOH for a 50 cm² α-Fe₂O₃ PE (open symbols, dashed lines) and for 8 small α-Fe₂O₃ PEs connected in parallel (full symbols, solid lines).

CoolPEC cell with the multi-PE window and a semi-transparent mask in front of PE #5



Appendix 4-q. CoolPEC cell assembled with the multi-PE window and a semi-transparent mask (Scotch tape) in front of PE #5; a) schematic representation of the location of the semi-transparent mask used to decrease sunlight reaching the surface of PE #5; b) picture of the CoolPEC cell in the test bench with the Scotch tape in front of PE #5.

J-V characteristics of PE #5-B



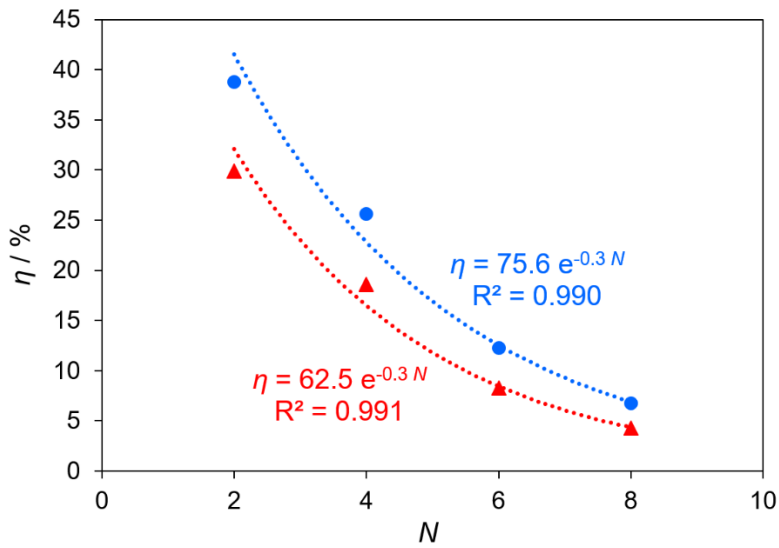
Appendix 4-r. J-V characteristics of PE #5 (solid lines, full symbols) and PE #5-B (dashed lines, open symbols) obtained under dark conditions and under simulated sunlight (500, 1000 and 2500 W·m⁻²) in 1.0 M KOH.

Photocurrent density @ 1.45 V produced by multiple PEs connected in parallel with PE #5-B and corresponding performance losses

Appendix 4-s. Photocurrent density @ 1.45 V under 500, 1000 and 2500 W·m⁻², for multiple PEs connected in parallel with PE #5-B, and the corresponding losses.

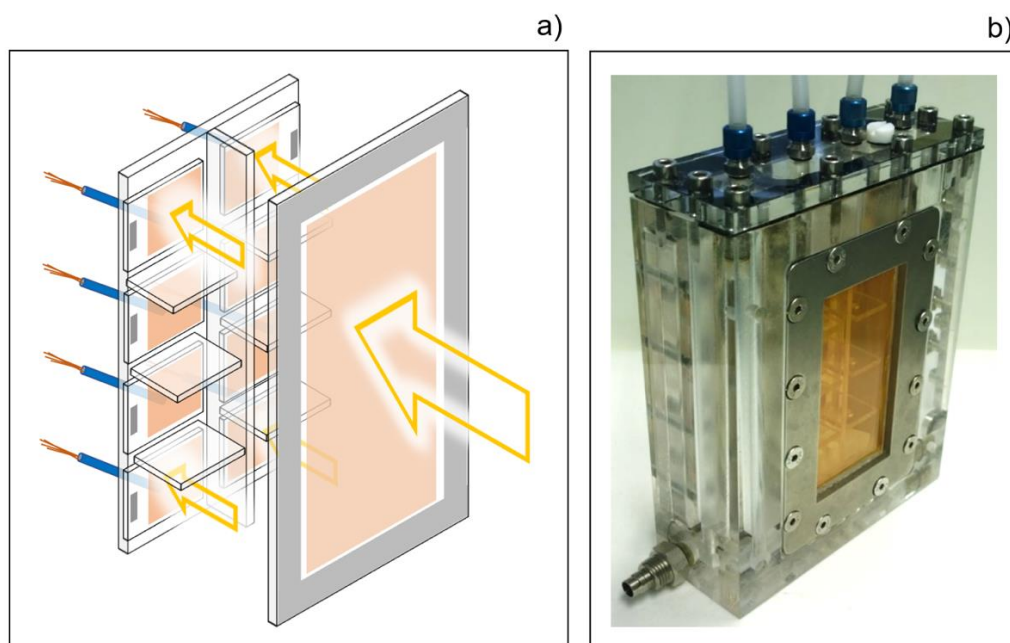
	Current density @ 1.45 V / mA·cm ⁻²					
	Standard configuration		PE #5 with mask in front		Performance losses	
	1.0-sun	2.5-sun	1.0-sun	2.5-sun	1.0-sun	2.5-sun
1 PE	0.699	1.140	0.483	0.777	44.7 %	46.7 %
2 PEs	0.659	1.120	0.498	0.807	32.3 %	38.8 %
4 PEs	0.625	1.060	0.547	0.844	14.3 %	25.6 %
6 PEs	0.639	1.080	0.568	0.962	12.5 %	12.3 %
8 PEs	0.648	1.110	0.626	1.040	3.5 %	6.7 %

Relation between the photocurrent losses and the number of PEs connected in parallel to an underperforming PE



Appendix 4-t. Photocurrent loss (η) as a function of the number of PEs connected in parallel (N), where one of them is the underperforming PE (PE #5-B).

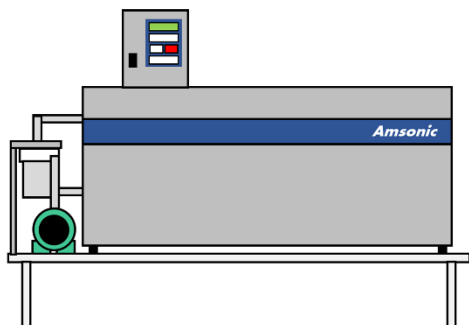
CoolPEC cell with a stack PE arrangement: multi-PE at the back and a 50 cm² α -Fe₂O₃ PE at the front



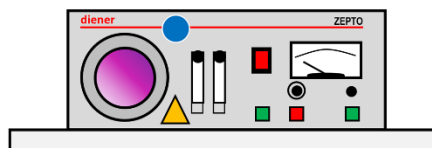
Appendix 4-u. CoolPEC cell assembled with the multi-PE window at the back and a 50 cm² α -Fe₂O₃ PE at the front; a) schematic representation of the α -Fe₂O₃ PEs assembled in a stack configuration; picture of the CoolPEC with a 50 cm² α -Fe₂O₃ PE assembled at the front.

5 APPENDIX 5

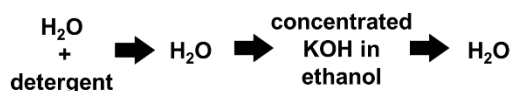
Cleaning procedure for FTO glass substrates



a) Ultrasonic cleaning at 45 °C, 8 min per step

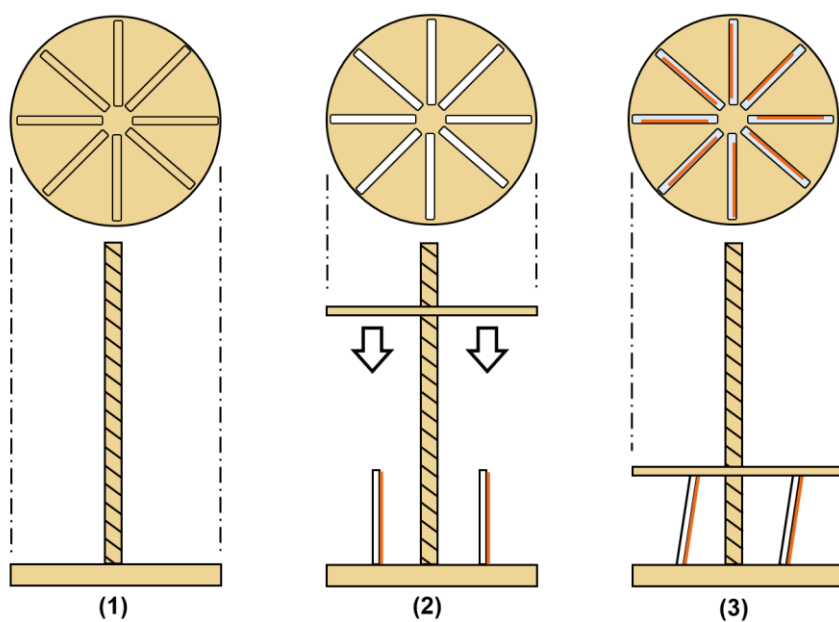


b) Plasma cleaning, 8 min with air

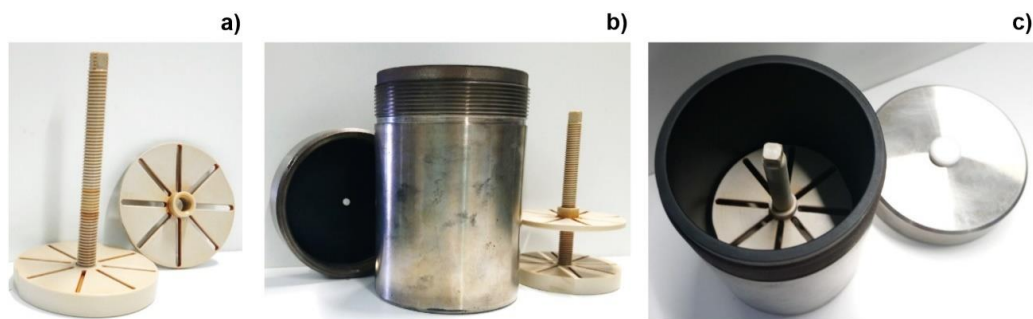


Appendix 5-a. Schematic representation of the steps included in the cleaning procedure for FTO glass substrates: a) sequential 8 min ultrasonic treatment (Amsonic TTc 2530) in soapy water (Alconox), distilled water, 2.0 M KOH (in a 70 % ethanolic solution), and distilled water; b) plasma treatment with air for 8 min (70 kW at 0.2 mbar; Diener electronic® Plasma Surface Technology).

Home-designed PEEK support and autoclave for the preparation of eight SPHA α -Fe₂O₃ PEs in a single batch

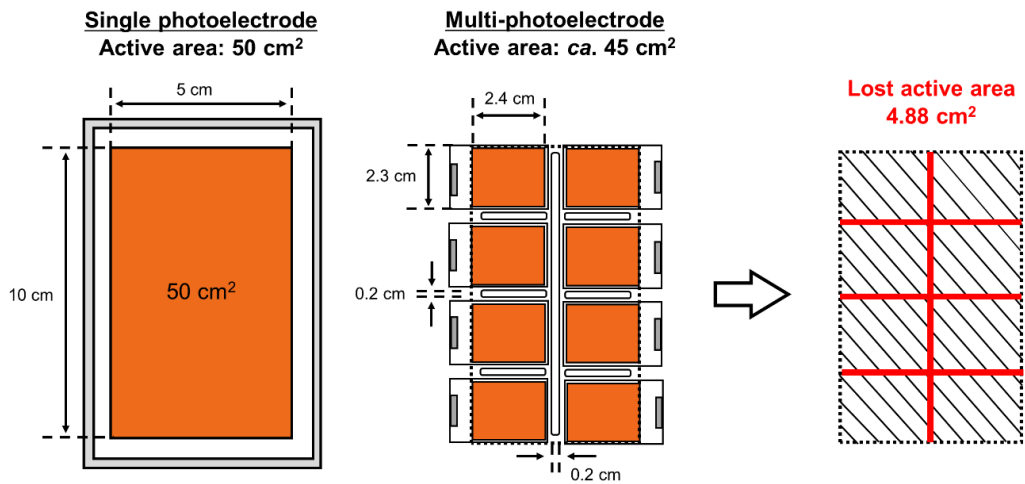


Appendix 5-b. Schematic representation of the assembly steps of SPHA-PEs in the home-designed PEEK support, before the hydrothermal synthesis inside the home-designed autoclave; PEs are fixed tilted at 80°.



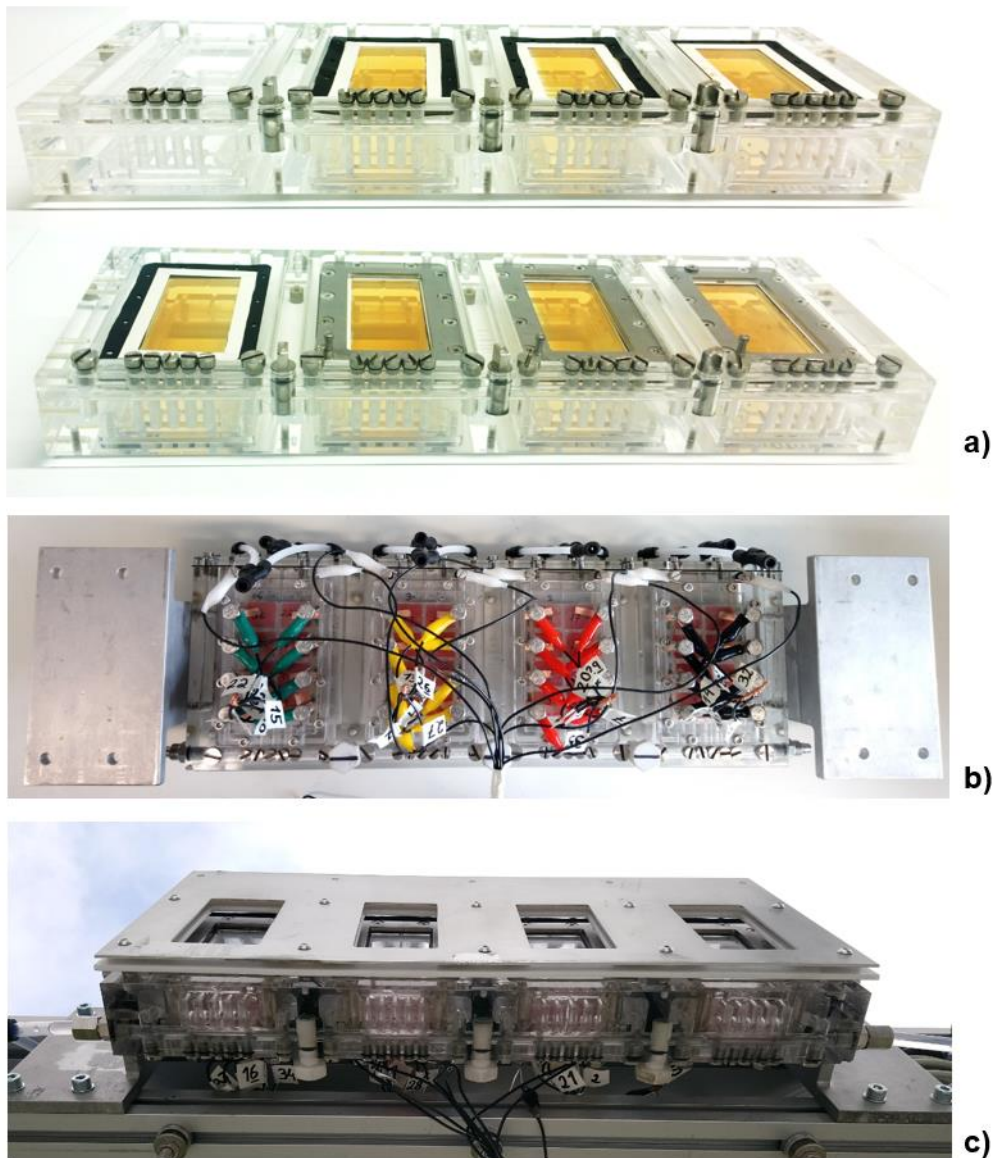
Appendix 5-c. Photos of the home-designed autoclave for the preparation of eight small-size SPHA-PEs in a single batch; a) internal PEEK support for holding the PEs; b) stainless steel autoclave placed side-by-side to the PEEK support with the two moving parts assembled; c) detailed view of the interior of the PEEK-coated stainless-steel autoclave with the PEEK support placed inside.

Active area losses due to the internal separators used in the multi-PE window



Appendix 5-d. Comparison between the active area of a single-large PE and the active area of eight small PEs assembled in the multi-PE support, both used in the CoolPEC module.

Additional photos of the CoolPEC module



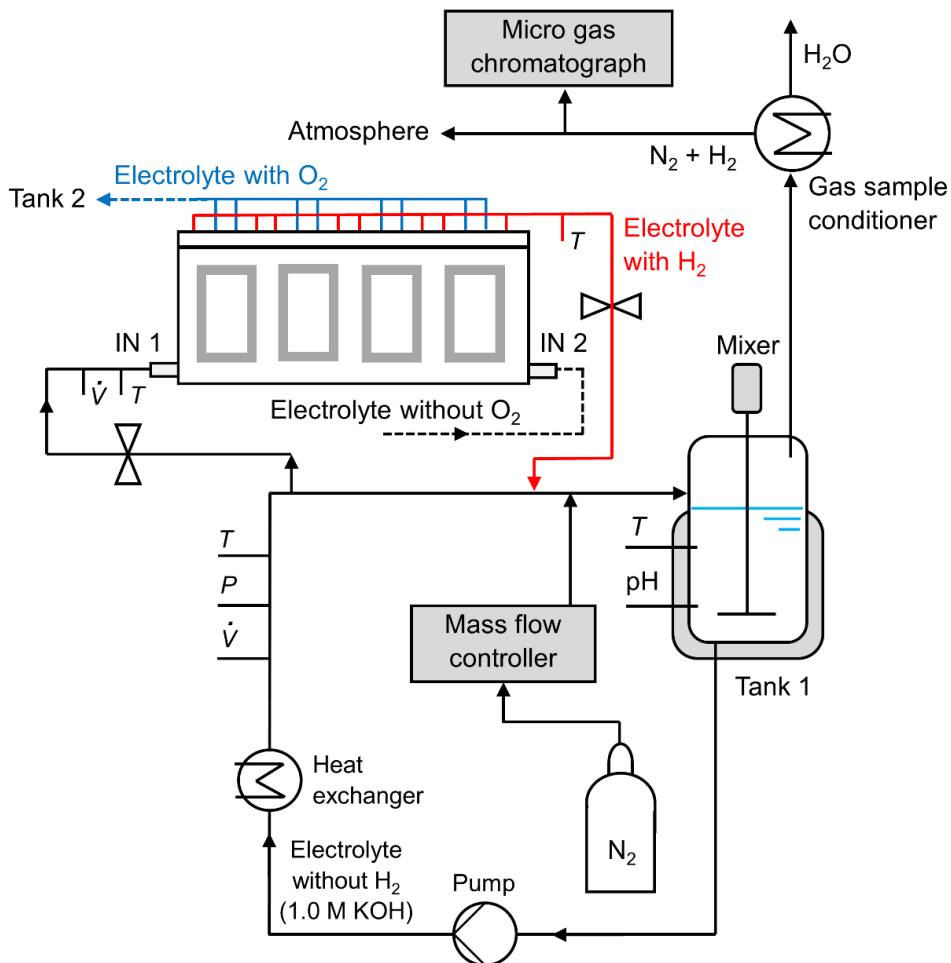
Appendix 5-e. CoolPEC module: a) assembly of single-large $\alpha\text{-Fe}_2\text{O}_3$ SP-PEs in the back side; b) back side with four multi-electrode windows (black cables – window 1; red cables – window 2; yellow cables – window 3; green cables – window 4; white cables – counter-electrodes); c) CoolPEC module assembled in the solar concentrator with the double-layer reflective shield.

Photos of the CoolPEC module during operation under concentrated sunlight



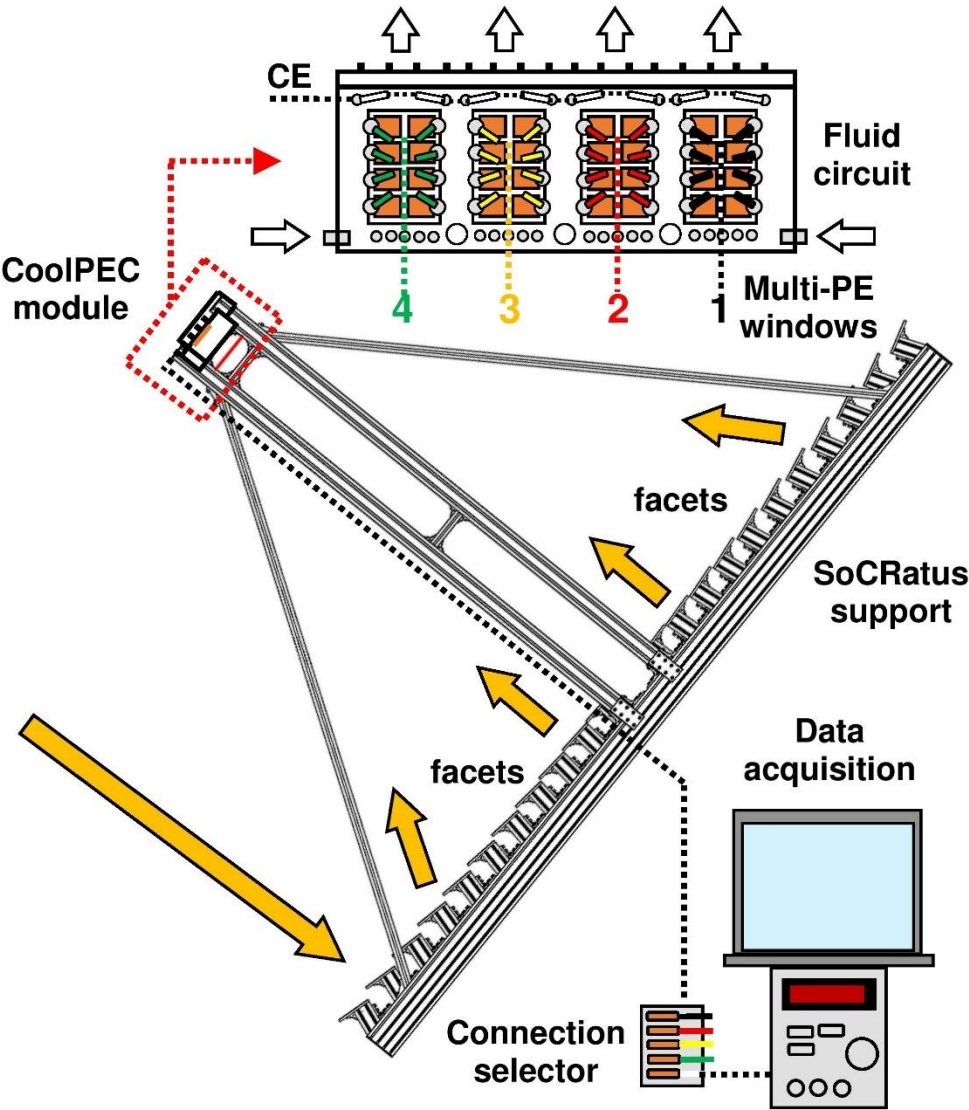
Appendix 5-f. CoolPEC module installed in the SoCRatus during operation under concentrated sunlight: a) front view of the module; b) view of the module from the back of the rectangular mirrors; c) SoCRatus being operated with 16 active mirrors; d) SoCRatus being operated with 6 active mirrors.

Fluid cycles in the SoCRatus testing facility



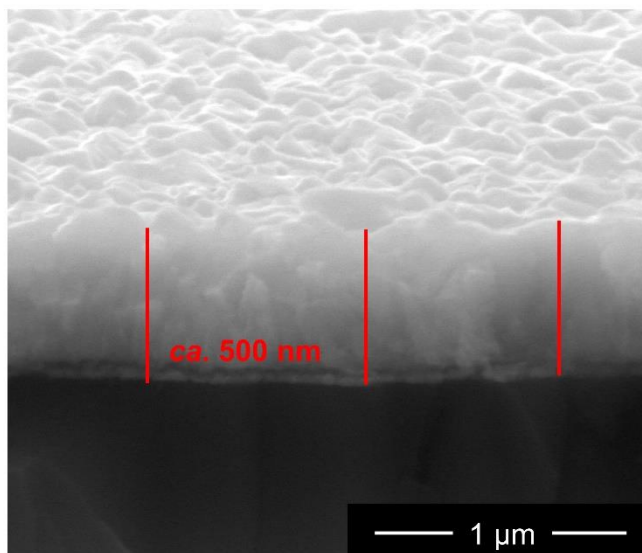
Appendix 5-g. Fluid cycles and auxiliary equipment of the SoCRatus testing facility when the CoolPEC module is installed; for better readability, only fluid cycle 1 (carrying the evolved hydrogen, corresponding to the CE compartments) is illustrated in detail. Dashed lines refer to fluid cycle 2 (carrying the evolved oxygen, corresponding to the PE compartments).

Electric connections in the SoCRatus testing facility



Appendix 5-h. Schematic representation of the electric wiring between the CoolPEC module and the data acquisition system in the SoCRatus testing facility. Since the CoolPEC module is inaccessible during operation, the connection selector allows doing measurements with any combination of the four windows.

SEM cross-section image of a non-tested (fresh) α -Fe₂O₃ PE prepared by spray pyrolysis



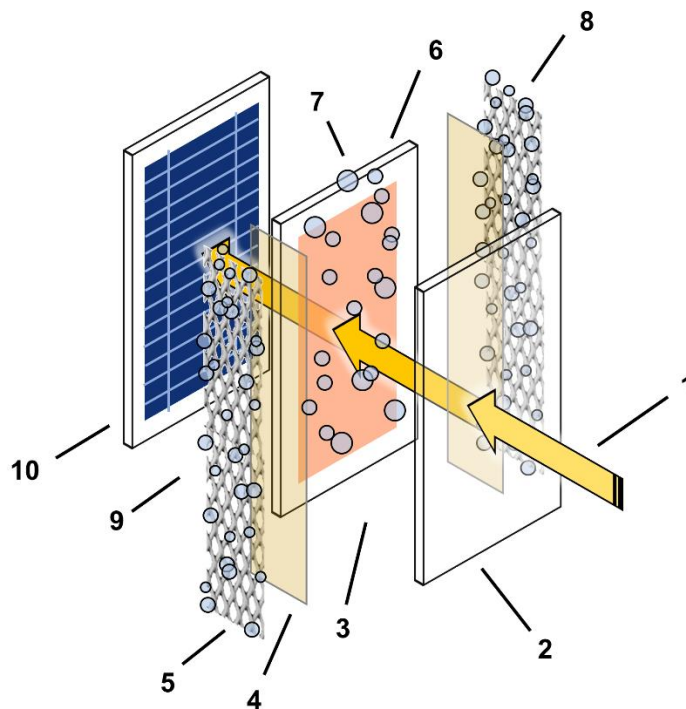
Appendix 5-i. Cross-section SEM image (mag. 100 000 ×) of a fresh (non-tested) α -Fe₂O₃ planar film prepared by spray pyrolysis on an FTO glass substrate. This image was obtained with a high-resolution scanning electron microscope (Quanta 400 FEG, FEI Company, USA), at CEMUP (Centro de Materiais da Universidade do Porto). The thickness of the underneath FTO layer is highlighted in red (ca. 500 nm). The planar α -Fe₂O₃ thin film is not visible, and its thickness cannot be clearly quantified.

List of values for the effective geometric concentration ratio on the PEs ($C_{g,eff}$)

Appendix 5-j. Values of effective geometric concentration ratio on the PEs ($C_{g,eff}$) as function of the number of active mirrors in the SoCRatus.

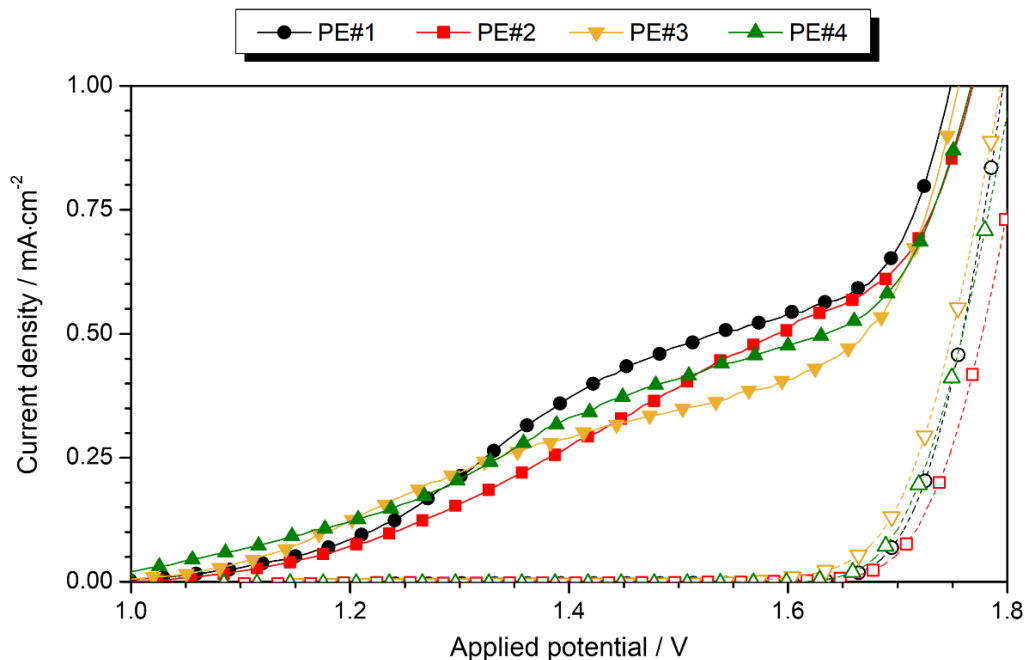
Number of exposed active mirrors	Effective geometric concentration ratio ($C_{g,eff}$)
2	1.67
4	3.59
6	5.47
8	7.29
10	9.04
12	10.7
14	12.3
16	13.9
18	15.3
20	16.7
22	17.9

Tandem arrangement in the CoolPEC module



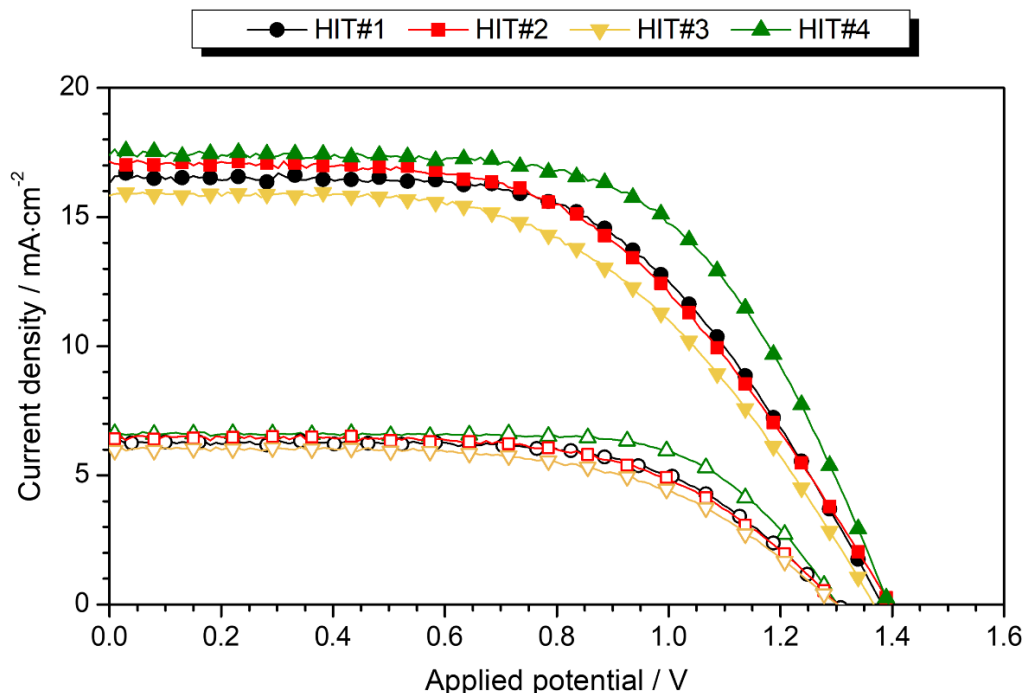
Appendix 5-k. Schematic representation of the tandem arrangement used in the CoolPEC module during the first set of tests under concentrated sunlight: 1 – concentrated sunlight provided by the active rectangular mirrors in the SoCRatus; 2 – front window (quartz); 3 – electrolyte (1.0 M KOH, aqueous solution); 4 – ionic exchange membrane (Fumatech Fumasep® FAA 3 PK 100); 5 – platinized-titanium mesh (CE); 6 – single-large $\alpha\text{-Fe}_2\text{O}_3$ SP-PE (prepared on a FTO glass substrate, Solaronix, 2.2 mm thick, $7\ \Omega\cdot\text{square}^{-1}$, 70 mm × 120 mm); 7 – evolved oxygen; 8 – evolved hydrogen; 9 – air gap; 10 – HIT silicon cell (prepared by PVcomB at the Helmholtz-Zentrum Berlin).

Individual performance of single large α -Fe₂O₃ SP-PEs



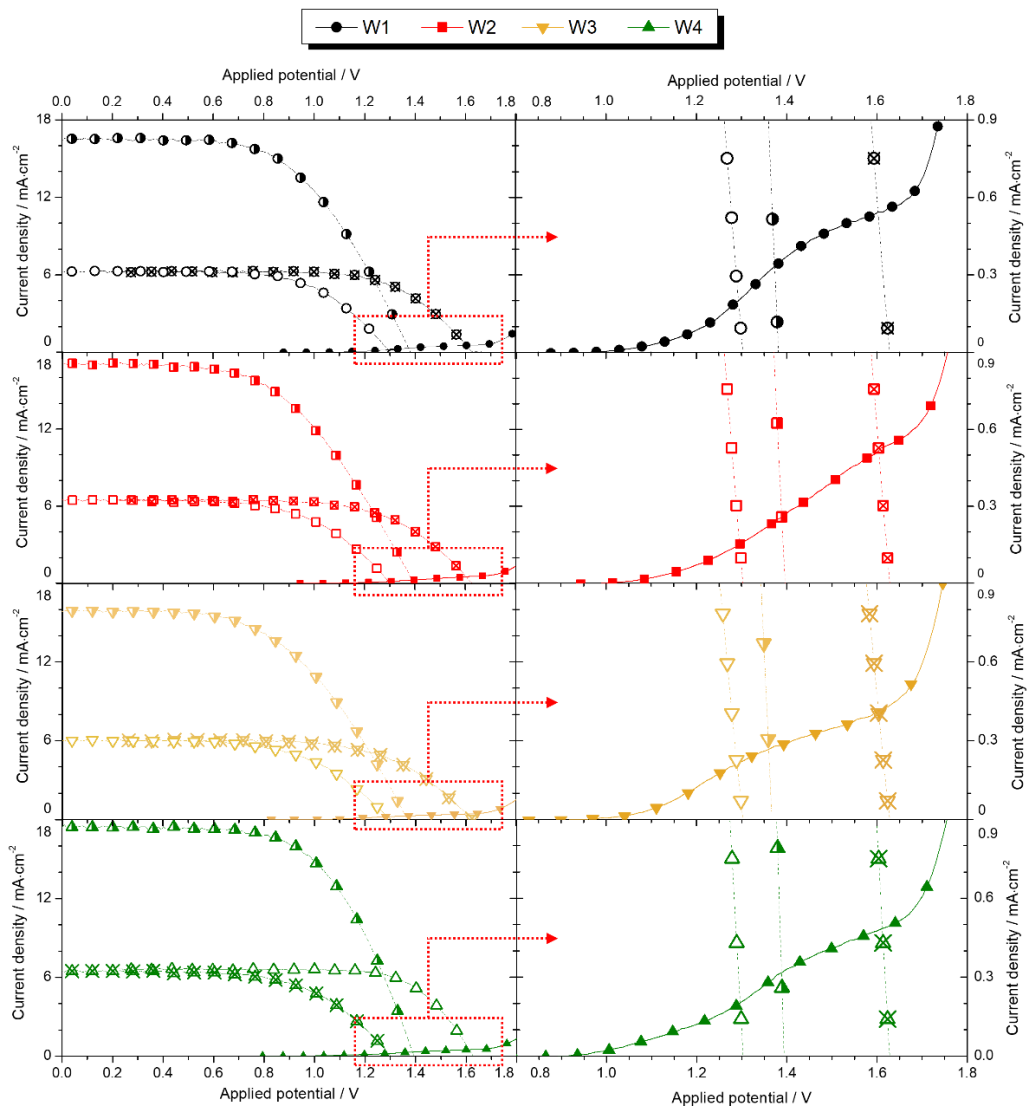
Appendix 5-I. *J-V* characteristics of single-large α -Fe₂O₃ SP-PEs, represented with the colours matching the windows where they were assembled: window 1, ●; window 2, ■; window 3, ▼; window 4, ▲. *J-V* measurements were performed between 0.8 and 2.2 V at a scan rate of 10 mV·s⁻¹, in 1.0 M KOH aqueous solution. The PEs were assembled in the CoolPEC cell and then characterized in the dark (open symbols, dashed lines) and under simulated sunlight (filled symbols, solid lines) provided by a class B solar simulator equipped with a 1600 W Xe lamp (Oriel, Newport, USA) and an AM 1.5 G filter (1000 W·m⁻², 25 °C; Newport, USA) calibrated with a c-Si photodiode (Newport, USA). The CoolPEC cell was assembled in a two-electrode configuration: the PE was operated as working-electrode and two nickel plates placed side-by-side to the PE were used as counter-electrodes. The characteristics curves were performed with an Autolab/PGSTAT302N workstation controlled by Nova software package (Nova version 1.11).

Individual performance of HIT silicon cells



Appendix 5-m. *J-V* characteristics of the HIT silicon cells (prepared by PVcomB at the Helmholtz-Zentrum Berlin) used in the CoolPEC module in a tandem arrangement for complete unbiased solar water splitting. *J-V* curves of each HIT silicon cell are represented with the colours matching the windows where they were assembled in the module: window 1, ●; window 2, ■; window 3, ▼; window 4, ▲; filled symbols correspond to standard measurements; open symbols correspond to measurements performed with a α -Fe₂O₃ SP-PE placed in front of the HIT cell, simulating a tandem arrangement. *J-V* measurements were made under simulated sunlight provided by a class B solar simulator equipped with a 1600 W Xe lamp (Oriel, Newport, USA) and an AM 1.5 G filter (1000 W·m⁻², 25 °C; Newport, USA) calibrated with a c-Si photodiode (Newport, USA). The characteristic curves were performed with an Autolab/PGSTAT302N workstation controlled by Nova software package (Nova version 1.11).

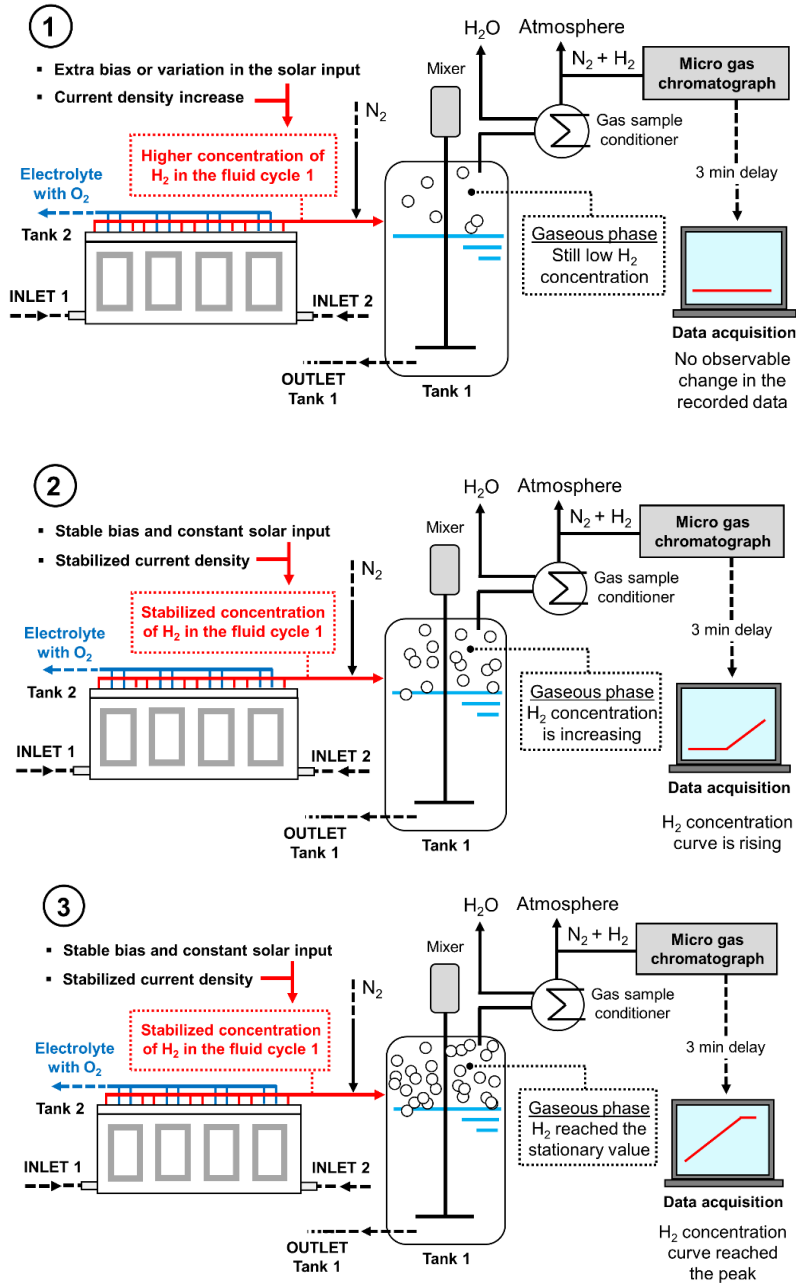
Intersection of J - V characteristics (α - Fe_2O_3 SP-PEs and HIT silicon cells)



Appendix 5-n. Intersection of J - V characteristics of HIT silicon cells (prepared by PVcomB at the Helmholtz-Zentrum Berlin) and the corresponding J - V characteristics of single-large α - Fe_2O_3 SP-PEs (in-house prepared). The intersection zone is zoomed on the right-side plots. J - V characteristics are represented with the colours matching the windows where the PE and the HIT cells were assembled in the CoolIPEC module: window 1, ●; window 2, ■; window 3, ▼; window 4, ▲; filled symbols correspond to J - V characteristics of α - Fe_2O_3 PEs, half-filled symbols correspond to the standard

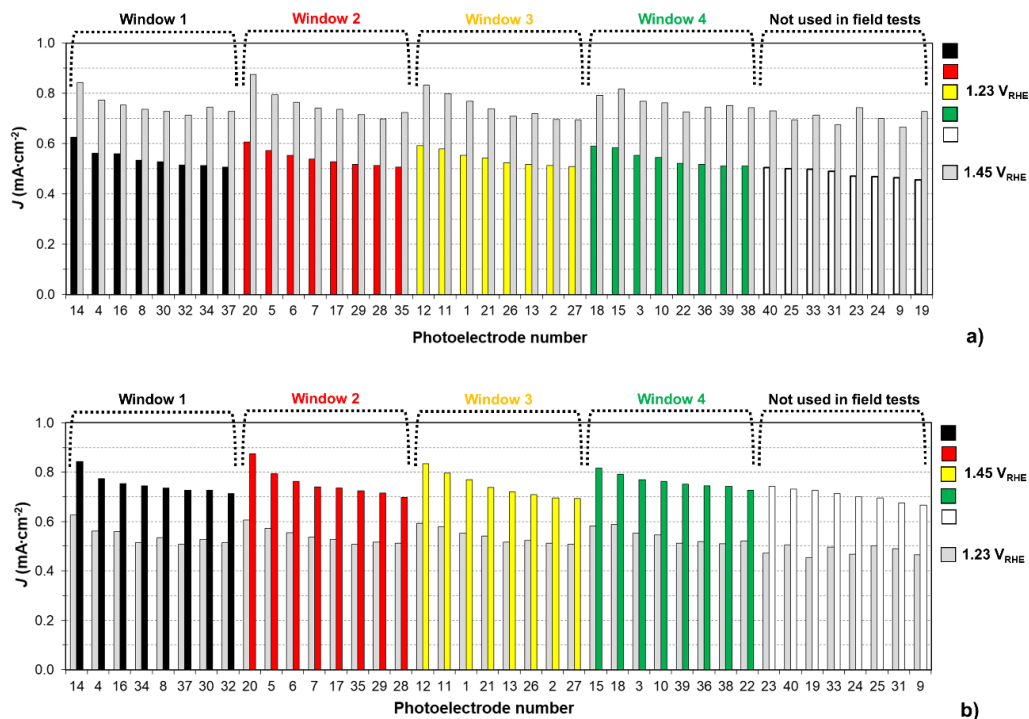
measurements of HIT cells, open symbols correspond to measurements performed with $\alpha\text{-Fe}_2\text{O}_3$ SP-PEs placed in front of the HIT cells, simulating a tandem arrangement and crossed-open symbols correspond to measurements performed with the tandem arrangement and an extra bias of 325 mV provided by the potentiostat. Detailed information concerning the experimental conditions under which the represented curves were obtained is available in the captions of Appendix 5-l and Appendix 5-m.

Gas mixing and saturation along fluid cycle 1



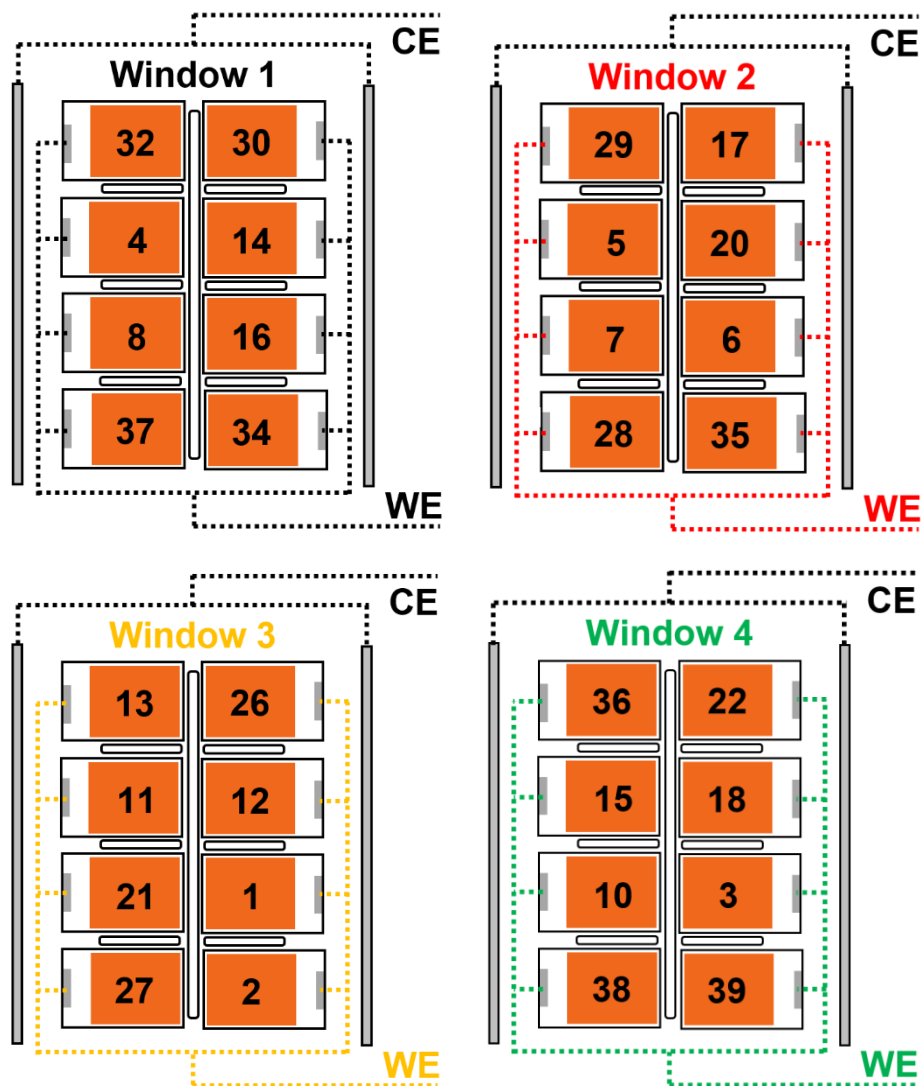
Appendix 5-o. Schematic representation of the mixing and saturation effects along fluid cycle 1; each number corresponds to the instants highlighted in the curve of molar flow of H_2 in the CE compartment, plotted in Figure 5.3 and Figure 5.4.

Individual performance of SPHA-PEs assembled in the multi-PE window



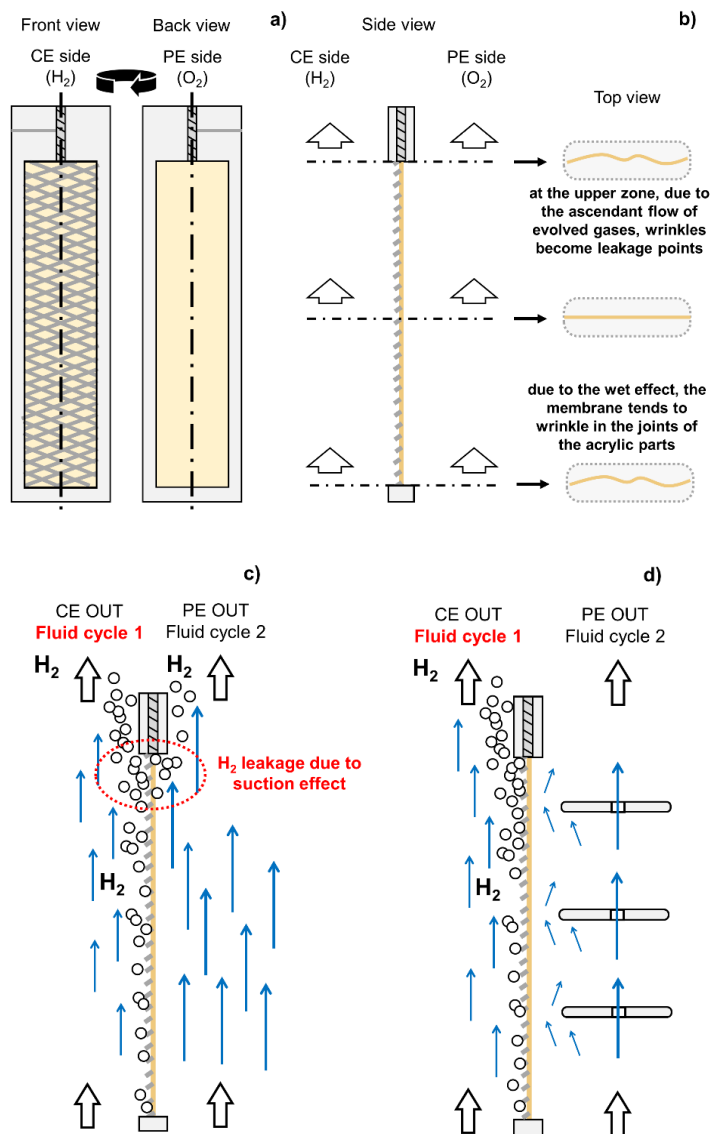
Appendix 5-p. Current density generated by SPHA-PEs at specific potentials: a) PEs ordered by the photocurrent recorded at 1.23 V_{RHE}; b) PEs ordered by the photocurrent recorded at 1.45 V_{RHE}. SPHA-PEs are grouped by the colour corresponding to the window on which they were assembled. The presented values were collected from J - V curves, performed between 0.8 and 2.0 V_{RHE} at a scan rate of 10 mV·s⁻¹, in 1.0 M KOH. J - V measurements were made in a cappuccino PEC cell, in the dark and under simulated sunlight provided by a class B solar simulator equipped with a 150 W Xe lamp (Oriel, Newport, USA) and an AM 1.5 G filter (1000 W·m⁻², 25 °C; Newport, USA) calibrated with a c-Si photodiode (Newport, USA). The cappuccino PEC cell was assembled in a three-electrode configuration, comprising the PE as working-electrode, 99.9 % pure platinum wire (Alfa Aesar®, Germany) as CE, and a Metrohm Ag/AgCl sat. KCl as reference electrode. A ZENNIUM workstation (Zahner Elektrik, Germany) controlled by a Thales software package (Thales Z 2.0) was used to obtain the J - V characteristics of each PE.

Arrangement of PEs in the multi-electrode windows



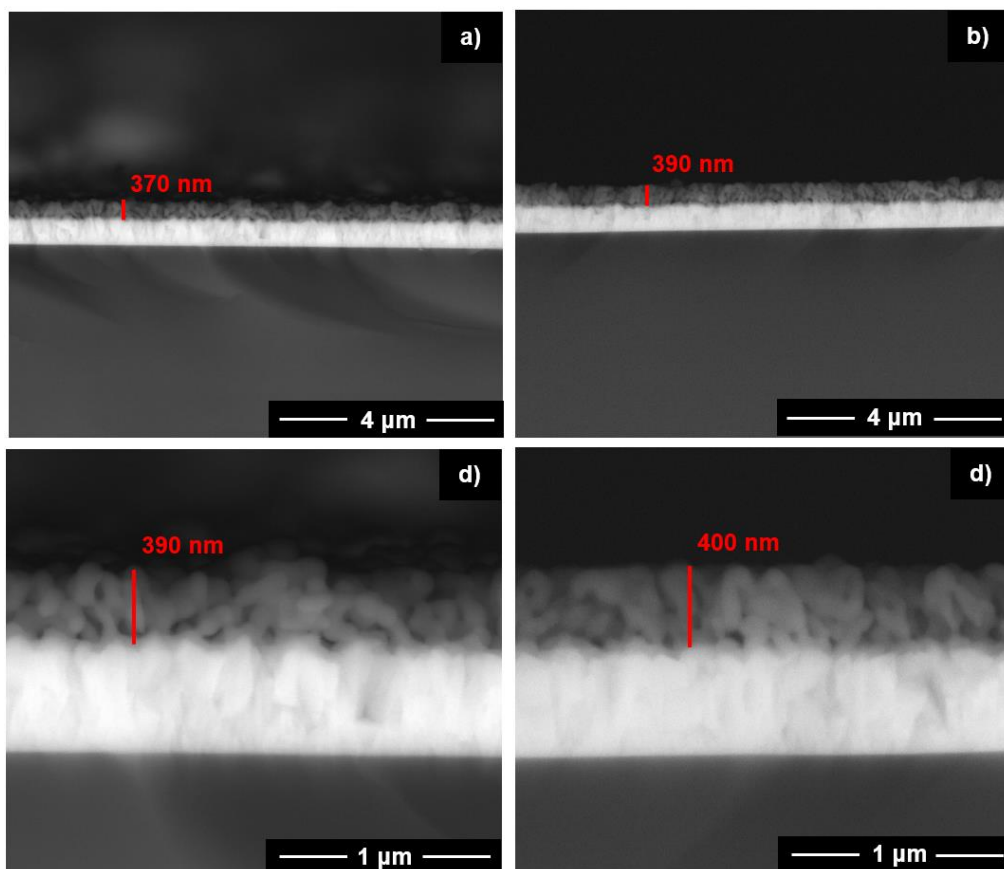
Appendix 5-q. Arrangement of SPHA-PEs in the multi-electrode windows. The PEs were gradually distributed by the four windows according to the recorded photocurrent at 1.23 V_{RHE} (see Appendix 5-p-a) aiming at having four multi-PEs with similar performances.

Evolved hydrogen leakage through the counter-electrode assembly parts



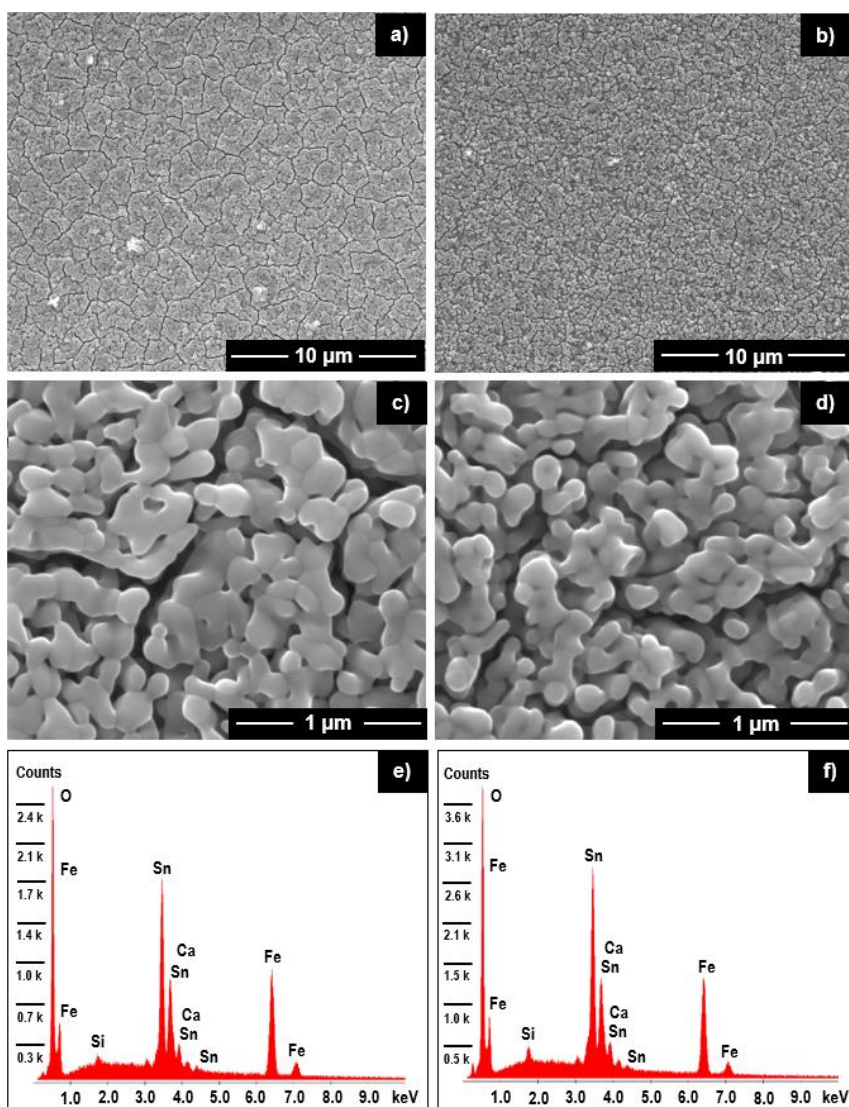
Appendix 5-r. Schematic representation of the hydrogen leakage in the CE: a) schematic view of the H₂ evolution side (comprising the CE mesh) and the O₂ evolution side; b) sectional view and detailed top view of the membrane after the immersion in the electrolyte; c) and d) sectional views of the acrylic holder with the membrane and the Pt-Ti mesh (CE) with the electrolyte flowpath generated when the cell is assembled with single-large PEs and with the multi-PE windows (comprising internal separators), respectively.

SEM cross-section images of fresh (non-tested) and tested SPHA-PEs (PE#33 and PE#16, respectively)



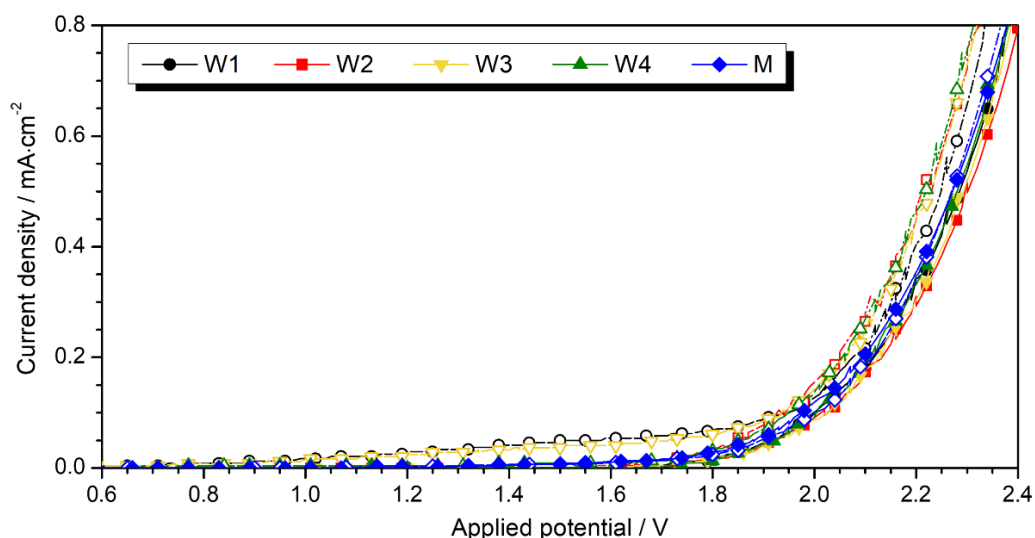
Appendix 5-s. Cross-section SEM images of worm-like α -Fe₂O₃ nanostructures collected from SPHA-PEs before [left-side – fresh PE] and after [right-side – used PE] the field tests under concentrated sunlight with continuous electrolyte recirculation; a) and b) mag. 25000 x; c) and d) mag. 100000 x.

SEM images and EDS analyses of fresh (non-tested) and tested SPHA-PEs (PE#24 and PE#34, respectively)



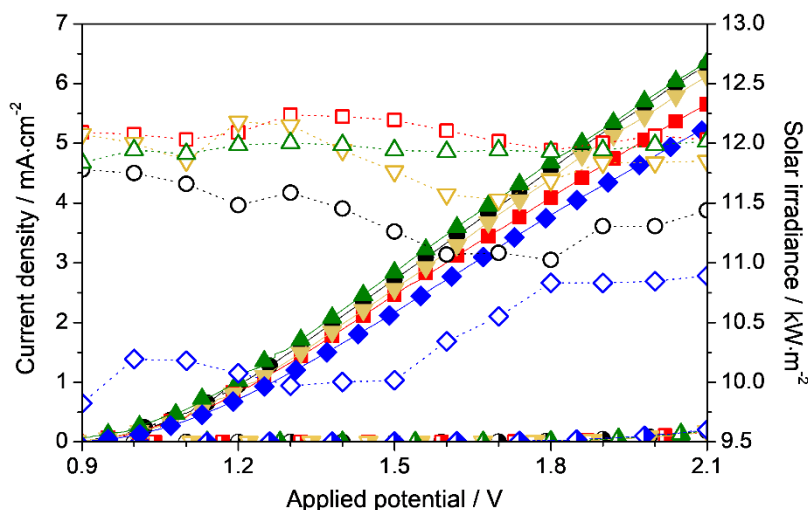
Appendix 5-t. Top-view SEM images and EDS analyses of worm-like nanostructures collected from other SPHA PEs than those reported in chapter 5. Images of the non-tested PE are presented on the left-side and images of the PE subjected to field tests under concentrated sunlight with continuous electrolyte recirculation tested are presented on the right-side: a) and b) mag. 10000 ×; c) and d) mag. 100000 ×; e) and f) EDS analyses.

J-V characteristics of multi-electrode windows and the complete module under dark conditions obtained before and after the field tests



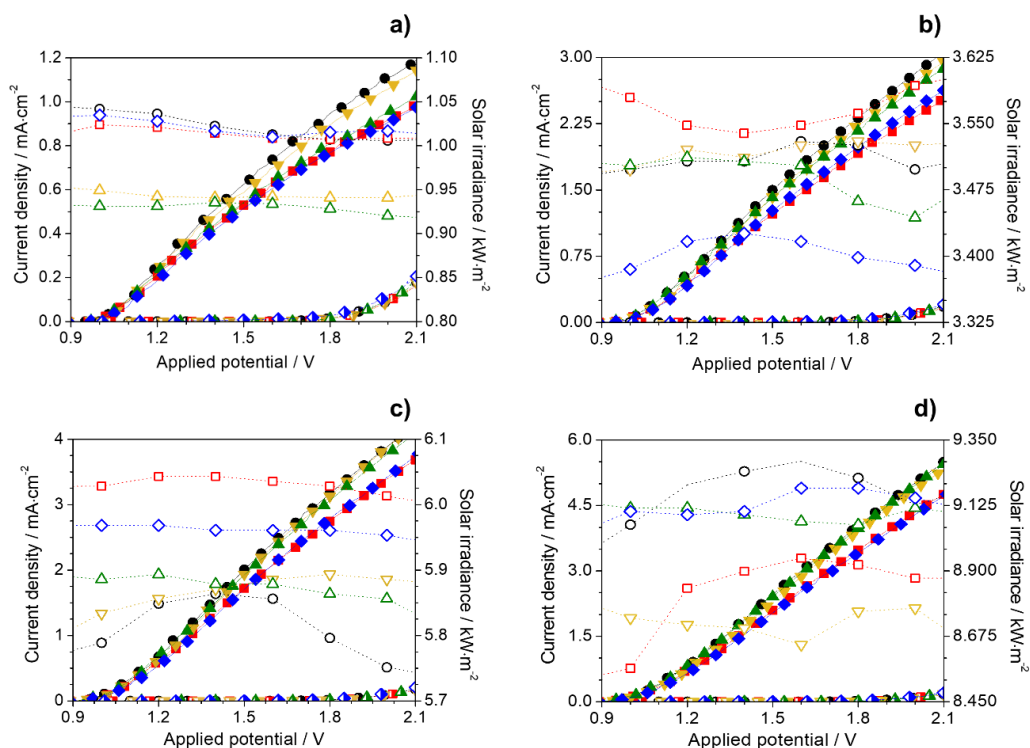
Appendix 5-u. J-V characteristics of each multi-electrode window (window 1, ●; window 2, ■; window 3, ▼; window 4, ▲), assembled with eight SPHA-PEs connected in parallel, and the complete module (◆), obtained under dark conditions with continuous electrolyte recirculation (1.0 M KOH, 25 °C, 0.5 L·min⁻¹). J-V curves with open symbols correspond to measurements performed before exposure to concentrated sunlight whereas J-V curves with filled symbols correspond to measurements performed after the testing period.

J-V characteristics of the multi-PE windows and the complete module under concentrated sunlight provided by 22 active mirrors



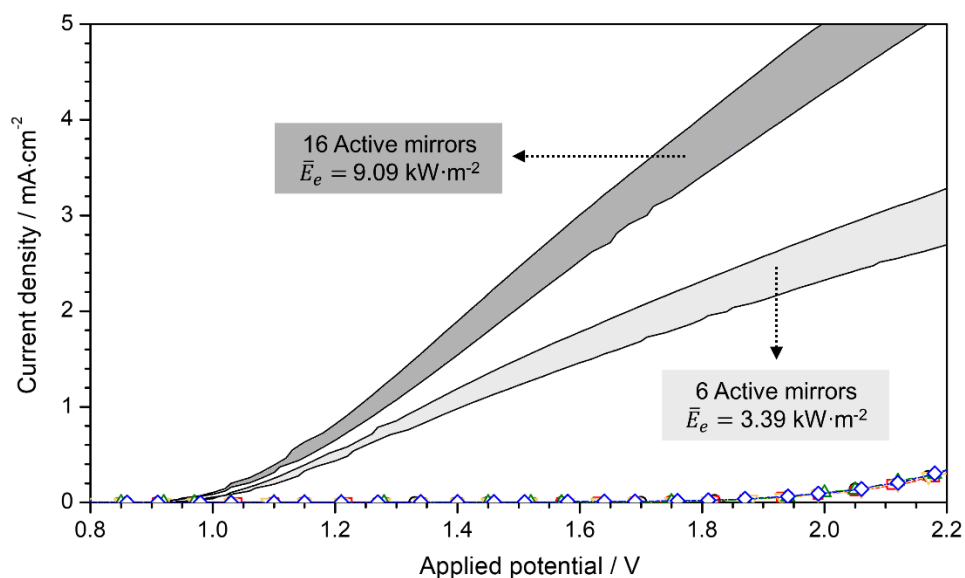
Appendix 5-v. J-V characteristics of each multi-PE window (window 1, ●; window 2, ■; window 3, ▼; window 4, ▲), assembled with eight SPHA-PEs connected in parallel, and the complete module (◆), obtained under dark conditions (dashed lines, half-filled symbols) and under concentrated sunlight (solid lines, filled symbols) provided by 22 rectangular active mirrors. These measurements were performed in the SoCRatus testing facility between 0 and 2.2 V at a scan rate of $10 \text{ mV}\cdot\text{s}^{-1}$, with electrolyte recirculation (1.0 M KOH , 25°C , $0.5 \text{ L}\cdot\text{min}^{-1}$ per cell). The real solar irradiance recorded during the J-V measurements is represented accordingly (dotted lines, open symbols), in the secondary y-axis. The testing period during which these measurements were made is highlighted in Figure 5.4.

J-V characteristics of multi-PE windows and the complete module under concentrated sunlight provided by 2, 6, 10 and 16 active mirrors



Appendix 5-w. J-V characteristics of each multi-PE window (window 1, ●; window 2, ■; window 3, ▼; window 4, ▲), assembled with eight SPHA-PEs connected in parallel, and the complete module (◆), obtained under dark conditions (dashed lines, half-filled symbols) and under concentrated sunlight (solid lines, filled symbols) provided by a specific number of active mirrors: a) 2 active mirrors; b) 6 active mirrors; c) 10 active mirrors; d) 16 active mirrors. These measurements were performed in the SoCRatus testing facility between 0 and 2.2 V at a scan rate of 10 mV·s⁻¹, with electrolyte recirculation (1.0 M KOH, 25 °C, 0.5 L·min⁻¹ per cell). The real solar irradiance recorded during the J-V measurements is represented accordingly (dotted lines, open symbols), in the secondary y-axis.

Shadowed bands comprising *J-V* characteristics of the multi-PE windows and the complete module obtained under concentrated sunlight



Appendix 5-x. *J-V* characteristics of multi-PE windows obtained under different solar irradiances with electrolyte recirculation (1.0 M KOH, 25 °C, 0.5 L·min⁻¹ per cell). Each shadowed band corresponds to a specific concentration factor, given by 6 and 16 active mirrors, and includes the *J-V* curves depicted in Appendix 5-w. *J-V* curves with open symbols correspond to measurements performed under dark conditions (window 1, O; window 2, □; window 3, ▽; window 4, △; and the module, ◇). The information represented hereby should be interpreted synchronously with the data provided in Appendix 5-y.

Current density, STH efficiency and mean solar irradiance values of the multi-PE windows and the complete module obtained under concentrated sunlight

Appendix 5-y. Values of current density (J , in $\text{mA}\cdot\text{cm}^{-2}$) recorded at applied potentials of 1.23 V, 1.45 V, 1.6 V and 1.8 V. These values were extracted from the J - V curves depicted in Appendix 5-w, performed for each window (W) and to the complete module (M), under concentrated sunlight provided by 6 and 16 active mirrors (m). The solar-to-hydrogen efficiency (STH, in %) and the mean solar irradiance ($\overline{E}_e$, in $\text{kW}\cdot\text{m}^{-2}$) are presented accordingly.

<i>m</i>	<i>V</i>	W1			W2			W3			W4			M		
		<i>J</i>	STH	$\overline{E}_e$	<i>J</i>	STH	$\overline{E}_e$	<i>J</i>	STH	$\overline{E}_e$	<i>J</i>	STH	$\overline{E}_e$	<i>J</i>	STH	$\overline{E}_e$
6	1.23	0.62			0.54			0.56			0.63			0.51		
	1.45	1.35	0.26	3.51	1.11	0.22	3.58	1.27	0.23	3.52	1.27	0.27	3.49	1.13	0.22	3.39
	1.60	1.78			1.46			1.71			1.68			1.51		
	1.80	2.31			1.91			2.24			2.17			1.98		
16	1.23	0.96			0.82			0.90			0.98			0.77		
	1.45	2.18	0.16	9.14	1.85	0.14	8.80	2.03	0.16	8.75	2.14	0.16	9.11	1.79	0.13	9.09
	1.60	3.01			2.57			2.87			2.95			2.53		
	1.80	4.03			3.48			3.91			3.97			3.41		