Solar-to-Hydrogen Production at 14.2% Efficiency with Silicon Photovoltaics and Earth-Abundant Electrocatalysts

Jan-Willem Schüttauf,a,*,z Miguel A. Modestino,b,*,z Enrico Chinello,b David Lambelet,b Antonio Delfino,d Didier Domíngë,a Antonin Faes,a Matthieu Despeisse,a Julien Bailat,a Demetri Psaltis,b Christophe Moser,b and Christophe Ballifª, b

Affordable, stable and earth-abundant photo-electrochemical materials are indispensable for the large-scale implementation of sunlight-driven hydrogen production. Here we present an intrinsically stable and scalable solar water splitting device that is fully based on earth-abundant materials, with a solar-to-hydrogen conversion efficiency of 14.2%. This unprecedented efficiency is achieved by integrating a module of three interconnected silicon heterojunction solar cells that operates at an appropriate voltage to directly power microstructured Ni electrocatalysts. Nearly identical performance levels were also achieved using a customized state-of-the-art proton exchange membrane (PEM) electrolyzer. As silicon heterojunction solar cells and PEM electrolysis systems are commercially viable, easily scalable and have long lifetimes, the devices demonstrated in this report can open a fast avenue toward the industrialization and deployment of cost effective solar-fuel production systems.

© 2016 The Electrochemical Society. [DOI:10.1149/2.0541610jes] All rights reserved.

Manuscript submitted June 30, 2016; revised manuscript received August 3, 2016. Published August 13, 2016.

The past decade has seen an increase in the urgency to substitute fossil fuels with clean and renewable energy sources. Among all of the renewable sources, solar irradiation is undeniably the most prominent option. The average accessible solar power accounts for over ~120 000 TW globally,2 several thousand times the current global energy needs.2 Photovoltaic cells can capture this vast energy resource and convert it into usable electrical energy at high efficiencies. Their implementation in the past years has seen a large growth driven by favorable environmental policies and a steady decrease in their production cost. Although the penetration of photovoltaics has been significant, some challenges for their integration into the electricity grid have started to become evident. Mainly, the intermittent nature of the solar electricity production prevents their large-scale grid implementation without compensation mechanisms that satisfy the demand during low-irradiation periods. Adding energy storage capacity to the grid could directly alleviate the fluctuations on power production. Electrochemical energy storage in batteries is already an interesting option for large-scale stationary energy storage. Electrochemical production of hydrogen from excess solar electricity is also an attractive option for storing solar energy in the form of a fuel which could be used at a later stage for electricity production back into the grid or transportation.3,4 Furthermore, hydrogen can be stored for prolonged periods of time, so that solar resources are harvested during high irradiation periods and used throughout the year. Because of these multiple advantages, solar-to-fuel approaches have attracted a lot of interest in the renewable energy field and project themselves as a critical technology to achieve large-scale utilization of solar-energy sources.3–5

Despite the strong research interest on solar-hydrogen materials and technologies, there have only been a limited number of demonstrations of solar water splitting devices. Most of these devices show short lifetimes (<1 day), low efficiencies, or use materials and designs that would prevent their practical and economical implementation.6,8 Deployable solar-hydrogen devices would need to function stably for years, produce robustly and continuously nearly pure H2 streams, incorporate economically viable photovoltaic and water-splitting components, and operate at high efficiencies so that the energy produced over their lifetime is much greater than the energy required to fabricate and operate the devices.9,10 Currently, the best performing systems implement GaAs-based photovoltaic materials to reach high conversion efficiencies.11 Although the solar-to-hydrogen efficiency (SHE) of these devices can reach values as high as 24.4%,11 the implementation of III–V semiconductors compromises their economic viability.12

An alternative to this approach was recently proposed where modules of three Copper Indium Gallium Selenide (CIGS) solar cells are connected in series to reach high performance.13 While these CIGS modules can reach ~17% solar-to-electricity efficiencies, when integrated with electrocatalysts the SHE is limited to 11% due to the low open circuit voltage (VOC) of the module. With a series-connected cell based on Perovskite photovoltaics, appropriate VOC values for water splitting can be obtained, which have led to their implementation in high-efficiency solar-hydrogen devices (up to 12.7% SHE).14,15 These materials are promising due to their performance and simple fabrication process, but their large-scale and long-term implementation is still hindered by serious stability issues.14,15 On the other hand, crystalline Silicon (c-Si) solar cells show high solar-to-electricity efficiencies, and have demonstrated stabilities in excess of 25 years. Propelled by their attractive performance, they have continuously dominated the market since their inception.16,17 with a current worldwide market share greater than 85%.17,18 Their high production volumes have largely contributed to a price drop of 80% since 2008, currently reaching levels below $1 per watt peak.18 Recently, c-Si modules have been implemented in solar-hydrogen devices, demonstrating SHE of 9.7%.19 As the VOC of the presented c-Si cells is only ~600 mV, four cells need to be connected in series to achieve stable water splitting performance.19 This results in lower operating currents and limited SHE efficiencies. Alternatively, c-Si-based heterojunction (SHJ) cells20,21 can reach VOC values in excess of 700 mV.21 These VOC values are the highest ones reported for silicon wafer-based technologies, and are predominantly obtained by an excellent interface passivation with a thin (~5 nm) film of hydrogenated intrinsic amorphous silicon (a-Si:H) between the c-Si wafer and the oppositely doped emitter, forming the p-n junction.20 We demonstrate in this study that, thanks to their high Voc, three series-connected SHJ cells can already stably drive the water splitting reaction at unprecedented SHE (Fig. 1).

**Experimental**

**Cell interconnection and module fabrication.**—We used 6-inch fully processed bifacial silicon heterojunction (SHJ) cells fabricated on 160 µm-thick Czochralski wafers,24 which have a front and back metallization pattern with three busbars at the same position on each side. The 6-inch cells are cut into small area (2 × 2 cm)2 cells using an infrared laser with a wavelength of 1064 nm in such a way that they have one busbar exactly on one of the edges of each side. The cells are subsequently interconnected one to another using a CB-450 conductive-adhesive paste from Hitachi Chemical Co. Ltd. in Japan, which enables to contact the edge of the front-side of one

---

*These authors contributed equally to this work.

*E-mail: jan-willem.schuettauf@csem.ch; miguel.modestino@epfl.ch
The cells were characterized under a Wacom WX5-220S-L2 class A+A+A+ solar simulator under standard test conditions (AM1.5g, 100 mW/cm², 25 °C). The modules were characterized under an in-house developed large-area class AAA solar simulator. For both cell and module measurements, the solar simulators were calibrated using certified SHJ cells and modules to obtain the current density of around 5% (absolute) over the entire relevant wavelength range (300–1100 nm), thereby leading to an increase in current density of around 5%. The (average) performance of the individual cells and modules is shown in Figures S1 and S2, and Table S1 of the Supplementary Information.

Cell and module characterization.—The cells were characterized under a Wacom WX5-220S-L2 class A+A+A+ solar simulator during the lamination process. After module fabrication, we plate. A rigid frame is used around the module to avoid breaking the glass during the lamination process. The modules were encapsulated with a 35 R&D membrane laminator using thermoplastic polyolefin (TPO) and low-iron solar-grade 3 mm-thick glass on both sides. The lamination process is performed at (165 ± 2) °C, during 300 s on pin, followed by 500 s at 100 mbar and 600 s at 1000 mbar on a heating plate. A rigid frame is used around the module to avoid breaking the glass during the lamination process. After module fabrication, we applied an anti-reflective foil on top of the module. Such an anti-reflective foil reduces the reflection losses at the air/glass interface by roughly 5% (absolute) over the entire relevant wavelength range (300–1100 nm), thereby leading to an increase in current density of around 5%. The (average) performance of the individual cells and modules is shown in Figures S1 and S2, and Table S1 of the Supplementary Information.

MEA electrolyzer fabrication, characterization and solar-driven operation.—The SHJ module captures sunlight and converts it into electricity directly feeding the electrochemical membrane electrode assembly water-splitting unit. Water is fed in the anodic side, where it is oxidized and oxygen molecules are generated; the simultaneously produced protons migrate across the membrane to the cathode, where they are reduced into molecular hydrogen. The gases can then be collected and stored in their pure form.

Alkaline electrolysis with Nickel electrocatalysts.—Ni-foam electrodes were obtained from Markatech International (thickness of 1.6 mm, surface density of 346 g/m², porosity >95%). Each Nickel electrode used in the experiments had a projected surface area of 60 cm². These electrodes were operated under basic electrolytes (1 M KOH) while coupled with the SHJ module. The integrated PV-electrolysis system showed stable and reliable performance for over 100 hours at SHE values ranging between 14.5% and 14.2%. In order to promote bubble detachment from the foam, the electrolyte was stirred during operation. Within these experiments, the electrodes co-evolved H₂ and O₂. In order to produce pure gases, anion exchange membranes (AEMs) can be used to separate the oxygen and hydrogen evolution sites. Similar results were attained with the implementations of an AEM between the anode and cathode side (see Figure S4 and S5).

Illumination of SHJ module during water splitting experiments.—The SHJ modules are illuminated with simulated sunlight using a 300 W solar simulator (Scientech SF300) containing an AM 1.5 filter. In order to illuminate uniformly the module area, a lens was used to enlarge the beam width and cover the module area. The simulator power was calibrated to obtain an irradiation of 1000 W/m² at the SHJ module surface. Due to illumination beam width limitations and in order to enhance the module performance reducing the peripheral charge recombination losses, the SHJ module was partially shadowed through a mask, which ensured the same illuminated area for the three cells (1.9 cm² each, 5.7 cm² total illumination area) and therefore guaranteed an overall high current density.

Light cycling stability tests.—In order to recreate the normal succession of daytime and nighttime, experiments under light and dark conditions were carried out at 30 minutes intervals. Both MEA-based and Nickel bulk water-splitting devices showed consistent operation in every cycle, with unaltered SHE during the illumination intervals. Results are reported in Figure S7 in the Supplementary Information.

The cells and modules were characterized at CSEM in Neuchâtel, Switzerland, and thereafter shipped to EPFL in Lausanne, Switzerland to be integrated and measured with electrolysis units.
In order to demonstrate the potential of SHJ cells in solar-hydrogen devices, a module consisting of three series-connected cells was fabricated following advanced and also scalable module manufacturing techniques. This module has suitable current-voltage characteristics (Fig. 2a) to drive the water splitting reaction at high current densities, as demonstrated by its high $V_{OC}$ (2.08 V), short-circuit current density ($J_{SC}$ = 11.9 mA/cm²), and solar-to-electricity conversion efficiency of 20.6% at its maximum power operating point ($J_{mpp}$ = 11.6 mA/cm², $V_{mpp}$ = 1.78). To trigger the generation of hydrogen, this module was integrated with a customized Nafion proton-exchange membrane (PEM) electrolysis unit. The flow plates used in the water splitting system were manufactured using a rapid-prototyping additive-manufacturing machine and the membrane electrode assembly implemented was based on Platinum (Pt) and Iridium Oxide (IrOx) electrocatalysts for the hydrogen and oxygen evolution reactions, respectively. PEM electrolysis units are widely used in commercial applications as they can operate at high current densities, only require pure water as the feed, produce nearly-pure hydrogen streams with faradaic efficiencies approaching 100%, and can operate continuously for over 5 years. For efficient and cost-effective solar-hydrogen production, these solar water-splitting units should be operated at voltages slightly lower than the $V_{mpp}$ of the PV components, which will avoid significant performance deterioration over the lifetime of the device. Fig. 2a shows that the SHJ module within the integrated solar-electrolysis device operates at a current density ($j_{op}$) of 11.8 mA/cm² and a corresponding potential of 1.67 V. This leads to an initial SHE of 14.5%, which after thermal equilibration of the PV module stabilizes at 14.2%. The Solar-to-Hydrogen Efficiency is calculated according to Eq. 1:

$$SHE = \frac{j E^0 \eta_F}{P_{solar}}$$

where $j$ is the current density of the PV module, $E^0$ is the standard thermodynamic water splitting potential (1.23 V), $\eta_F$ is the faradaic efficiency and $P_{solar}$ is the power illuminating the SHJ modules (1000 W/m²). Also, as the components used within this system are intrinsically stable, we have shown that the system can continuously produce H₂ without performance degradation for over 100 h (Fig. 2b). Furthermore, as the overall hydrogen collection efficiency approaches 100% with minimum crossover across the membrane, these devices could be truly deployed for large scale solar-hydrogen production. Hydrogen and oxygen production rates over time are shown in Figure S6 in the Supplementary Information.

While the device described above represents a viable solution for solar-fuel generation in the short term, reaching scales of solar-hydrogen production that satisfy the global energy needs would not be viable with the use of scarce noble-metals such as Platinum and Iridium. Alkaline water-splitting systems have historically dominated the electrochemical hydrogen production landscape, as they implement stable, inexpensive and earth-abundant Nickel (Ni) electrocatalysts. Since these systems operate at lower current density levels than their Pt/IrOx counterparts, larger active electrocatalysis areas are required for their integration into solar-hydrogen generators. To achieve the current levels required by SHJ modules at potentials lower than $V_{mpp}$, a set of two high-surface area microstructured Ni electrodes was used in an electrolysis cell operated under a 1 M potassium hydroxide electrolyte. Based on the photoelectrochemical characteristics of the integrated PV and electrocatalyst components (Fig. 3a), this device operated at an average SHE of 14.2%. As the Ni electrocatalysts are intrinsically stable under basic electrolytes, this high-efficiency level of solar to hydrogen conversion was sustained for more than 100 h (Fig. 3b). This high efficiency demonstration suggests that Si-based solar-hydrogen generators with earth-abundant electrocatalysts can have the potential to trigger deployment of reliable solar-hydrogen systems at large scale.

Technological Outlook and Conclusions

The SHJ module developed and implemented in this study led to a 44% efficiency increase from the previous highest performing Si-based solar-hydrogen system. By series-connecting three SHJ solar cells with an advanced interconnection method, we fabricated a module that operated at an appropriate voltage to directly power the electrolysis unit without using any further electronics between both components. This approach led to the demonstration of an intrinsically stable, silicon-based solar-driven water splitting system with the unprecedented SHE of 14.2% for a duration of at least 100 h. Furthermore, the solar-fuel conversion efficiencies achieved in this study surpass those of recently demonstrated perovskite based systems. Alternative systems involving physically integrated photo-electrochemical (PEC) cells have attracted the attention of the scientific community, even when their practical implementation faces significant challenges.
PEC components have poor stability under strong electrolytes, constrain the positioning of the electrocatalysts to the surface of light-absorber materials, face parasitic irradiation losses in the catalysts, electrolyte, protection layers, and generated bubbles, and inherently require longer pathlengths for ion migration. On the other side of the spectrum, approaches that implement grid-distributed PV components and electrolysis units will suffer from efficiency losses in power inverters, as well as directly affect the operation of the electrical grid. Stand-alone electrically-coupled PV-electrolysis approaches, such as the one proposed in this work, circumvent these issues and have the potential to significantly disrupt the clean energy storage landscape.

Additional efficiency improvements can be achieved by using interdigitated back contacted SHJ cells\(^{23,33}\) or fine-line electrophoretically metallized;\(^{24}\) improving the infrared light management\(^{35}\) the transparency of the front side of the device\(^{6,16-20}\) and implementing thinner a-Si:H passivation and doped layers on the front side of the device. SHJ cells fabricated in the same configuration as the ones used in this study (i.e. with contacts on both sides of the device) have reached certified current densities up to 39.5 mA/cm\(^2\);\(^{22}\) which could lead to Solar-H\(_2\) generators with SHE approaching 16%.

Furthermore, the highest certified efficiencies and current densities (Eff = 25.6%; \(J_{SC} = 41.8\) mA/cm\(^2\); \(V_{OC} = 740\) mV; FF = 82.7%) for SHJ cells have so far been obtained in a back contacted configuration.\(^{23,33}\) In such cells, both electrical contacts are placed on the back of the device. As there is no metallization on the front side of the cells, shadowing losses are avoided, leading to enhanced current densities. Within this configuration, and considering similar interconnection losses to the ones presented in our study, modules based on these cells could lead to SHEs as high as 16.6%. This proposed pathway of efficiency improvements in SHJ-based solar water-splitting devices could disruptively change the prospect for the implementation of solar-fuel technologies. Furthermore, the growth, scalability, availability and stability of silicon heterojunction photovoltaics in combination with earth-abundant catalysts can lead to large-scale solar-to-hydrogen conversion systems that operate at high efficiencies and produce clean fuels at affordable price levels.

Acknowledgments

The authors acknowledge the support from the Swiss National Science Foundation: Nano-Tera project 20N21_145936 “Solar integrated Nano Electrolyzer: SHINE”. The authors also thank Roland Dupuis (EPFL) for his help with the additive manufacturing process and Jonathan Champliaud (CSEM) for his help with the module fabrication.

References