

## Solar Water Splitting

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# A Stable Integrated Photoelectrochemical Reactor for H<sub>2</sub> Production from Water Attains a Solar-to-Hydrogen Efficiency of 18 % at 15 Suns and 13 % at 207 Suns

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**Abstract:** The major challenge in solar water splitting to H<sub>2</sub> and O<sub>2</sub> is in making a stable and affordable system for large-scale applications. We have designed, fabricated, and tested a photoelectrochemical reactor characterized as follows: 1) it comprises an integrated device to reduce the balance of the system cost, 2) it utilizes concentrated sunlight to reduce the photoabsorber cost, and 3) it employs an alkaline electrolyte to reduce catalyst cost and eliminate external thermal management needs. The system consists of an III-V-based photovoltaic cell integrated with Ni foil as an O<sub>2</sub> evolution catalyst that also protects the cell from corrosion. At low light concentration, without the use of optical lenses, the solar-to-hydrogen (STH) efficiency was 18.3 %, while at high light concentration (up to 207 suns) with the use of optical lenses, the STH efficiency was 13 %. Catalytic tests conducted for over 100 hours at 100–200 suns showed no sign of degradation nor deviation from product stoichiometry (H<sub>2</sub>/O<sub>2</sub>=2). Further tests projected a system stability of years.

## Introduction

Hydrogen is an important raw material for chemical and refinery industries, which is primarily used for the production of ammonia and methanol, and secondly for hydrotreating in refineries.<sup>[1]</sup> Presently, almost half of the world's population depends on food made from ammonia-based fertilizer,<sup>[2]</sup> making the availability of low-cost hydrogen a critical issue. Moreover, hydrogen may play a future role in the energy sector and in conversion of CO<sub>2</sub> into useful fuels and

chemicals. Currently, steam methane reforming (SMR) is the most widely used process for H<sub>2</sub> production with a cost of approximately 0.8–2.0 \$ kg<sup>-1</sup> H<sub>2</sub> (without accounting for carbon capture, use, and storage (CCUS)), depending on geographic location.<sup>[3–5]</sup> A major drawback of the SMR process are the CO<sub>2</sub> emissions. Dependent on the nature of feedstock (natural gas, rich gases, naphtha, and so on), one ton of hydrogen simultaneously produces 8 to 12 tons of CO<sub>2</sub> (the weight ratio of CO<sub>2</sub> to H<sub>2</sub> produced by the combined processes of SMR and the water–gas shift reaction is 5.5).<sup>[6]</sup>

Solar-driven water splitting is a clean and sustainable route for H<sub>2</sub> production and it has been the subject of intense research efforts over the last few decades.<sup>[7–9]</sup> Photovoltaic (PV)–electrolysis systems that use PV modules connected physically and electrically in series with electrolyzers present the most mature technology for solar H<sub>2</sub> production. There are several relatively small-scale demonstrations of PV–electrolysis systems with more than 15 % solar-to-hydrogen (STH) efficiency.<sup>[10–12]</sup> However, the use of power electronics and a significant number of other auxiliary control components leads to a high balance of system (BOS) cost. This increases the cost of H<sub>2</sub> production and the latest techno-economic studies indicate that PV–electrolysis will result in a H<sub>2</sub> cost between 5 and 15 \$ kg<sup>-1</sup>, depending on the PV technology and location.<sup>[13,14]</sup> While this progress is promising, it is very challenging to compete with SMR technology in terms of cost.

For this reason, photoelectrochemical (PEC) systems that integrate the photoabsorber (as a multijunction high-concentration solar cell) with catalysts provide an opportunity for the necessary cost reduction.<sup>[8,15]</sup> However, there are several challenges associated with developing practical PEC systems for industrial scale H<sub>2</sub> production. PEC devices are less developed and have efficiencies lower than PV–electrolysis systems.<sup>[8,16]</sup> This is because of their instability in harsh electrolytes.<sup>[17–19]</sup> Another development challenge is to scale up these PEC devices so as to reach the same H<sub>2</sub> production capacity as that of the PV–electrolysis system. Therefore, high efficiencies are not the sole target, but high power and cell-current densities are needed. These would allow reductions in the size of the PEC elements, and consequently, a decrease in the cost of hydrogen produced over the device lifetime.<sup>[20,21]</sup> This can be achieved by increasing photocurrents under concentrated light. However, working at elevated operating current densities bring other complexities given the significant increase in temperature and overpotential, which exacerbate degradation of the photoabsorber and catalysts.<sup>[21–23]</sup>

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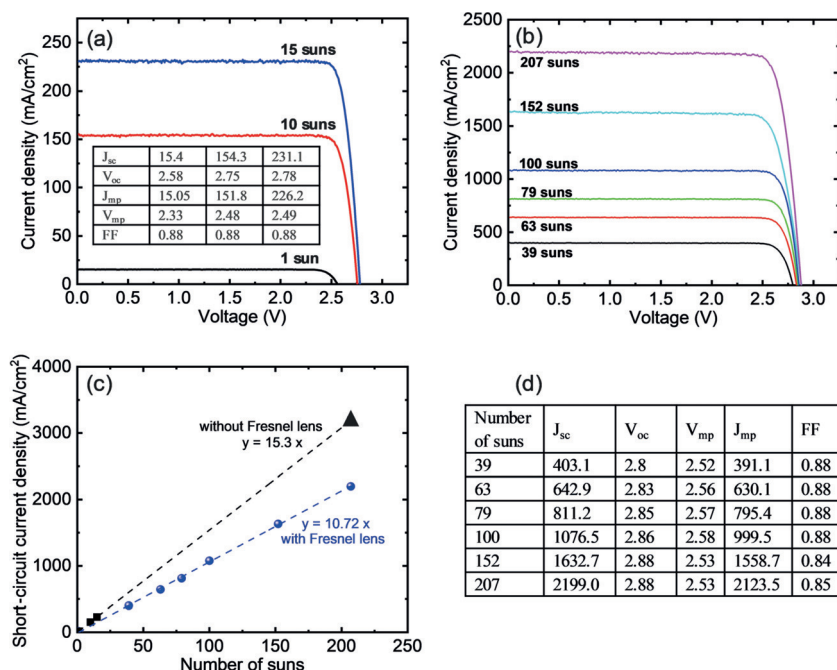
In one of the earliest reports on developing PEC reactors for operation under high ( $>100$  suns) concentrated light, Peharz and co-workers<sup>[24]</sup> developed a reactor for water splitting at approximately  $500 \text{ kW m}^{-2}$ . The system consisted of a III–V multijunction cell coupled externally with a proton exchange membrane (PEM) electrolyzer. While the reactor had a high STH efficiency of about 15%, the reported stability was for a few of hours. To calculate the STH, the authors assumed that all energy needed to split water comes from electricity because of the high current density; in this case the thermoneutral potential of 1.48 V per H atom was used for the efficiency calculation ( $285 \text{ kJ mol}^{-1}$  at 1 bar,  $25^\circ\text{C}$ ,  $2.39 \text{ kWh kg}^{-1}$ ). Furthermore, the system was designed using expensive current collectors, flow plates, and catalysts. Recently Haussener and co-workers<sup>[25]</sup> reported a PEC reactor for water splitting at  $474 \text{ kW m}^{-2}$  with a STH efficiency of 15%. The experiment was conducted using a high-power solar simulator (that is, without the use of optical concentrators) but the reported stability was for a few minutes. Furthermore, the use of a copper cooling plate and titanium flow plate would increase the cost of the reactor. There have also been a few reports<sup>[26–31]</sup> on the use of lower sun concentrations (2 to 42 suns) for  $\text{H}_2$  production, but again, with maximum reported stabilities of a few hours.

Herein, we address these combined challenges and demonstrate a PEC hydrogen reactor that works under high concentrated light. We propose a design that allows the reactor to perform at high efficiency and is at the same time stable. Firstly, we have directly integrated the III–V-based PV cell with the oxygen evolution reaction (OER) catalyst to avoid ohmic losses that can potentially reduce the efficiency

of the system. This also helped to eliminate expensive current collector components, as used in previous reports.<sup>[24,25]</sup> Secondly, we worked with an alkaline electrolyte to avoid using expensive OER catalysts, thereby allowing for a non-zero gap configuration as opposed to PEM-based systems. The design also used the electrolyte to cool the PV cell, therefore eliminating the need for external thermal management.<sup>[25]</sup> Equally important, the reactor was designed in such a way to ensure that the PV cell is isolated from the electrolyte, and thereby protecting it from possible corrosion. Without the contribution of optical losses from Fresnel lens, we were able to reach close to maximum theoretical STH efficiency at approximately  $18.3 \pm 0.7\%$  under light fluxes of  $10 \text{ kW m}^{-2}$  and  $15 \text{ kW m}^{-2}$ . At higher light flux up to  $207 \text{ kW m}^{-2}$ , we reached photocurrent densities up to  $2.24 \text{ A cm}^{-2}$  and associated  $\text{H}_2$  production rates of approximately  $3.10 \text{ mL min}^{-1}$ , corresponding to  $13\% \pm 0.6\%$  STH efficiency. The decrease in STH is a consequence of optical loss upon using the Fresnel lenses and is independent of sun concentration. Constant  $\text{H}_2$  and  $\text{O}_2$  production with time, and with a ratio equal to 2, is an indication of system stability.

## Results and Discussion

Figure 1a presents the PV characteristics of the GaInP/GaInAs/Ge triple junction (3J) PV cell under 1, 10, and 15 suns, respectively, without the use of the optical concentrator (that is, the Fresnel lens). The solar light flux was obtained by adjusting the distance and power of the solar simulator, and calibrated using a silicon photodetector, as described in the



**Figure 1.** a) PV characteristics of the GaInP/GaInAs/Ge PV cell under concentrated light without the use of a Fresnel lens. b) PV characteristics of the GaInP/GaInAs/Ge PV cell under concentrated light with the use of a Fresnel lens. c) Short-circuit current density ( $J_{sc}$ ) as a function of the number of suns with (●) and without (■) the use of a Fresnel lens. The difference in the slope of both lines indicates losses arising from use of the Fresnel lens (ca. 30%). An extrapolated linear point as a visual guide (▲). d) Summary of PV characteristics shown in (b).

Experimental Section. Under 1 sun, the short-circuit current density ( $J_{sc}$ ), the open-circuit voltage ( $V_{oc}$ ), maximum power current density ( $J_{mp}$ ), maximum power voltage ( $V_{mp}$ ), and fill factor (FF) were  $15.4 \text{ mA cm}^{-2}$ ,  $2.58 \text{ V}$ ,  $15.05 \text{ mA cm}^{-2}$ ,  $2.33 \text{ V}$ , and  $0.88$ , respectively. Practical solar light concentration is achieved using either parabolic mirrors or Fresnel lenses, which focus the light onto smaller area light absorbers.<sup>[32]</sup> Figure 1b displays the PV characteristics of the GaInP/GaInAs/Ge/Au 3J cell under concentrated light coming from a poly(methyl methacrylate) (PMMA) Fresnel lens (area  $A_1 \approx 19.6 \text{ cm}^2$ ; see Figures 4a–c in the Experimental Section for depictions of the PEC reactor. The concentrated light spot had a diameter of roughly  $0.5 \text{ cm}$ ; thus, the spot size area  $A_2$  was approximately  $0.196 \text{ cm}^2$ , leading to a geometric concentration ratio of  $100$ . By controlling the light intensity incident on the Fresnel lens ( $0.39, 0.63, 0.79, 1.0, 1.52$ , and  $2.07 \text{ suns}$ ) light fluxes of  $39, 63, 79, 100, 152$ , and  $207 \text{ suns}$  were thus obtained, respectively.

Under uniform irradiance and constant temperature, the short-circuit current density is considered linear with respect to light concentration, as expressed in Equation (1):<sup>[23]</sup>

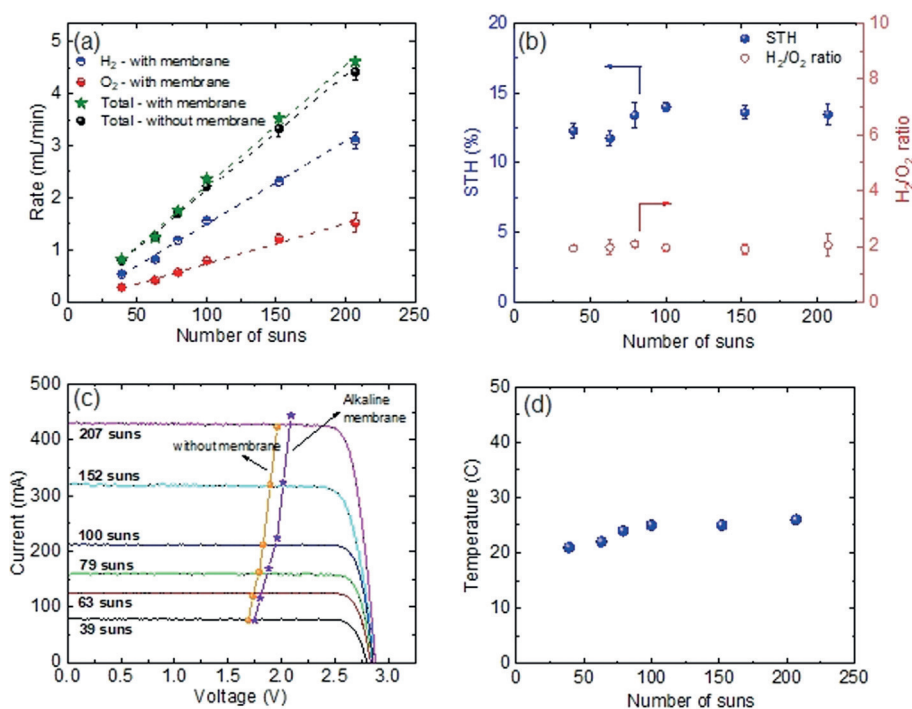
$$J_{sc} = X J_{sc-1\text{sun}} \quad (1)$$

where  $X$  is the light concentration factor, and  $J_{sc-1\text{sun}}$  is the short-circuit current density at one sun ( $1 \text{ kW m}^{-2}$ ). While there is a linear increase of  $J_{sc}$  as a function of light concentration (Figure 1c), the use of Fresnel lens leads to optical losses of about  $30\%$ , as indicated by the difference in

slope of the two curves in Figure 1c (for a detailed calculation of optical losses, see the Supporting Information, Table S1). The PV characteristics are summarized in Figure 1d. There is a small drop in FF at high concentrations that we attribute to the non-uniform light flux (Supporting Information, Figure S2). The concentrated light from the Fresnel lens has a non-uniform Gauss-like intensity distribution resulting in a decreased FF.<sup>[33,34]</sup>

Results of the integrated PEC reactor under concentrated light are presented in Figure 2. The first set of experiments were carried out without using an anion exchange membrane (AEM). The electrolyte ( $5 \text{ M KOH}$ ) was flowed into the reactor from one side only and the  $\text{H}_2/\text{O}_2$  gases were collected together in a single eudiometer. Figure 2a presents the combined  $\text{H}_2$  and  $\text{O}_2$  production rates, which increased linearly as a function of light concentration. We have also measured, in parallel, the activity at  $100 \text{ suns}$  using different concentrations of  $\text{KOH}$  ( $0.5, 1$ , and  $5 \text{ M}$ ) and flow rates ( $2$  to  $40 \text{ mL min}^{-1}$ ); both showed marginal effect, within experimental errors (Supporting Information, Figure S3).

Upon incorporating the alkaline membrane directly on top of the Pt/Ti mesh, and keeping all other reactor components unchanged,  $\text{H}_2$  and  $\text{O}_2$  gases were collected separately in two different eudiometers. The  $\text{H}_2$  production rates were initially checked by gas chromatography (GC) measurements to remove any errors arising from water vapor (water partial pressure at  $25^\circ\text{C}$  is about  $0.031 \text{ atm}$ ) and possible dissolved molecular  $\text{O}_2$  (Supporting Information, Note S1). GC measurements indicated that the contribution



**Figure 2.** a)  $\text{H}_2$  and  $\text{O}_2$  production rates (with and without an anion exchange membrane). b)  $\text{H}_2/\text{O}_2$  ratio and STH efficiency as a function of light concentration using an anion exchange membrane (Sustainion® 37–50); the top dashed line represents the average STH of  $13\%$ , the bottom dashed line represent the  $\text{H}_2$  to  $\text{O}_2$  stoichiometric ratio of  $2$ . c) IV characteristics of the 3J GaInP/GaInAs/Ge cell overlapped with  $\text{H}_2$  production rates (a) converted to the corresponding current values (Supporting Information, Note S3). Electrolyte =  $5 \text{ M KOH}$ , flow rate =  $8 \text{ mL min}^{-1}$ . d) Cell temperature measured during the reaction at the given sun concentration.



of water vapor into the volumetric measurement was negligible and no crossing of molecular O<sub>2</sub> was observed into the H<sub>2</sub> side. H<sub>2</sub> and O<sub>2</sub> production rates increased linearly as a function of light concentration (Figure 2a). The reaction at each light concentration was carried out for a total of 2 hours with five separate measurements for H<sub>2</sub> and O<sub>2</sub> rates. The STH efficiencies (Figure 2b) were calculated using Equation (2) after each measurement, and the error bars were calculated at the end of the experiment based on a 95 % confidence interval.

System efficiency = STH

$$= \frac{\text{Power from H}_2 \text{ produced}}{\text{Power of light incident on the Fresnel lens}} \quad (2)$$

$$= \frac{r_{\text{H}_2} \Delta G_r}{A_{\text{PV}} \Phi}$$

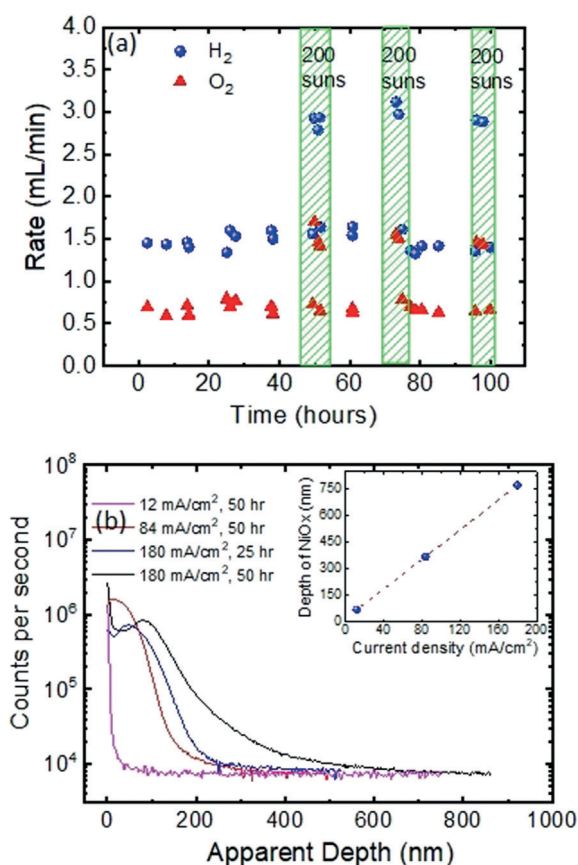
Where  $r_{\text{H}_2}$  is the H<sub>2</sub> production rate in mol s<sup>-1</sup>,  $\Delta G_r$  is the free energy of reaction (H<sub>2</sub>O → H<sub>2</sub> + 1/2 O<sub>2</sub>; 237 000 J mol<sup>-1</sup>),  $A_{\text{PV}}$  is the PV cell area (cm<sup>2</sup>), and  $\Phi$  is the light flux (J s<sup>-1</sup> cm<sup>-2</sup>).

The H<sub>2</sub>/O<sub>2</sub> ratio of 2:1, as shown in Figure 2b, indicates a stable system. The average STH efficiency at different light concentrations was found to be approximately 13 ± 0.7 %. An example of how the system efficiency for 100 suns was calculated is given in Note S2 of the Supporting Information. The maximum possible STH efficiency upon using these PV cells is about 18.8 % based on a faradaic efficiency ( $\eta_F$ ) of 100 %. The drop in STH is a result of 30 % optical losses coming from the Fresnel lens (Figure 1c). This was confirmed by performing experiments under low concentrations (10 and 15 suns) without the use of a Fresnel lens (for which an STH efficiency of 18.3 % was obtained; Supporting Information, Figure S4).

The H<sub>2</sub> production rates upon incorporating a membrane were identical to the case without using it. The use of a membrane introduces some resistance because  $V_{\text{mp}} > E_{\text{cell}}$ . H<sub>2</sub> production is not affected. This is evident in Figure 2c, where we overlap the PV cell performance of Figure 1b and PEC device performance of Figure 2a. The PV cell performance was plotted as current versus voltage so that it can be plotted together with the PEC data. The voltage of the PEC device was measured under incident concentrated light and the H<sub>2</sub> produced was converted into current (Supporting Information, Note S3). From Figure 2c we observe that the H<sub>2</sub> produced is very close to  $J_{\text{sc}}$  from the PV cell, indicating faradaic efficiencies of about 100 %. Furthermore, the difference in performance of the PEC reactor with and without membrane is seen by the increase in required voltage for the catalytic reaction. The resistance calculated from difference in voltage ( $\Delta V$ ) and current ( $I_{\text{sc}}$ ) is in the range of 0.5–0.7 Ω for the various light concentrations. It is important to mention that, while we are not operating at the maximum power point (MPP), the H<sub>2</sub> production rates and efficiency are dictated by the  $I_{\text{sc}}$ . Optimizing the catalyst amount to operate at MPP does not increase the H<sub>2</sub> production rate or efficiency in an integrated PEC system.<sup>[35]</sup> On the contrary, decreasing the catalyst amount to operate at MPP might be detrimental for the stability of the catalyst and increases risk of drop in

efficiency over time. This extra voltage can be utilized in a decoupled PV–electrolysis setup using a DC–DC converter. However, the use of a DC–DC converter and corresponding electronics increases the BOS cost. Figure 2d presents the recorded temperature of the cell under working conditions using a thermocouple at the edge of the cell. The recorded temperature was about 30 °C. Good thermal management is supported by the PV characteristics (Figure 1), a linear increase in current, and logarithmic increase in voltage with increasing sun concentration. An increase in cell temperature would have resulted in a deviation from this behavior.

Figure 3a displays the long-term stability data of the integrated PEC reactor under alternating 100 and 200 suns light fluxes. The PEC reactor showed stable performance with constant H<sub>2</sub>/O<sub>2</sub> production (ratio of 2:1) at a STH efficiency of approximately 13 % for the duration of the test without degradation, which is the highest reported stability for PEC H<sub>2</sub> production under concentrated light. The reactor demonstrated good thermal management at high operating photo-currents. Any potential failure of the system would be



**Figure 3.** a) Stability tests of integrated PEC reactor under alternating 100 and 200 suns light flux using a Fresnel lens together with H<sub>2</sub> and O<sub>2</sub> production rates plotted as a function of time. The green shaded area shows the data when operating under 200 suns. The current density at 200 suns is 107.5 mA cm<sup>-2</sup>. b) Depth profile of the Ni surface where the <sup>90</sup>NiO<sub>x</sub><sup>+</sup> secondary ion signal was monitored after the electrochemical oxidation reaction. Inset: the oxide layer thickness measured from the SIMS experiment plotted against electrochemical current density.

because of a leak into the seal, which is a manufacturing rather than a conceptual issue.

While stoichiometric  $\text{H}_2/\text{O}_2$  production indicates true water splitting,<sup>[36]</sup> the role of the Ni catalyst in protecting the 3J PV cell from the electrolyte needed further study. For this purpose, the Ni surface was analyzed using dynamic secondary ion mass spectrometry (SIMS). The Ni foil was subjected to electrochemical oxidation in conditions similar to those of the PEC tests under different current densities. Figure 3b displays the depth profile of the Ni surface, where the  $^{90}\text{NiO}_x^-$  secondary ion signal was monitored. The point at which the signal from the  $^{90}\text{NiO}_x^-$  secondary ion fragment becomes constant represents the oxide/bulk Ni interface. SIMS results indicate that the oxide layer thickness increases linearly with time at constant current; see for example the difference between 25 and 50 hour samples at  $180\text{ mA cm}^{-2}$ . From these data, the rate of Ni oxidation can be extracted and is found to be  $0.088\text{ nm per mA cm}^{-2}$  per hour. This oxidation rate is negligible and does not disturb the stoichiometry of  $\text{H}_2/\text{O}_2$  (Supporting Information, Table S2). To confirm Ni oxidation is an electrochemical process we have also carried out SIMS depth profiling of Ni dipped in alkaline electrolyte under dark conditions, and no oxidation with time was seen (Supporting Information, Figure S5). The results highlight that, when working under concentrated light (higher currents), it would be better to dilute the photocurrents from the PV cell onto a larger area catalyst, not only to maximize efficiency<sup>[21]</sup> but also for longer stability of the catalysts.

For long-term stability projections, the oxidation rate derived from the SIMS experiment at  $0.088\text{ nm per mA cm}^{-2}$  per hour may be used to calculate the expected stability of such systems. For example, under 200 suns, with a photocurrent of  $430\text{ mA}$ , and an electrochemical current density of  $107.5\text{ mA cm}^{-2}$  ( $4\text{ cm}^2$  area Ni in our PEC reactor), the oxidation time for a  $250\text{ }\mu\text{m}$  thick Ni layer may be calculated to approximately 9.1 years based on 8 hours of daily operation. This number can be taken as a projection for commercial use. Accelerated stability tests, for example, at a much higher concentration of 1000 suns, are needed for further verification.

## Conclusion

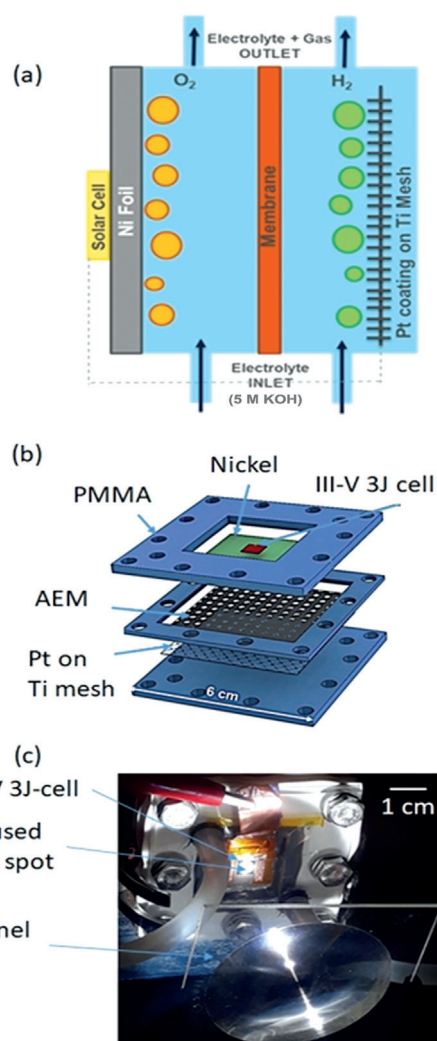
Herein, we have presented a PEC reactor for  $\text{H}_2$  production from water that operates under concentrated sunlight close to the maximum theoretical efficiency (ca.  $18.3 \pm 0.7\%$ ) at low light flux (10 and 15 suns). Under higher light flux, obtained using a Fresnel lens,  $\text{H}_2$  production rates linearly increased at a constant STH efficiency of approximately  $13 \pm 0.6\%$ , reaching  $3.10\text{ mL min}^{-1}$  at 207 suns (short-circuit current density =  $2.24\text{ A cm}^{-2}$ , electrochemical current density =  $107.5\text{ mA cm}^{-2}$ ). The reactor was stable with a stoichiometric  $\text{H}_2/\text{O}_2$  ratio for the duration of the tests ( $>100$  hours) with an extrapolated lifetime of  $>9$  years. The development of active and stable integrated PEC reactors with  $\text{H}_2/\text{O}_2$  separation may represent a step forward toward the realization of „green“ hydrogen with affordable cost. Because the system works well in an alkaline environ-

ment using Ni-based catalysts, an excess amount of catalyst with respect to cell area would be beneficial,<sup>[37]</sup> since the determining geometric factor is that of the total sunlight area before concentration. Therefore, working with low electrochemical current density ensures stability while producing the same amount of  $\text{H}_2$ . The  $\text{H}_2$  production rate and STH efficiency of such systems can be improved by optimizing the growth/performance of III–V PV cells to obtain a maximum cell current density and optimal  $V_{\text{mp}}$  (ca.  $1.8\text{--}2.0\text{ V}$ ) for solar water splitting. The optical losses under concentrated light can also be reduced ( $<20\%$ ) by selecting an appropriate Fresnel lens similar to that in commercial concentrator PV (CPV) modules. With the development of such reactors, the design of large-scale PEC modules and techno-economics studies (Supporting Information, Note S3), similar to that for CPV–electrolysis<sup>[38]</sup> are needed. Moreover, it is necessary to address the long-term stability of the membranes (stability of many years is required), as well as that of the different components of the electrodes. Moreover, assessment of the safety hazards associated with use of a KOH base in a much larger plumbing and distribution system needs to be compared to that of a MW-scale conventional alkaline electrolyzer stack.

## Experimental Section

**PEC reactor fabrication.** Figures 4a and b present a schematic and illustration of the integrated PEC reactor designed for use under concentrated light. The reactor was fabricated using a transparent PMMA ideal for use in alkaline conditions ( $\text{pH} \approx 14$ ). A 3J GaInP/GaInAs/Ge PV cell ( $5.0 \times 5.0\text{ mm}^2 = 0.25\text{ cm}^2$ ) from Azure Space was used as the photoabsorber. The reactor area was  $6 \times 6\text{ cm}^2$  ( $36\text{ cm}^2$ ) and fabricated using a  $\text{CO}_2$ -based laser (Epilog Fusion M2; wavelength =  $10.6\text{ }\mu\text{m}$ ) at a power setting of  $75\text{ W}$ . Electrical connection from the front of the 3J PV cell was done using ball wire bonding with  $25\text{ }\mu\text{m}$  gold wire (HB16, TPT Wire Bonder GmbH & Co) onto a copper foil. The back of the 3J PV cell was integrated with a  $0.25\text{ mm}$  thick Ni foil (Alfa Aesar, 99.5% purity) using silver paste (Alfa Aesar 42469), which was cured at  $60^\circ\text{C}$  for 2 hours in air. The Ni geometric area was kept at approximately  $4\text{ cm}^2$  and the hydrogen evolution reaction (HER) catalyst used was approximately  $50\text{ nm}$  thick Pt sputtered onto both sides of a porous titanium mesh (Goodfellow TI008710, nominal aperture =  $0.19\text{ mm}$ , wire diameter =  $0.23\text{ mm}$ , open area =  $20\%$ ). Prior to sputtering, the Ti mesh was cleaned with  $0.2\text{ M}$  oxalic acid for 10 min before loading into the sputter chamber. Pt was sputtered using a radio frequency (RF) sputtering method at a constant RF power of  $400\text{ W}$  at  $5\text{ mTorr}$  Ar pressure during deposition. The thickness of Pt was verified using a stylus profiler for a film deposited on silicon, which was kept in the sputter chamber along with the Ti mesh. An alkaline anion exchange membrane (Sustainion® 37–50, dioxide materials) with area  $\approx 12.96\text{ cm}^2$  was used for ion transfer and gas separation. The membrane was activated by dipping it in a  $1\text{ M}$  KOH electrolyte solution for 12 h. Sustainion® 37–50 is a new imidazole-functionalized membrane with a polystyrene-based backbone, which is stable in strong alkaline solutions. Dioxide materials have demonstrated long-term stability in thousands of hours at high current densities ( $1\text{ A cm}^{-2}$ ).<sup>[39]</sup>

**PEC testing.** Figure 4c shows the experimental setup for the PEC reactions. An Asahi Spectra HAL-320W solar simulator ( $350\text{--}1800\text{ nm}$ ) was used as the light source. A PMMA (Edmund Optics, #43-025) Fresnel lens with an area of approximately  $19.6\text{ cm}^2$  was used



**Figure 4.** a) Schematic and b) illustration of the integrated PEC reactor in which the components from which the reactor is fabricated are displayed. c) Photograph of the integrated PEC reactor and Fresnel lens under illumination. The ratio  $A_1/A_2$  of the Fresnel lens area ( $A_1 = 19.6 \text{ cm}^2$ ) and that of the focused light spot area ( $A_2$ ) gives the geometric light concentration. In (a) the gap between the membrane and the Ni foil is ca. 2.5 mm, while that between the membrane and the Ti mesh is close to 1 mm.

to concentrate light onto a 3J PV cell kept at the focal distance from the lens (5 cm). The light flux was measured using a precalibrated monocrystalline silicon reference cell (Newport, 91150-KG5) and a precalibrated high concentration 3J GaInP/GaInAs/Ge reference cell (Azure space, 3C42A). The light flux measurements were further verified using a spectroradiometer (Spectral Evolution SR-500) in a range of 350–1100 nm (Supporting Information, Figure S1). For reactions performed without the use of a concentrating Fresnel lens (10 and 15 suns), the irradiation was adjusted by the distance to the PV cell and the power of the solar simulator. Specifically, the experiments conducted at 10 suns were performed at a distance of 8 cm and 60 % intensity, and for 15 suns at 8 cm and 90 % intensity. A peristaltic pump was used to flow 5 M KOH as the electrolyte for the reaction and the  $\text{H}_2/\text{O}_2$  gases were collected using two separate inverted eudiometers. The total volume of the KOH in the collection system was about 0.5 L. At 5 M concentration, the solubility of  $\text{O}_2$  is approximately  $0.1 \times 10^{-3} \text{ moles L bar}^{-1}$ .<sup>[40]</sup> Thus, maximum dissolved  $\text{O}_2$  at 1 atm is approximately  $0.2 \times 10^{-3} \text{ moles} = 0.00892 \text{ mL O}_2$ , which

is negligible when compared to the amount of  $\text{O}_2$  detected. The temperature of the cell was measured at the corner with a type K thermocouple. To monitor  $\text{H}_2$ , a gas chromatograph (Agilent Technologies, 7890A) equipped with a thermal conductivity detector (TCD) connected to a Porapak Q packed column (2 m long, 1/8 in. external diameter) at  $45^\circ\text{C}$  was used with  $\text{N}_2$  as the carrier gas (flow rate =  $20 \text{ mL min}^{-1}$ , pressure = 8 psi).  $\text{O}_2$  was monitored using another GC (Thermo Scientific, Trace1300) equipped with a TCD connected to a packed molecular sieve ( $5\text{\AA}$ ) column (2 m long, 1/8 in. external diameter) with He as the carrier gas (flow rate =  $1.5 \text{ mL min}^{-1}$ , pressure = 22 psi). The complete system is available upon request.

**SIMS depth profiling.** Depth-profiling experiments were performed on a dynamic SIMS instrument from Hiden analytical company (Warrington-UK) operated under ultrahigh vacuum (UHV) conditions (typically  $10^{-9}$  torr). A continuous  $\text{Ar}^+$  beam of 4 keV energy was employed to sputter the surface while the selected ions were sequentially collected using a MAXIM spectrometer equipped with a quadrupole analyzer. The sputtered area is estimated to be  $750 \times 750 \mu\text{m}^2$ . To avoid the edge effect during depth-profiling experiments, it is necessary to acquire data from a small area located in the middle of the eroded region. Using an adequate electronic gating, the acquisition area was scaled down to approximately  $75 \times 75 \mu\text{m}^2$ . The conversion of the sputtering time to sputtering depth scale was carried out by measuring the depth of the crater generated at the end of the depth profiling experiment using a stylus profiler from Veeco Company, with a calculated average sputtering rate of approximately  $5.5 \text{ nm min}^{-1}$ .

The Ni samples for SIMS were prepared in a two-electrode setup with Pt as the counter electrode. The electrolyte used was 5 M KOH and was continuously purged with high-purity (99.999 %)  $\text{N}_2$  during the reaction. The Ni was oxidized using chronopotentiometry measurements at different currents. After measurements, Ni samples were washed with deionized water and dried with  $\text{N}_2$  gas before loading into the UHV chamber for SIMS depth-profiling experiments.

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## Conflict of interest

The authors declare no conflict of interest.

**Stichwörter:** concentrated sunlight · hydrogen production · nickel oxide · OER catalyst stability · photoelectrochemistry

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