Large-area photoelectrochemical water splitting using a multi-photoelectrode approach

António Vilanova, Tânia Lopes, Adélio Mendes*
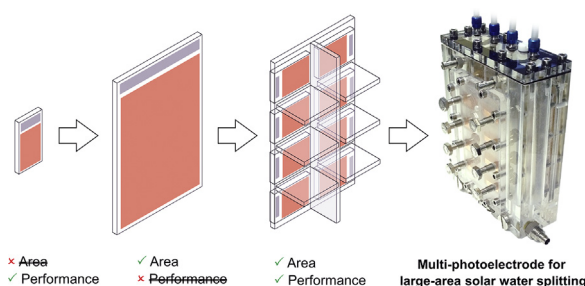
LEPABE - Faculdade de Engenharia, Universidade do Porto, rua Dr. Roberto Frias, 4200-465, Porto, Portugal

HIGHLIGHTS

- A segmented support was developed for holding 8 photoelectrodes in parallel.
- No current losses occurred when 8 photoelectrodes were operated in parallel.
- CFD simulations were used to optimize the electrolyte flow path inside the cell.
- The negative effect of an underperforming photoelectrode was assessed.

GRAPHICAL ABSTRACT

× Area
✓ Performance

✓ Area
× Performance

✓ Area
✓ Performance

Multi-photoelectrode for large-area solar water splitting

ARTICLE INFO

ABSTRACT

In the field of photoelectrochemical hydrogen 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 $3.2\,cm^2$ 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 hematite photoelectrodes 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 photoelectrode in the overall performance of the cell decreases exponentially with the number of photoelectrodes connected in parallel.

1. Introduction

Modern society has an increasing dependence on energy use. The present economic development is still based on the intensive use of fossil fuels to supply the constant growing of energy demand, resulting in high emissions of greenhouse gases (GHG) [1]. Therefore, climate change and social problems became important issues in global policies, imposing the need for replacing fossil fuels by renewable energy sources [2].

Solar energy is the most abundant, clean and renewable source of energy [3]. The solar energy irradiating the surface of the Earth every year is approximately $5.0 \times 10^{12}\,TJ$ [4], enough to supply the human annual energy consumption, *ca.* $5.67 \times 10^8\,TJ$ [5]. Photoelectrochemical (PEC) hydrogen is a promising route to harvest and store

---

the solar energy [6,7], which can be directly consumed as a fuel or used for producing energy-rich chemical fuels, such as hydrocarbons [8,9]. Photoelectrochemical hydrogen produced from solar water splitting has been pointed as a quite competitive and promising option for the transportation and industry sectors [10,11]. However, the lack of a commercial prototype for continuous production of PEC hydrogen is often considered the main obstacle to accurately demonstrate the advantages of PEC devices [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 for solar water splitting at lab scale, upscaling highly efficient photoelectrodes 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 ($\geq 50\,cm^2$), which compromises the upscaling process [18,19]. Record-performing photoelectrodes usually have few square centimetres [20,21] and the demonstration of their applicability in large-area devices is still missing [15,22].

Transparent conducting oxides (TCOs) such as fluorine doped tin oxide (FTO) are commonly used as substrates for making photoelectrodes (PEs) for PEC water splitting [23,24]. These substrates allow using tandem photoelectrodes/photovoltaic (PV) cells, which is considered the most feasible arrangement for reaching the required solar-to-hydrogen (STH) efficiency targets [25,26]. Overcoming the high ohmic losses in large-area photoelectrodes due to the electronic resistance imposed by this type of substrates is a key requirement to bring upscaled PEC cells to the commercial market [27]. Hankin et al. [28] demonstrated that the performance of PEC reactors that use large photoelectrodes 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 point [29]. Although this approach can be easily implemented in solar cells, its implementation in photoelectrodes for PEC cells is more complex. Since the photoelectrode is immersed in an electrolyte, metal lines need to be protected against corrosion [30,31]. 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 protection [27].

This work addresses an innovative approach to overcome the main constrains of upscaling photoelectrodes for photoelectrochemical hydrogen production (Fig. S1). A segmented support was developed for holding multiple photoelectrodes connected in parallel, used as PEC cell window. Therefore, highly efficient nanostructured photoelectrodes with small dimensions can be prepared using the state-of-the-art equipment and then connected in parallel to fulfil large-area requirements.

2. Experimental

2.1. Preparation of hematite photoelectrodes

Hematite photoelectrodes were prepared by spray pyrolysis technique, following the procedure developed by the authors and reported elsewhere [32]. First, a TEOS (tetraethyl orthosilicate) pre-treatment was applied to the FTO glass substrates (120 mm × 70 mm; Solaronix TCO 22–7) [33]. 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 mL min^{-1} considering a time gap of 45 s between sprays and a total volume of 70 mL. Finally, the hematite thin films were annealed for 30 min at 550 °C and cooled down to the room temperature.

2.2. J–V measurements

J-V measurements were performed in an Autolab/PGSTAT302 N 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, 500–2500 W 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 mV s^{-1} and 10 mV 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 supplementary material (SM), Fig. S2.

3. Theory/calculation

3.1. Model and simulation

Ansys® Workbench Academic 18.2 was used for assisting the design of the segmented support that holds the photoelectrodes 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 [34], the electrochemical option in Fluent was enabled. The reaction rate was determined using the Butler-Volmer equation [35,36]:

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

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, $Y_{k,r}^{ref}$ 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 (96 487 C mol^{-1}), R is the universal gas constant (8.314 J mol^{-1} 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:

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

where $S_{Faradaic,i}^r$ is the species production/consumption rate, $v_{i,r}^{'}$ and $v_{i,r}^{''}$ are the stoichiometric coefficients of the kth 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: