Photoelectrochemical Demonstrator Device for Solar Hydrogen Generation

Project Deliverable Report – D6.4

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1. EXECUTIVE SUMMARY

Project PECDEMO considers environmentally friendly production of hydrogen via water splitting in hybrid photoelectrochemical-photovoltaic (PEC-PV) devices. These devices comprise photoelectrodes (or working electrodes) in contact to an electrolyte, which absorb incoming high energy photons from sunlight and lead to the formation of electron-hole pairs, as well as PV-modules behind, which capture photons associated with the low energy part of the solar spectrum. This tandem configuration potentially allows very efficient exploitation of the solar input.

Based on previous cell designs, detailed in the public report D4.3, an innovative PEC-PV prototype was developed and built within the framework of the project. The final device design covers all the PECDEMO requirements and embodies the concept of hybrid PEC-PV technology. This prototype features a 1 x 4 module array allowing each compartment to hold a 50 cm$^2$ photoelectrode and two counter electrodes located side by side. Accordingly, the open light path from the front to the back window adequately allows irradiating PV cells behind the latter.

The prototype performance under non-concentrated sunlight was assessed at UPorto with an individualized cell identical to the ones that comprise the large-area prototype. The medium term test under non-concentrated sunlight was performed in two sets of experiments: i) with bare hematite produced at UPorto and ii) with bismuth vanadate prepared at HZB within the framework of WP1. In the first medium term test, the PEC-PV device was equipped with a 50 cm$^2$ hematite photoelectrode connected in series with two 50 cm$^2$ HIT silicon modules, that supplied the PEC cell with the necessary bias to promote water electrolysis. The hematite photoelectrode remained stable over 1,000 h delivering a constant photocurrent of ca. 0.43 mA cm$^{-2}$ at 1.6 V. The ultra-thin hematite film was resistant to corrosion in contact with the electrolyte at 45 °C. The HIT silicon solar cells also remained stable over the 1,000 h period, generating a constant $V_{oc}$ of ca. 2.7 V. When the PEC-PV cell was equipped with a 50 cm$^2$ bismuth vanadate photoelectrode an average photocurrent density of 0.41 mA cm$^{-2}$ was recorded at 1.28 V bias potential given by a single HIT silicon solar cell. The photocurrent density produced by the bismuth
vanadate continuously decreased over the 24 h operation under simulated sunlight conditions (1,000 W m$^{-2}$) at 25 °C.

The prototype array equipped with hematite and dual bismuth vanadate photoelectrodes was tested under about 17.5-fold concentrated sunlight on DLR’s test facility SoCRatus. A HIT silicon mini module in series to each photoelectrode was installed to provide a bias voltage and promote the water splitting reactions occurring at the working electrode and the counter electrodes that lead to the formation of hydrogen as well as oxygen as a by-product. In case of hematite a further voltage of 325 mV was applied to allow operation under a total bias of 1.6 V. The system had been operated under concentrated sunlight for about 63 h. Maximum current densities of about 0.58 mA cm$^{-2}$ and 1.88 mA cm$^{-2}$ were achieved for hematite and bismuth vanadate respectively. Congruently, the estimated maximum flow of generated hydrogen reached 2,078 µmol h$^{-1}$ and 6,741 µmol h$^{-1}$. A certain degradation could be observed in case of bismuth vanadate, which was operated longer than hematite. Though, both configurations remained active during the experimental campaigns, the measured current densities and hydrogen generation rates were lower than expected. The observations suggest that further efforts with respect to photoelectrode characteristics and cell design have to be made to utilise the complete potential of performance also under concentrated sunlight.
2. DETAILED REPORT ON THE DELIVERABLE

2.1. Background and Objectives

Light-driven water splitting in hybrid photoelectrochemical-photovoltaic (PEC-PV) devices is the subject of project PECDEMO; this is considered a promising route to produce hydrogen using intermittent solar energy. One of the main goals of the project is to develop and demonstrate a stand-alone water splitting device with an active area of ≥50 cm² and a solar-to-hydrogen efficiency of 8-10% that is stable for more than 1,000 h.

Within the project various cell designs were analysed and tested with respect to optical efficiency and electrolyte flow characteristics before developing the optimised cell concept applied in the final prototype array, which features four compartments with an active area of 50 cm² each. A 1 x 4 array configuration was realised instead of an initially planned 2 x 2 array due to the better compatibility to the test facility SoCRatus described below.

The final demonstration phase began end of Nov 2016, when Milestone 7 was successfully accomplished by starting the field test of the prototype module.¹ The assessment of performance and stability of the prototype as well as ageing effects represented important parts of the work; the project aimed stability periods of ≥1,000 h under non-concentrated sunlight and ≥5,000 h/concentration ratio under concentrated sunlight respectively. Due to the low number of available sunshine hours in the reporting period, it was decided a) to use the developed 1 x 4 array prototype with a total active area of 200 cm² in the experiments under concentrated solar radiation at the German Aerospace Center (DLR)² in Cologne and b) to use an individualised 50 cm² cell, identical to the four cells forming the prototype, for simultaneous tests under non-concentrated, artificial sunlight at the University of Porto (UPorto)³.

¹ see PECDEMO website: http://pecdemo.epfl.ch/page-113308.html
² Institute of Solar Research
³ LEPABE - Laboratory for Process, Engineering, Environment Biotechnology and Energy, Faculty of Engineering
2.2. Results and Discussion

This deliverable reports on the final demonstration experiments conducted to assess the performance of the developed PEC-PV prototype array under non-concentrated and concentrated sunlight. Details about the prototype design as well as experimental results gained under non-concentrated and concentrated sunlight are presented in the subsequent sections.

2.2.1. Large-area prototype design

The final demonstrator comprising four tandem PEC-PV cells, each with an active area of 5 cm × 10 cm is presented in Figure 1.4

![Prototype module images](image)

*Figure 1. Final prototype module images. This device has an acrylic embodiment composed of four individual 50 cm² PEC cells. A reflective shield can be screwed in the front for operation under concentrated sunlight. The electrolyte feed is assured by two main inlets located at the bottom and on/off valves control the flow for each cell allowing individual or combined tests.*

The optimized design incorporates an open light path from the front to the back window.5 This allows placing a PV cell in the back of the photoelectrode

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providing the PEC cell with the necessary bias to promote water electrolysis. Counter electrodes (CE) are placed side-by-side to the photoelectrode (PE), but physically separated by an ion exchange membrane to avoid product gas mixing. The photoelectrode (working electrode – WE) can work as front or/and back window, depending on the preferred to operation mode: back-illumination or front-illumination. In both configurations the photoelectrode has a conductive metal frame at the semiconductor side, directly connected to the back side of the substrate where the electrical cables are connected or the PV cell is installed.

For operation under concentrated sunlight a double-layer (PTFE and aluminum) reflective shield is screwed close to the front side preventing the acrylic embodiment of overheating due to the solar input.

The cell body is made of transparent acrylic, assuring resistance to corrosive electrolytes and a very acceptable range of operating temperatures – from 0 °C to 65 °C. The final design also assures an easy to assemble and mechanically robust construction. Each cell compartment was built based on the electrolyte geometry optimized with CFD simulations – Figure 2.

![Figure 2](image-url)  
**Figure 2.** 3-D project of the modular prototype embodiment: 1 – acrylic body; 2 – acrylic cap; 3 – holder for the membrane and counter-electrode mesh; 4 – acrylic plate dividing the photoelectrode compartment; 5 – PE compartment; 6 – CE compartment; 7 – electrolyte free volume.
The CFD-based software was used to test the electrolyte flowpath of several designs varying: i) the number of inlets and outlets; ii) the location of the inlets and outlets in the bottom and in the top; and iii) their diameter. Following a step-by-step approach, it was possible to obtain the optimized design presented in Figure 2-7.

The electrolyte flowpath inside each compartment of the cell was improved for good heat dissipation (especially when concentrated sunlight is used) and for efficient gas bubbles collection in the top. The electrolyte free volume geometry comprises a main feeding channel with two inlets located at the bottom. This channel feeds 10 inlets located in the bottom of the PE compartment, 5 inlets close to the back window and 5 inlets close to the front window; it also feeds two inlets located at the bottom of each CE compartment. Four electrolyte outlets are located in the cell cap, two on top of the PE compartment and one on top of each CE compartment. This arrangement of inlets and outlets allows creating a uniform upward flow valid for a wide range of electrolyte feeding flow rates (between 500 and 1500 ml min⁻¹). The electrolyte flowpath generated in the CFD software was experimentally validated in a two-step approach: i) a tracer test with a blue dye to validate the flowpath lines, and ii) water electrolysis at 5.4 mA cm⁻² to assess the gas bubbles movement towards the outlets of the cell – Figure 3.

As Figure 3 shows, the non-optimized cell comprises several stagnant flow zones inside the electrolyte reservoir, as well as large turbulent areas with backflow. In the optimized cell design this stagnant flow zones were eliminated and fluid turbulence became negligible, being observed only in a quite restricted part at the bottom of the cell. In the non-optimized design, as the blue dye flows through the cell, the turbulent areas delay the upward movement towards the cell outlets and the dye is concentrated in stagnant zones becoming darker. In the optimized cell the tracer flows continuously towards the outlets, without any evidence of turbulence or stagnant zones. An optimized electrolyte flowpath is also crucial to avoid the accumulation of gas bubbles during operation. Stagnant and turbulent zones increase gas accumulation inside the cell, decreasing the optical transparency in the path that the sunlight needs to cross. In the non-optimized design – Figure 3-a), the
accumulation of bubbles is considerably higher than in the optimized cell design – Figure 3-b).

The optimized electrolyte flowpath is also crucial to assure good heat dissipation, mainly when the prototype operates under concentrated sunlight. CFD simulations were performed to predict the effectiveness of each individual cell of the modular prototype to maintain a specific electrolyte temperature and dissipate heat – Figure 4. Two different scenarios were considered: a) operation under 17,000 W m\(^{-2}\) with a feeding flow rate of 1,000 ml min\(^{-1}\) at 25 °C and the outside air at 25 °C; b) operation under 17,000 W m\(^{-2}\) with a feeding flow rate of 500 ml min\(^{-1}\) at 45 °C and the outside air at 25 °C.

As shown in Figure 4 the electrolyte temperature is mostly uniform in both compartments of the cell - anode and cathode. Only in the areas close to the windows a slight increase in the electrolyte temperature is observed. For example, when the electrolyte enters the cell at 45 °C (Figure 4-b) a maximum difference of only 2 K is observed inside the electrolyte container. For the most common scenario (electrolyte entering the cell at 25 °C) a maximum difference of only 1 K was observed in the electrolyte free volume.
2.2.2. Tests under non-concentrated sunlight

To assess the performance of the optimized hybrid photoelectrochemical-photovoltaic (PEC-PV) device under non-concentrated sunlight an experimental setup was assembled at UPorto – Figure 5. The stability tests under non-concentrated sunlight were performed in a 50 cm² PEC cell identical to the ones that comprise the large-area prototype. Two experimental campaigns were conducted: i) with bare hematite during 1,000 h operation at 1.6 V (bias potential given by 2 HIT-Si cells), 1,000 W m⁻², and 45 °C and ii) with bismuth vanadate covering 24 h continuous operation at 1.28 V (bias potential given by 1 HIT-Si cell), 1,000 W m⁻², and 25 °C.
Figure 5. Test bench to perform the long-term stability test: 1 – PEC-PV device; 2 – auxiliary PV cell; 3 – peristaltic pump; 4 – cooling fan; 5 – Sulphur plasma lamp system AS 1300 V 2.0, Plasma International GmbH; 6 – Autolab potentiostat; 7 – data acquisition software; 8 – water bath.

2.2.2.1. Medium term test with hematite

Hematite was first selected to conduct the stability test due to its high stability under continuous operation. Hematite thin films (ca. 20 nm thick) were prepared by spray pyrolysis at UPorto on a FTO glass substrate (7 Ω square\(^{-1}\)). Continuous electrolyte feeding of ca. 200 ml min\(^{-1}\) was promoted using a peristaltic pump (Figure 5–3). A water bath (Figure 5–8) was used to keep the electrolyte at a constant temperature of ca. 45 °C, which was the temperature agreed by PECDEMO partners to conduct this test.

To supply the hematite photoelectrode with the necessary bias potential of ca. 1.6 V, two 50 cm\(^2\) PV modules prepared by HZB\(^7\) were connected in series – Figure 6. An Autolab potentiostat was used to continuously monitor the photocurrent produced by the semiconductor – Figure 6.

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\(^7\) Helmholtz-Zentrum Berlin für Materialien und Energie GmbH
Figure 6. Schematic representation of the connections between the main components of the tandem PEC-PV device used in the medium term test with hematite.

The photocurrent density history over 1,000 h operation is plotted in Figure 7.

Figure 7. Polarization curve of the hematite photoelectrode obtained under a constant bias of 1.6 V and simulated solar irradiance under simulated sunlight, sulphur plasma lamp system AS 1300 V 2.0, Plasma International GmbH (1,000 W m$^{-2}$).

From Figure 7 it can be concluded that the PEC-PV device remained stable over 1,000 h (approximately 42 days) delivering an average photocurrent density of ca. 0.43 mA cm$^{-2}$, which corresponds to a STH efficiency of 0.64% (based on the HHV of hydrogen). Although the recorded photocurrent over this period was not particularly high, this study aims at to demonstrate that it is possible to have a stand-alone PEC-PV device continuously working over 1,000 h under similar operating conditions to the ones of a pilot plant.

The individual performance of the hematite photoelectrode and the PV modules was monitored over time with $J$-$V$ characteristic curves acquired at
specific periods during the stability test. The J-V characteristic curves obtained for both components at the beginning and at the end of the test show no significant decrease in their performance occurred after 1,000 h of continuous operation – Figure 8.

Finally, after the stability test was finished the PEC-PV cell was disassembled and it was possible to confirm that none of the elements had undergone any visible degradation, as Figure 9 shows.

**Figure 8.** J-V characteristics curves: a) 50 cm² hematite photoanode prepared by spray pyrolysis, before starting the stability test, 0 h (●), and after operating 1005 h (●) under simulated sunlight (1,000 W m⁻²) and in 1 M KOH, obtained in a 2-electrode configuration; b) two 50 cm² Si-PV HIT modules connected in series before starting the stability test, 0 h (●), and after operating 1,005 h (●) under simulated sunlight, sulphur plasma lamp system AS 1300 V 2.0, Plasma International GmbH (1,000 W m⁻²).

**Figure 9.** Main components of the PEC cell embodiment after the 1,000 h stability test; a) acrylic embodiment; b) stainless steel frame; c) hematite photoanode prepared by spray pyrolysis (before and after stability test) and d) Si-PV cells.
2.2.2.2. Medium term test with bismuth vanadate

Bismuth vanadate photoelectrodes prepared at HZB were tested at UPorto using the test bench presented in Figure 5. Continuous electrolyte feeding of ca. 200 ml min\(^{-1}\) was promoted using a peristaltic pump (Figure 5–3). A water bath was used to keep the electrolyte at a constant temperature of ca. 25 °C (Figure 5–8). Considering the characteristic performance of BiVO\(_4\) a single 50 cm\(^2\) PV module was enough to provide the necessary bias to the PEC cell for promoting water electrolysis – Figure 10.

**Figure 10.** Schematic representation of the connections between the main components of the tandem PEC-PV device used in the medium term test with bismuth vanadate.

In this test the setup operated at the interception point of the J-V curves of BiVO\(_4\) photoelectrode and HIT PV module – Figure 11. At the starting point (0 h) this interception corresponds to a photocurrent density of ca. 1.55 mA cm\(^{-2}\) at 1.28 V resulting in a solar to hydrogen (STH) efficiency of 2.30%.

**Figure 11.** J-V characteristics curves: 50 cm\(^2\) bismuth vanadate photoelectrode (●) under simulated sunlight (1,000 W m\(^{-2}\)) and in 0.1 M KPi, obtained in a 2-electrode configuration; single 50 cm\(^2\) Si-PV HIT module (●) under simulated sunlight, sulphur plasma lamp system AS 1300 V 2.0, Plasma International GmbH (1,000 W m\(^{-2}\)).
An Autolab potentiostat was used to continuously record the photocurrent produced by the PEC-PV device. The photocurrent history over 24 h operation is plotted in Figure 12.

![Figure 12](image12.jpg)

**Figure 12.** Polarization curve of the bismuth vanadate photoelectrode obtained in a 2-electrode configuration under simulated sunlight, sulphur plasma lamp system AS 1300 V 2.0, Plasma International GmbH (1,000 W m$^{-2}$).

From Figure 12 the PEC-PV device performance decreased over time. During the 24 h test an average photocurrent density of 0.41 mA cm$^{-2}$ was recorded, corresponding to a STH efficiency of 0.61%. Similarly to the test with hematite the individual performance of BiVO$_4$ photoelectrode and the PV module was assessed at the beginning and at the end of the test with J-V measurements – Figure 13.

![Figure 13](image13.jpg)

**Figure 13.** J-V characteristics curves: a) 50cm$^2$ bismuth vanadate photoelectrode, before starting the stability test, 0 h (∗), and after operating 24 h (∗) under simulated sunlight (1,000 W m$^{-2}$) and in 0.1 M KPi, obtained in a 3-electrode configuration; b) 50 cm$^2$ Si-PV HIT module before starting the stability test, 0 h (∗), and after operating 24 h (∗) under simulated sunlight (1,000 W m$^{-2}$).
During the stability tests it was possible to observe material detachment from the glass substrate, Figure 14. This may explain why the photoelectrode performance decreased continuously over the 24 h test.

2.2.3. Tests under concentrated sunlight

The performance tests under concentrated sunlight were carried out using DLR’s test facility SoCRatus\(^8\) in Cologne starting end of Sept 2016. This solar concentrator provides homogeneous, concentrated irradiation in the rectangular focal plane and is characterised by a geometric concentration factor of 20.2. Main components and a schematic of the concentration principle are depicted in Figure 15. Taking the solar-weighted hemispheric reflectance of the aluminium based mirror material (87%) into account 17.5-fold concentrated sunlight effectively reached the prototype mounted in the focal plane.

The prototype installed in the focus of the solar concentrator without reflective shields is shown in Figure 16. Sensitive parts of the PEC-PV array and surrounding equipment were protected by reflective shields during the experiments. The prototype operating with bismuth vanadate photoelectrodes under concentrated sunlight can be seen in Figure 17, in which also the grid lines of the front photoelectrodes are clearly visible.

Figure 15. DLR’s test facility SoCRatus with its main components.

Figure 16. Modular prototype with hematite photoelectrodes mounted in the focal plane of the SoCRatus (here without reflective shields).

Figure 17. Modular prototype equipped with bismuth vanadate photoelectrodes irradiated with concentrated sunlight in the focal plane of the SoCRatus with reflective shields to protect sensitive parts of the setup.
The modular prototype was implemented in the set-up using two fluid cycles of the SoCRatus as shown in Figure 18. In bypass operation the two fluid cycles feed the inlets of the prototype, where the flow is distributed to the oxygen (O\textsubscript{2}) and hydrogen (H\textsubscript{2}) chambers. The outlets of the hydrogen chambers are connected to the Fluid Cycle 1, whereas the outlets of the oxygen chambers are connected to Fluid Cycle 2. Evolved hydrogen is transported by the electrolyte of Fluid Cycle 1 to the tank where it leaves the system together with nitrogen (N\textsubscript{2}) introduced upstream as a purging gas. Evolved oxygen leaves the system similarly from the tank of Fluid Cycle 2. The two tanks were connected to each other at the bottom part in order to allow compensation of slightly different volume flows of Fluid Cycle 1 and 2. Temperatures, pressures, volume flows, pH values as well as product gas composition, direct normal irradiance (DNI) and spectral irradiance were measured and processed by the data acquisition and control system.

![Figure 18. Modular prototype implemented in Fluid Cycle 1 and 2 of the SoCRatus.](image)

2.2.3.1. Preparing tests

To assess the CFD results considering operation under concentrated sunlight (Figure 4) two sets of experiments were conducted in the first field test...
campaign – Figure 19 and Figure 20. First, the prototype was exposed to concentrated sunlight (max. 15 suns) considering a constant electrolyte feeding flow rate of around 500 ml min\(^{-1}\) at a constant feed temperature of ca. 25 °C. As expected, when exposed to concentrated sunlight a slight electrolyte temperature increase was observed in the photoelectrode compartment, being recorded a maximum difference of 4 K between the inlets and the outlets of the cell due to the solar input - Figure 19-a). During this period the temperature in the cell body was continuously recorded at four distinct points. As Figure 19-b) shows only the front part of the cell was affected by the concentrated solar radiation and a maximum temperature of ca. 120 °C was reached on the aluminium shield. In the back window, where the semiconductor was located, the maximum temperature recorded was ca. 40 °C. These results confirm that the developed prototype can safely operate with highly concentrated sunlight without damaging the semiconductor film or damaging any part of the embodiment by critical temperatures.

![Figure 19](image.png)

**Figure 19.** Temperature monitoring in the prototype operating under concentrated sunlight with a constant electrolyte temperature of 25 °C and a constant feeding flow rate of 500 ml min\(^{-1}\): a) temperature monitoring in the electrolyte circuit; (\(\rightarrow\))IN1 – electrolyte inlet 1; (\(\rightarrow\))IN2 – electrolyte inlet 2; (\(\rightarrow\))PE OUT – electrolyte outlets in the photoelectrode compartments; (\(\rightarrow\))CE OUT – electrolyte outlets in the counter-electrode compartments; b) temperature monitoring in the prototype embodiment; BS (\(\rightarrow\)) – back side of the aluminum shield; (\(\rightarrow\))AB – acrylic body; (\(\rightarrow\))FW – front window; (\(\rightarrow\))BW – back window.
Another set of tests was conducted to assess the capability of the prototype to maintain a certain electrolyte temperature inside independently from the feeding flow rate and from the solar irradiance. In these tests the feeding flow rate was gradually changed from 0.4 to 0.6 l min\(^{-1}\); the initial electrolyte feeding temperature was 45 °C being changed to 25 °C afterwards – Figure 20.

![Figure 20](Figure 20. Temperature monitoring in the prototype operating under concentrated sunlight with variation of the feeding flow rate and tilted position in the SoCRatus: a) temperature monitoring in the electrolyte circuit; (-)IN1 – electrolyte inlet 1; (-)IN2 – electrolyte inlet 2; (-)PE OUT – electrolyte outlets in the photoelectrode compartments; (-)CE OUT – electrolyte outlets in the counter-electrode compartments; b) electrolyte flow rate; (-)IN1 – electrolyte inlet 1; (-)IN2 – electrolyte inlet 2.)

The obtained results showed that after exposure to concentrated sunlight (ca. 15 suns) the electrolyte temperature slightly increased in the photoelectrode compartment. A maximum difference of ca. 4 K was recorded between the inlets and the outlets of the cell due the solar input, namely when the electrolyte was entering the cell at 45 °C, which is in accordance with the CFD results – Figure 4-b). These tests clearly demonstrated that the prototype is capable of maintaining a desired electrolyte temperature under different operating scenarios.

Field tests in the SoCRatus facility were also performed to assess the ability of the prototype to collect the generated hydrogen separately from oxygen – Figure 21.
Figure 21. Hydrogen flow monitoring in the prototype at 5.4 mA cm\(^{-2}\) without sunlight exposure, with variation of the feeding flow rate and tilted position: a) evolved hydrogen monitoring; (—) H2 CE – hydrogen collected in the counter-electrode compartments; (—) H2 PE – hydrogen collected in the photoelectrode compartment; b) electrolyte flow rate monitoring at the inlets; (—) feeding flow 1 – electrolyte inlet 1 and outlets from the photoelectrode compartment; (—) feeding flow 2 – electrolyte inlet 2 and outlets from the counter-electrode compartments.

The feeding flow rate and the tilted position of the prototype were changed to simulate different operating scenarios. When the SoCRatus operates with solar tracking the tilted position of the prototype is continuously changed to maximize the solar irradiance, which may contribute to some hydrogen crossover through the membrane. Despite this, as Figure 21 shows, the prototype can safely operate with different tilted positions (from about 80° to 25° corresponding to elevation angles of ca. 10° to 65°, respectively), avoiding gas mixture inside. The evolved hydrogen was continuously collected at the CE compartment.

2.2.3.2. Medium term tests

The prototype with its photoelectrodes and PV-modules was wired and connected to a power source in order to allow the measurement of diverse parameters such as voltage and current as well as the application of an additional bias voltage as partly done in experiments with hematite photoelectrodes.
The first experimental campaign was conducted with front illuminated hematite photoelectrodes, whereas in the second campaign two bismuth vanadate photoelectrodes in each compartment were installed – the first one being back illuminated as part of the front window, the second one being front illuminated as part of the back window. Some details of the experimental conditions can be extracted from Table 1.

**Table 1. Comparison of experimental conditions for Campaign 1 with hematite photoelectrodes and Campaign 2 with bismuth vanadate photoelectrodes.**

<table>
<thead>
<tr>
<th>Campaign</th>
<th>1: Hematite</th>
<th>2: Bismuth vanadate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photoelectrode</td>
<td>4 × 50 cm², front illuminated, UPorto</td>
<td>8 × 50 cm², 4 front + 4 back illuminated (in parallel), with grid-lines, HZB^a</td>
</tr>
<tr>
<td>PV module</td>
<td>HIT silicon mini modules, 4 × 50 cm², $J_{sc}$: 16.95-17.55 mA cm⁻², $V_{oc}$: 1.38-1.40 V, PVcomB^a</td>
<td></td>
</tr>
<tr>
<td>Additional bias</td>
<td>partly +325 mV^b</td>
<td>none</td>
</tr>
<tr>
<td>Membrane</td>
<td>8 × FAA^c</td>
<td>Comp. 1: 1 × FAA + 1 × NE^d</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Comp. 2: 2 × NE^d</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Comp. 3+4: none</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>1 M KOH</td>
<td>0.5 M K₂SO₄ + 0.1 M K₂HPO₄/KH₂PO₄ buffer with pH 7</td>
</tr>
<tr>
<td>Temperature</td>
<td>about 25 °C</td>
<td>about 30 °C</td>
</tr>
<tr>
<td>Product gas purging</td>
<td>2 lN min⁻¹ N₂ in both fluid cycles</td>
<td></td>
</tr>
</tbody>
</table>

^a Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, ^b by power supply AIM-Ti QL355-P in series, ^c Fumasep® FAA-3-PK-130, ^d Nafion® NE-1110 Comp. = compartment

The total irradiation on the prototype, the achieved average current density, and the estimated molar flow of generated hydrogen relative to respective mean values is shown in Figure 22 for the experiments with hematite photoelectrodes. A total experimental time of nearly 15 h was reached, thereof more than 8.5 h without additional bias and close to 6.5 h with 325 mV additional bias as indicated. A total irradiance of 12.4 kW m⁻² on average and up to 14.0 kW m⁻² was applied. Current densities of about 0.2 mA cm⁻² and 0.5 mA cm⁻² were reached without and with the additional bias respectively. Within the duration of operation the prototype featured stable performance.
The hydrogen flow generally follows the current density with a certain delay due to mixing and saturation effects in the fluid cycle. Maximum hydrogen flows of 924 μmol h⁻¹ and 2,078 μmol h⁻¹ were detected without and with bias respectively. A major fraction of about 90% of the produced hydrogen could be found in Fluid Cycle 1, whereas only about 10% was detected in Fluid Cycle 2 (connected to the outlets of the oxygen chambers) indicating efficient product gas separation and minor cross over.

Figure 22. Total irradiation on the prototype (smoothed ± 30 s), average current density (smoothed ± 30 s), and hydrogen flow relative to respective mean values as well as average solar-to-hydrogen efficiencies (STH, based on the HHV of H₂) without and with bias voltage of the particular days associated with Campaign 1 (hematite photoelectrodes), gray field refers to test of single compartments.

The corresponding results for Campaign 2 with bismuth vanadate photoelectrodes, which covered a duration of about 48 h, can be found in Figure 23. An applied total irradiance of 7.85 kW m⁻² on average and up to 16.5 kW m⁻² was estimated. The mean current density could be calculated to 0.88 mA cm⁻² while a maximum value of 1.88 mA cm⁻² was measured on Day 2 at about 13 kW m⁻². As for hematite the hydrogen flow corresponds well to the current density taking the aforementioned delay into account. Production rates up to 6,741 μmol h⁻¹ reached on Day 2 were estimated. Since part of the membranes was removed for Campaign 2 a larger portion of the produced
hydrogen could be found in Fluid Cycle 2. With 0.42% the maximum daily solar-to-hydrogen efficiency (STH) was calculated for Day 5 at comparably low levels of irradiance which suggests a non-proportional dependency of hydrogen formation on the solar input. This can be confirmed by comparing achieved current densities under non-concentrated and concentrated sunlight respectively. Moreover, the graphs indicate degradation of the photoelectrochemical system within the duration of the campaign since relative figures of the current density undercut the total irradiance at the end of the campaign whereas they exceed them at the beginning of the campaign. However, even after 48 h operation under challenging conditions the bismuth vanadate system was still active. A significant influence of membranes on the performance of particular compartments could not be observed in the current set-up.

Figure 23. Total irradiation on the prototype (smoothed ± 30 s), average current density (smoothed ± 30 s), and hydrogen flow relative to respective mean values as well as average solar-to-hydrogen efficiencies (STH, based on the HHV of H\textsubscript{2}) of the particular days associated with Campaign 2 (bismuth vanadate photoelectrodes).
2.2.4. Medium term tests overview and comparison

An overview and comparison of the medium term tests is provided in Table 2.

<table>
<thead>
<tr>
<th>DLR</th>
<th>Hematite</th>
<th>Bismuth vanadate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photoelectrodes</td>
<td>4 × 50 cm², front illuminated, UPorto</td>
<td>8 × 50 cm², 4 front + 4 back illuminated (in parallel), with grid-lines, HZB</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>1.0 M KOH pH 14 at 25 °C</td>
<td>0.5 M K₂SO₄ + 0.1 M K₂HPO₄/KH₂PO₄ buffer with pH 7 at 30 °C</td>
</tr>
<tr>
<td>Stability time</td>
<td>8.5 h without bias; 6.5 h with 325 mV bias</td>
<td>Stability time: 48 h</td>
</tr>
<tr>
<td>PV modules</td>
<td>HIT silicon mini modules, 4 × 50 cm², Jsc: 16.95-17.55 mA cm⁻², Voc: 1.38-1.40 V, PVcomB</td>
<td>HIT silicon mini modules, 1 × 50 cm², Jsc: 16.95 mA cm⁻², Voc: 1.39 V, PVcomB</td>
</tr>
<tr>
<td>Average photocurrent</td>
<td>0.20 mA cm⁻² without bias; 0.46 mA cm⁻² with 325 mV bias</td>
<td>0.87 mA cm⁻² without bias</td>
</tr>
<tr>
<td>Maximum photocurrent</td>
<td>0.52 mA cm⁻² without bias; 0.58 mA cm⁻² with 325 mV bias</td>
<td>1.88 mA cm⁻² without bias</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>UPorto</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Photoelectrodes</td>
<td>1 × 50 cm², front illuminated, UPorto</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>1.0 M KOH pH 14 at 45 °C</td>
</tr>
<tr>
<td>Stability time</td>
<td>Stability time: 1,000 h</td>
</tr>
<tr>
<td>PV modules</td>
<td>HIT silicon mini modules in series, 2 × 50 cm², Jsc: 16.95-17.37 mA cm⁻², Voc: 1.390-1.399 V, PVcomB</td>
</tr>
<tr>
<td>Average photocurrent</td>
<td>0.43 mA cm⁻² (with 250 mV bias from auxiliary PV module)</td>
</tr>
<tr>
<td>Maximum photocurrent</td>
<td>0.60 mA cm⁻² (with 250 mV bias from auxiliary PV module)</td>
</tr>
</tbody>
</table>

2.3. Conclusions and next steps

The main objective of WP6 activities was to develop, build, and assess the performance of a sub-module prototype consisting of four identical cells, each with a photoactive area of 50 cm². The optimal design assures an open path for the sunlight to reach the PV cell placed in the back of the PEC cell. The counter-electrodes are placed side-by-side to the working-electrode and an
ion exchange membrane physically separates the O₂ and H₂ evolution compartments. CFD simulations were performed to obtain an optimized electrolyte flowpath that assures good heat dissipation and efficient collection of evolved gas bubbles. These simulations showed that under a solar concentration factor of 17, the expected maximum temperature inside each cell is ca. 55 °C in the front window and ca. 52 °C in the back window (assumed electrolyte temperature at the inlet of 45 °C with a feeding flow rate of 500 ml min⁻¹ and external air at 25 °C), perfectly suitable for the materials used in its construction and for the temperature range of the semiconductor film. Pre-characterization tests allowed confirming that the developed prototype assures an efficient separation of the evolved gases and is capable of maintaining the electrolyte temperature constant at the desired value independently from the tilted position angle and the feeding flow rate.

The prototype performance under non-concentrated sunlight was assessed at UPorto with an individualized cell, identical to the ones that comprise the large-area prototype. The PEC-PV device continuously operated with a 50 cm² hematite photoelectrode connected in series with two 50 cm² HIT silicon solar cells, which supplied the PEC cell with the necessary bias to promote water electrolysis. The hematite photoelectrode remained stable over 1,000 h delivering a constant photocurrent of ca. 0.43 mA cm⁻² at 1.6 V. The ultra-thin hematite film was resistant to corrosion with the electrolyte at 45 °C. The HIT silicon solar cells also remained stable over the 1,000 h period, generating a constant Voc of ca. 2.7 V. In what concerns bismuth vanadate, an average current density of ca. 0.41 mA cm⁻² was obtained during the 24 h operation at 1.28 V. Over time the bismuth vanadate performance obtained in 0.1 M K₂HPO₄/KH₂PO₄ at 25 °C and 1-sun simulated solar conditions continuously decreased.

The developed 1 x 4 prototype PEC-PV array was tested under about 17.5-fold concentrated sunlight on DLR’s test facility SoCRatus. Hematite and dual bismuth vanadate photoelectrodes with HIT silicon solar cells in series were considered. The experimental runs lasted 15 h and 48 h regarding hematite and bismuth vanadate photoelectrodes, respectively. A maximum current density of 0.58 mA cm⁻² was observed for hematite at a total irradiance of nearly 13 kW m⁻² when an additional bias of 325 mV was applied; hydrogen was
produced at up to 2,078 µmol h⁻¹. Within the test duration, stable performance was observed and efficient separation of product gases was reached. The bismuth vanadate configuration was operated without additional bias and led to current densities up to 1.88 mA cm⁻² at about 13 kW m⁻². Corresponding hydrogen production rates of up to 6,741 µmol h⁻¹ were determined. Degradation of bismuth vanadate photoelectrodes was observed.

In both campaigns under concentrated sunlight lower current densities and hydrogen production rates than expected were achieved taking into account that the tests under non-concentrated irradiation led to current densities of around 0.43 mA cm⁻² for hematite and 0.41 mA cm⁻² for bismuth vanadate. This suggests a non-proportional dependency of hydrogen formation on the solar input and that further efforts have to be made in order to allow efficient exploitation of the higher photon flow provided by the solar concentrator, which deserve further investigation.