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1. EXECUTIVE SUMMARY

PECDEMO’s goal of developing a large scale hybrid photoelectrochemical-photovoltaic (PEC-PV) solar water splitting device showing high efficiency (8-10%) and long term stability is particularly important to show the applicability of solar water splitting in our future energy system. The first work package (WP1) focuses on a small-area device (< 1cm²), which forms as a basis for our up-scaling efforts. In this deliverable report (D1.4), we focus on the stability aspect of such a device, by showing long-term stability data of our metal oxide photoelectrodes and solar cells. The main aim is to demonstrate less than 10% performance decrease within the first 100 hours of measurement. The results are summarized in the following:

- \textit{Fe}_2\textit{O}_3\) photoanode is known to be highly stable, and we show for the first time a stability data of up to 1000 hours. No noticeable degradation was observed.
- \textit{BiVO}_4\) photoanode is expected to be stable in neutral pH electrolyte, but we observed a photocurrent decrease within the 100-hour measurement period. The decrease is, however, not related to material degradation, but due to sub-optimal PEC cell design. Bubbles formed rapidly and trapped at the surface of BiVO₄, causing decreased effective surface area. More optimal cell design is expected to fully resolve this issue. In alkaline environment, protection layer consisting of TiO₂ and Ni successfully improves the stability, although it is still limited to less than one hour.
- \textit{Cu}_2\textit{O}\) photocathode’s stability is shown to be enhanced with the protection layer strategy that we developed. Although 10% performance decrease is observed within ~55-60 hours, the improvement in stability is unprecedented for Cu₂O photocathodes.
- \textit{Perovskite} solar cell shows increasing efficiency within the first 500 hours of measurement, with no noticeable change of efficiency afterwards, up to more than 2000 hours of operation.
- \textit{HIT silicon} solar cell shows stable short-circuit current and open-circuit potential within 100 hours, and a slight decrease of fill factor is observed. Overall, the efficiency decreases only by less than 4%.

The deliverable target has been satisfactorily met by \textit{Fe}_2\textit{O}_3\) photoanode, perovskite and \textit{HIT silicon} solar cell; efforts will be continued in the next couple of months in achieving the same level of stability with BiVO₄ and Cu₂O.
2. DETAILED REPORT ON THE DELIVERABLE

2.1. Background and Objectives

One of the main advantages of using metal oxides as photoelectrode materials lies in their relative stability in aqueous solutions. This is indeed a rather widely held view in the solar water splitting field. However, it is not necessarily true, certainly not under all conditions. The solution’s pH is an important pre-requisite. For example, TiO$_2$ and Fe$_2$O$_3$ are reported to be stable except in acidic pH. In contrast, WO$_3$ is only stable in acidic (pH < 3) solution. BiVO$_4$ is known to be stable in neutral pH (between 3 and 11). Finally, some oxides are also known to be unstable in all pH range, e.g., ZnO and Cu$_2$O. Since material’s stability is an important factor that in the end determines the applicability and cost of the final solar water splitting device, we set out to report the long-term stability of our metal oxide photoelectrodes in this deliverable report.

The benefit of these stability data is two-fold. First, they clearly serve as important evaluation metric of our photoelectrode materials. Second, these rather long-term (100 hours) stability measurements are not currently done by researchers in the solar water splitting field. These data will then fill this void, and additional problems—commonly unknown due to the short-term nature of our standard measurements—will be able to be identified. Adequate solutions can then be implemented at a much earlier stage.

Finally, although the solar cells are not considered as the limiting factor in terms of the stability of a tandem PEC-PV water splitting device, we also report the long-term stability of the solar cells used in this project: silicon and perovskite solar cells.

2.2. Results and Discussion

2.2.1. Fe$_2$O$_3$ photoanode

Photoelectrodes that are efficient, highly stable, made from low cost materials and easily prepared using inexpensive techniques are required for commercially viable solar photoelectrochemical (PEC) water-splitting technology. Hematite is one of few materials that is being considered for this application. The performance of hematite photoanodes is very sensitive to the deposition method, either in terms of efficiency and stability. In this work, bare hematite thin films were prepared by spray pyrolysis
and systematically optimised following a design of experiments approach. The optimised hematite photoelectrode showed a photocurrent density of ca. 0.94 mA cm$^{-2}$ at 1.45 $V_{\text{RHE}}$, without dopants or co-catalysts, which is remarkable for a thin film of ca. 19 nm. The stability of this photoelectrode was assessed over 1000 h of PEC operation under 1-sun of simulated sunlight. A record-breaking result was obtained with no evidences of hematite film degradation neither of current density loss. These results open the door to turn PEC cells into a competitive technology in the solar fuel economy. The result of this $\text{Fe}_2\text{O}_3$ section is published in the journal of Nano Energy.$^1$

**EXPERIMENTAL**

**Hematite photoanodes preparation**

The synthesized materials were prepared by spray pyrolysis in an in-house assembled setup consisting of: (i) spray pyrolysis chamber; (ii) automatic syringe pump; (iii) liquid and air feeding system; and (iv) spray nozzle and its control system; (v) heating plate and its control system. The spray nozzle (Spraying Systems Co. model SU J4B-SS) was fed with an ethanolic solution of iron (iron (III) acetylacetonate - $\text{Fe(}\text{AcAc})_3$) and mixed with compressed air, directing the spray to the substrates at ca. 2 bar. An automatic syringe pump (Cronus programmable Sigma 2000 C, SMI-Labhut Ltd, UK) was used to deliver 1 mL of 10 mM of $\text{Fe(}\text{AcAc})_3$ (99.9 %, Aldrich) in EtOH (99.5 %, Aga) to the spray head, at a flowrate of 12 mL min$^{-1}$ (spray length of 5 s). The heated plate, 18 $\times$ 18 cm$^2$, displayed a uniform surface temperature regulated up to 550 °C. The substrates were placed on the heated plate at constant temperature; a range of 400 °C to 500 °C was tested. After the spray deposition, the hematite samples were air-annealed for 30 min at 550 °C, before being cooled down to the room temperature. This setup allows depositing homogeneous films up to 10 $\times$ 10 cm$^2$. For each set of parameters tested, three samples were prepared to assess the reproducibility.

The photoanodes were prepared on 2.2 mm thick, 7 Ω·square$^{-1}$ fluorine-doped tin oxide (FTO) coated glass substrates (Solaronix, Switzerland). The FTO-glass substrates were heated at 450 °C and ca. 1.5 mL of a diluted TEOS solution (10 % volume in ethanol) were hand-sprayed with a glass atomizer onto the heated substrates. These samples were cooled down before heating again to deposit the hematite film.
Electrochemical characterization
A PEC cell device known as “cappuccino” was chosen to perform the electrochemical characterization of the prepared hematite photoanodes. This cell was filled with a 1.0 M NaOH (25 °C, pH = 13.6) electrolyte solution in which the photoelectrode was immersed. The surface area illuminated was ca. 0.5 cm² defined by an external mask. A standard three-electrode configuration was used: Ag/AgCl/Sat KCl electrode (Metrohm, Switzerland) used as a reference electrode, 99.9 % pure platinum wire (Alfa Aesar®, Germany) as counter-electrode and hematite photoanodes as working electrodes.

J-V characteristic curves were performed using a ZENNIUM workstation (Zahner Elektrik, Germany) controlled by Thales software package (Thales Z 2.0). The applied potential bias was reported as a function of the reversible hydrogen electrode (RHE). The stability test was performed using an AUTOLAB electrochemical station (Metrohm Autolab B.V., Netherlands) and a Plasma-I AS1300 light engine (Plasma International, Germany) lamp power equipped with a standard sulphur lamp (SS0); a c-Si photodiode was used for calibration. The photocurrent history of the prepared hematite photoanodes was assessed over 1000 h under continuous 1-sun illumination (100 mW·cm⁻²) and applying a potential of 1.45 V_RHE.

RESULTS AND DISCUSSION
A design of experiments (DoE) approach was used to optimise the bare hematite deposition; the selected response variable was the photocurrent density (J, in mA·cm⁻²) generated by the prepared material at a bias potential of 1.45 V_RHE. A response surface methodology was applied to factors: (i) sprayed volume of solution (v); (ii) temperature of the glass substrate during the deposition (T); and (iii) time gap between sprays (t). The set of preparation conditions found to maximize the photocurrent density were: v = 42 mL, T = 425 °C and t = 35 s.

The performance of the bare hematite photoanodes prepared using the optimised conditions was assessed based on the photocurrent-voltage (J-V) curves in dark and under simulated solar illumination (AM 1.5 G, 100 mW·cm⁻²) conditions - Figure 1. Under dark conditions the current steeply increased for a potential higher than 1.66 V_RHE, indicating the electrochemical water oxidation onset potential. Under sunlight conditions the sample showed an onset potential at 0.95 V_RHE and photocurrent densities of ca. 0.67 mA·cm² at the potential of reversible oxygen
electrode (1.23 V$_{RHE}$) and ca. 0.94 mA·cm$^{-2}$ at 1.45 V$_{RHE}$. These performance values represent one of the highest photocurrents ever reported for bare hematite photoanodes. Among hematite samples prepared by spray pyrolysis, the present result is ca. 65% greater. The film thickness of the optimised sample was ca. (18.8 ± 0.1) nm; the literature refers that a film thickness of ca. (20.0 ± 2.2) nm maximizes the internal quantum yield.

Figure 1. J-V characteristics of the optimised hematite sample prepared by spray pyrolysis, before starting the stability test, 0 h (■), and after 500 h (●) and 1000 h (▲), in the dark (dashed lines) and under simulated solar illumination conditions (AM 1.5 G, 100 mW·cm$^{-2}$, solid lines).

Recent studies have increasingly mentioned the importance of obtaining highly stable photoelectrodes as a critical objective to achieve commercial viability of photoelectrochemical hydrogen production devices. Therefore, the stability of the optimised hematite sample was evaluated during a period of time of 1000 h under a bias potential of 1.45 V$_{RHE}$ and simulated solar illumination (100 mW·cm$^{-2}$). The photocurrent history is plotted in Figure 2, showing a stable performance over 1000 h (approximately 42 days) with an average photocurrent density of ca. 0.95 mA·cm$^{-2}$. To the best knowledge of the authors there are no published results for stability of hematite photoanodes for such long period. Figure 1 shows the J-V characteristic curves obtained before performing the stability test and after 500 and
1000 h of simulated sunlight exposure; no significant differences were observed for the response under light conditions. On the other hand, the dark current onset potential shifted slightly to lower potentials.

Figure 2. Polarization curve of the optimised hematite samples prepared by spray pyrolysis (solid blue line) obtained under a constant bias of 1.45 \( V_{\text{RHE}} \) and simulated solar illumination (100 mW cm\(^{-2}\)).

Figure 3 shows SEM images and EDS analyses of the fresh and aged hematite photoelectrode. The optimised hematite photoanode displays a very uniform surface fully covering the underneath FTO layer. The film growth follows a layer-plus-island growth, known as a Stranski-Krastanov mode.\(^6,7\) The morphology is in straight agreement with previous hematite structures deposited by spray pyrolysis.\(^8\) No significant differences are observed between the fresh and aged sample (see Figure 3c and Figure 3d, respectively). Moreover, the global EDS analyses are also similar, as shown in Figure 3e and Figure 3f.
The electrolyte solution used in the stability test was also analysed by inductively coupled plasma (ICP) spectroscopy; a fresh electrolyte sample was also analysed as control. Since an iron concentration of ca. 88 μg L⁻¹ was detected in the control, the results were merely supportive of the film corrosion hypothesis. The electrolyte used in the aging test showed an iron concentration of ca. 143 μg L⁻¹ suggesting minimal material detachment from the film surface, probably resulting
from the mechanical erosion by the oxygen evolution. Literature reports considerably high iron concentration increase during the aging tests; for example, Mendes et al. reported an increase of 1 mg L\(^{-1}\) only after 72 h of aging.

### 2.2.2. BiVO\(_4\) photoanode

Although BiVO\(_4\) is known to be stable between pH 3 and 11, most publications have only shown stability data (photocurrent-time curve) in the range of one hour. Only one report is known to have reported 48-hour stability data, which shows relatively no change of photocurrent within these 2 days of measurement.

In our previous report, we have employed cobalt phosphate (Co-Pi) as a co-catalyst on BiVO\(_4\), and the photocurrent seems to be stable for one hour. However, a recent report compares a long term stability of BiVO\(_4\) catalyzed with Co-Pi and cobalt carbonate (Co-Ci). There, it was shown that while Co-Pi catalyzed BiVO\(_4\) results in higher photocurrent, the stability is much better when Co-Ci is used as a co-catalyst. We therefore deposited Co-Ci on our W,Mo-BiVO\(_4\) via photo-assisted electrodeposition (PED). 0.3 mM \(\text{Co(NO}_3\)\(\text{)}_2\cdot 6\text{H}_2\text{O}\) was dissolved in 50 mL solution of 0.1M sodium bicarbonate (NaHCO\(_3\)) and used as the PED solution. The PED step utilized AM1.5 solar simulator as the illumination source and applied potential of -0.27 V vs Ag/AgCl until total charge of 3 mC/cm\(^2\) was obtained (corresponds to deposition time of \(\sim\)6 minutes). Longer deposition time and/or larger applied potential was found to give larger transient currents and reduced steady-state photocurrents.
Figure 4. (a) Chronoamperometry (photocurrent-time) curve of Co-Ci catalyzed, W,Mo-doped BiVO₄ at an applied potential of 1.23 V vs. RHE. (b) Photograph of the PEC cell containing the BiVO₄ sample under operation, where bubbles are shown to be formed and stucked at the surface of BiVO₄. (c) Photocurrent-voltage curves of the BiVO₄ sample prior to long term measurement, at t=10 h, and after completing the 100-hour measurement.

Figure 4a shows the photocurrent-time curve for Co-Ci catalyzed, W,Mo-doped BiVO₄ at an applied potential of 1.23 V vs RHE in a 0.1 M potassium carbonate buffer solution (pH ~8.6). It can be seen that the photocurrent decreases rapidly within the first few hours of the measurement. This is surprising, especially considering that BiVO₄ is known to be stable at this neutral pH and 48 hour stability has been shown in the literature. A closer look to the sample under measurement reveals that bubbles (presumably oxygen) were extensively formed in our PEC cell. Due to the geometry of the PEC cell that we used, some bubbles were unable to leave the surface of BiVO₄ (see Fig. 4b). This creates a void and essentially reduces the active area of the BiVO₄ photoelectrode. This turns out to be the reason for the photocurrent decrease we observed; in fact, physical removal of these bubbles results in an increase of photocurrent, back to the initial value (see Fig. 4a). Photocurrent-voltage (j-V) curves of the BiVO₄ photoelectrode at t= 0, 10, and 100 hour are relatively unchanged (Fig. 4c). This suggests that BiVO₄ is indeed stable within the 100 hour measurement period, and the photocurrent reduction that we
observed in the photocurrent-time plot is merely a result of sub-optimal PEC cell engineering.

![Photocurrent-time plot](image)

**Figure 5.** Chronoamperometry (photocurrent-time) curve of Co-Ci catalyzed, W-doped BiVO$_4$ at an applied potential of 1.23 V vs. RHE.

In an attempt to prevent bubbles being trapped at the surface of our BiVO$_4$ photoelectrode, we then performed the photocurrent-time measurement using an excessive stirring and a flow pump to ensure the convection of the electrolyte. Figure 5 shows the result of such measurement; here, we only used a 1% W-doped BiVO$_4$ (catalyzed with Co-Ci), which explains the lower photocurrent density observed. While it is not yet 100% stable, we already observed a significant improvement, as compared to the data shown in Fig. 4a, even without the need to manually removing the bubbles. However, some bubbles were still trapped on our BiVO$_4$ surface, albeit for a much shorter period of time; the oscillations of photocurrent in Fig. 5 indicate bubbles growing and leaving the surface of BiVO$_4$. We are currently working on a better PEC cell design, and we hope to show a 100-hour stability data for BiVO$_4$ photoelectrode in the next couple of months.
Figure 6. (a) Normalized photocurrent (It/I0) as a function of time for BiVO₄, BiVO₄ protected with TiO₂, and BiVO₄ protected with TiO₂ and Ni. (b) Longer-term stability measurement for BiVO₄ protected with TiO₂ and Ni. Both (a) and (b) were measured in 0.1 M KOH (pH ~13) and at an applied potential of 1.23 V vs RHE.

In addition to measurements in neutral electrolyte, efforts are also ongoing in improving the stability of BiVO₄ in alkaline electrolyte. This is motivated by the expected built-up pH gradient problems when a solar water splitting device is operated in neutral pH electrolyte. We therefore developed surface protection layer (ALD deposited TiO₂ and vacuum evaporated Ni) for BiVO₄ in order to prevent its corrosion in alkaline electrolyte, as already reported in the D2.1 and midterm report. Figure 6a shows the normalized photocurrent plot for bare BiVO₄, BiVO₄ protected with only TiO₂ layer (10 nm), and BiVO₄ protected with both TiO₂ layer and Ni layer (1 nm). Within the 15 minutes measurement time, it is clear that the stability of BiVO₄ photodeelectrode in alkaline solution is improved dramatically with the simultaneous deposition of both TiO₂ and Ni layers. However, longer term measurements in the order of one hour (Fig. 6b), reveals that even the TiO₂/Ni-protected BiVO₄ is not entirely stable: 50% reduction of photocurrent is observed. This degradation is caused by the presence of pin-holes in our ALD-TiO₂ layer; efforts are currently ongoing in order to prevent this and create a deposition condition that results in a fully dense TiO₂ layer.

### 2.2.3. Cu₂O photocathode

We have adopted an overlayer strategy on the Cu₂O photocathode for preventing its degradation in the aqueous solution. It was demonstrated that this strategy is
effective in the near-neutral solution, while it is still not fully effective in the harsh conditions such as acid and alkaline solutions (See Deliverable 2.1 and WP2 Mid-term reports). Therefore, we have focused on the stability of Cu$_2$O photocathode in the near-neutral solution (pH 5) for the goal of Deliverable 1.4. In this report, we look into the protective layers deposited planar Cu$_2$O photocathode, as well as the Cu$_2$O nanowire (NW) photocathode, which shows the highest performance in the pH 5 solution (See Deliverable 1.3 and WP1 Mid-term reports).

**Planar Cu$_2$O photocathode**

In our conventional planar Cu$_2$O photocathode, atomic layer deposited amorphous TiO$_2$ overlayer has been introduced as a protective layer. Around 100 nm amorphous TiO$_2$ thin film efficiently prevented the degradation of Cu$_2$O over several hours of continuous operation in pH 5 electrolyte. In addition, we found that a hydrothermal steam treatment at low temperature can further improve the stability of Cu$_2$O photocathode.

![Figure 7](image)

**Figure 7.** Stability measurement of RuO$_x$ catalyzed and TiO$_2$ overlayered Cu$_2$O photocathode with the steam treatment at 150 °C for 3 h in the pH 5 electrolyte biased at 0V vs RHE under the light chopping (1 sun).

Consequently, the RuO$_x$ catalyzed and TiO$_2$ overlayered Cu$_2$O photocathode with the steam treatment at 150 °C for 3 h showed the initial performance with a photocurrent density of 5.5 mA cm$^{-2}$ biased at 0V vs RHE in the pH 5 electrolyte under 1 sun illumination. The performance was stable with less than 10% photocurrent
decrease over 50 h operation under chopped illumination (Fig. 7). This result was published in *Energy and Environmental Science (2014)*.\textsuperscript{15}

![Figure 8](image)

**Figure 8.** (a) I-V characteristics in the pH 5 electrolyte under 1 sun illumination and (b) Stability measurements biased at 0V vs RHE of Cu$_2$O/SnO$_2$/RuO$_x$ photocathodes without and with the steam treatment at different temperatures for 3 h.

A SnO$_2$ overlayer was also explored as a protective layer for the planar Cu$_2$O photocathode. It was also deposited by atomic layer deposition. Sequentially, the hydrothermal steam treatment was carried out with different temperatures (100 °C, 125 °C and 150 °C). The initial performance of all samples including onset voltage and plateau current density was similar in the pH 5 electrolyte (Fig. 8a). However, the stability trend was quite different depending on the steam treatment conditions. The samples with the steam treatment were more stable, compared to the sample without the steam treatment. Among them, the sample with the steam treatment at 125 °C for 3 h showed the highest stability. Its photocurrent density operated at 0 V vs RHE was remained as 90 % of the initial value even after 57 h of operation under continuous illumination (Fig. 8b).

**Cu$_2$O NW photocathode**

We recently developed the high-quality Cu$_2$O NW photocathode, showing a considerable efficiency improvement compared to the planar Cu$_2$O photocathode (See Deliverable 1.3 and WP1 Mid-term reports in details). In this photocathode, AZO and TiO$_2$ overlayers were also adopted for forming a p-n junction and protecting the photocathode, respectively. In addition, electrodeposited RuO$_x$ was used as a HER catalyst on the surface, like the conventional planar Cu$_2$O photocathode.
Figure 9. (a) Photocurrent density and Faradaic efficiency for hydrogen evolution of Cu$_2$O NW photocathode biased at 0V vs RHE under 1 sun illumination in the pH 5 during the stability test. (b) Current-potential characteristics of Cu$_2$O NW photocathode before and after stability test. (c) Transmission electron microscopy image of Cu$_2$O NW photocathode after stability test.

For evaluating the stability, we measured the current density and the Faradaic efficiency for hydrogen generation using a gas chromatograph in the pH 5 electrolyte operated at 0 V vs RHE under 1 sun illumination. As a result, the Cu$_2$O NW photocathode showed a stable photocurrent density remaining 90 % of the initial photocurrent density over 50 h with a constant Faradaic efficiency of ~ 100 % (Fig. 9a). Although the photocurrent density was gradually decreased during the stability test, the performance was almost fully recovered to its initial level when the electrolyte was exchanged after stability test (Fig. 9b). Furthermore, no significant degradations were observed in each components (Cu$_2$O, AZO, TiO$_2$ and RuO$_x$) of the Cu$_2$O NW photocathode even after 55 h stability test, as evidenced by TEM-EDX elemental mapping analysis (Fig. 9c). Therefore, the gradual photocurrent density
drop during the stability test was probably caused by the local pH change of electrolyte, not the degradation of Cu$_2$O NW photocathode itself. This result was recently published in *Nano Letters* (2016).\textsuperscript{16}

**Outlooks**

We demonstrated the stable Cu$_2$O photocathode with less than 10% performance decrease in the near-neutral solution (pH 5) as below.

1. Planar Cu$_2$O with TiO$_2$ protection layer over 50 h
2. Planar Cu$_2$O with SnO$_2$ protection layer over 57 h
3. Cu$_2$O NW with TiO$_2$ protection layer over 50 h

Unfortunately, we could not achieve the goal of Deliverable 1.4 (Stable device with less than 10% performance decrease after 100 hours of operation) using our Cu$_2$O photocathode. Nevertheless, we demonstrated that overlayer strategy effectively prevents the intrinsic Cu$_2$O degradation in the aqueous solution. We have observed that pinholes originating from the imperfect synthesis of Cu$_2$O and the ALD overlayers represent the primary points of degradation, representing point defects which lead to corrosion of the Cu$_2$O material. We believe that these defects are not inherent to the materials and configuration we are using, but rather just a byproduct of the synthetic methods. Going forward, we will manually passivate pinholes which emerge during testing (using insulating epoxy resin) to hopefully arrest this degradation pathway and enable evaluation of the intrinsic device stability. Therefore, we are optimistic that we will soon be able to meet the Deliverable 1.4 target on our Cu$_2$O photocathodes.

2.2.4. Perovskite solar cell

Lack of proven stability has become a major obstacle on the path of metal halide perovskite solar cells (PSCs), in particular methylammonium lead triiodide (MAPbI$_3$), towards commercial viability. This correlates with the intrinsic affinity of MAPbI$_3$ towards moisture and ambient air in particular, leading to its degradation in ambient conditions. At Solaronix, we performed extensive stability tests using the module to
prove the durability of hole-conductor-free PSCs based on a triple-layer architecture employing carbon as a back contact.

Modules were glass sealed in order to protect perovskite absorber from moisture or ambient air. The devices were subjected to constant AM1.5G (100 mW cm\(^{-2}\)) illumination using a Solaronix Sunirad A45 and the modules were kept at 50°C during the whole experiment. J–V curves were recorded to determine the time evolution of the photovoltaic metrics. The efficiency tends to increase during the first 500 h. The photon to current efficiency remains then constant during the following 2000 h (Fig. 10).

![Figure 10. Normalized I-V characteristics and efficiency of PSC module during the light soaking stability test under AM 1.5G illumination.](image)

These results show no evidence for device degradation under the test conditions, confirming that the triple-layer device architecture provides a promising path towards realizing efficient and stable perovskite photovoltaics.

2.2.5. HIT solar cell

Compared to the previously reported results on the HIT solar cells, the main innovation is the implementation of the screen printing process for the front side metallization. Previous cells were metallized by means of thermal evaporation.
Screen printing allows a faster, more reproducible and more industrial like processing and gives more freedom regarding grid design. For the long term stability tests, three cells of 2 x 2 cm² area were measured with the standard grid design. As the screen printing process is still in the development phase, different screen openings were tested (40 and 50 µm). Also, unlike before, silicon wafers fabricated by the Czochralski (Cz) method instead of float zone material was used. Figure 11 shows the photograph of such a pseudo-Cz silicon wafer with seven different screen-printed solar cells.

![Finger width in µm](image)

**Figure 11.** Photograph of a 5" pseudo square Cz-silicon wafer with seven different screen printed solar cells (cell area 2 x 2 cm²).

The long term tests were performed at the light soaking bench at room temperature and an illumination of one sun under open circuit conditions. The cells were taken out of the light soaking bench every 25 h in order to perform current density voltage measurements.
Figure 12. The results of light-soaking experiment on our HIT solar cells. (a) Fill factor (FF), efficiency (η), (b) short-circuit current density (J_{sc}), and open-circuit voltage (V_{oc}) are shown.

Figure 12a and b shows the long term stability result for our HIT solar cells. Presumably due to the not yet-optimized screen printing process as well as a relatively poor ITO front TCO performance related to a recent target change, a maximum of 18.7% solar to electricity conversion efficiency was measured for the tested cells (Fig. 12a), which was lower than for the previously reported cells. The cells with 50 µm screen opening performed better than the ones with 40 µm. This is due to the lower series resistance losses, which results to higher fill factor, despite the lower short circuit current density resulting from higher amount of grid shading. A slight but apparently systematic decrease in FF of 1.5 to 2.2 percent points was observed (Fig. 12a). Scattering in J_{sc} is most likely related to the solar simulator lamp which approached the end of its life cycle during our measurement (Fig. 12b). Fig. 12b also shows that the V_{oc} remained stable. Overall, the relative decrease in efficiency was not more than 4%, which fulfils the deliverable target. A lamination process, which is currently under investigation could further improved stability.

2.3. Conclusions and next steps

In summary, we have performed long-term stability measurements on our metal oxide photoelectrodes as well as our HIT silicon and perovskite solar cells. The deliverable target, which is less than 10% performance decrease after 100 hours of operation, is fully met by the Fe_{2}O_{3} photoanode, perovskite solar cell, and HIT solar cell. There is no noticeable degradation for the Fe_{2}O_{3} photoanode, even when
measured up to 1000 hours. Perovskite solar cell interestingly show an increase of performance within the first 500 hours, with no decrease in efficiency up to > 2000 hours. HIT solar cell only shows overall efficiency decrease of ~4% within the 100 hours of measurement.

The deliverable target is partially met with both BiVO₄ photoanode and Cu₂O photocathode. BiVO₄ photoanode, in principle, shows no degradation of performance when operated in neutral pH electrolyte, other than the case of sub-optimal PEC cell engineering (bubbles formation and adhesion to the surface). This issue will be addressed in the next couple of months, by new more optimized PEC cell design. In alkaline electrolyte, protecting BiVO₄ with TiO₂ and Ni layer results in improved stability, although it is limited to less than one hour. Cu₂O photocathode shows ~50-60 hours stability (10% performance decrease). While this has not reached the deliverable target, our overall protection layer strategy has improved the Cu₂O stability significantly; such a long-term stability for a Cu₂O photocathode was previously unheard of. The remaining degradation that we still see is believed to be caused by pinhole formation, and efforts will be focused in the next few months in order to remove these pinholes and extend the stability up to the deliverable target.
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