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Direct Water Electrolysis

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Executive Summary

Current green hydrogen production approaches, connecting renewable power plants to electrolyser facilities, grapple with low conversion efficiencies and high production costs, limiting broad adoption. Direct solar hydrogen photoelectrochemical (PEC) systems, that combine photovoltaic and electrocatalytic elements into a single system, aim to combat this by bypassing energy conversion stages and reducing balance of system requirements.

The aim of this project was to develop solutions to the challenges that hinder the potential of III-V semiconductors for PEC hydrogen generation, namely their high cost and poor stability. Despite enabling record energy conversion efficiencies, III-V-based PEC systems indeed typically involve sophisticated growth techniques, expensive co-catalyst materials and short lifetimes. Overcoming these challenges is crucial to promote the commercial prospects of solar hydrogen systems, which have been identified as a key element to the energy transition.

The project investigated several research directions to reduce the balance of costs of III-V-based PEC systems.

- (1) The optimisation of the electronic structure with the use of multijunction cells and their connection in series led to increased solar-to-hydrogen (STH) efficiencies to counterbalance the fabrication costs.
- (2) The spalling technique, optimised for III-V materials, yielded large-area thin-film lift-off, in an effort to enable substrate recycling.
- (3) The Ni-based earth-abundant co-catalyst foils developed in the project exhibited high catalytic efficiency for both the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER), as well as adaptability to multiple III-V-based photoanodes.
- (4) Two different approaches were implemented to improve the stability of PEC systems: the use of sulphide passivation layer and the physical decoupling of the photoactive and catalytic components.

The project thus focused on the design and development of a robust integrated III-V-based solar-driven water splitting system. The final prototype consisted of three InGaP/InGaAs/Ge triple-junction solar cells combined with four electrolysers based on NiFe(OH)_x and NiMo_x Ni-foil-supported earth-abundant co-catalysts. The prototype demonstrated >20% STH conversion efficiency and stability over 200 h. The project concluded with the techno-economic assessment of the developed techniques, demonstrating a pathway towards a long-term levelised cost of hydrogen (LCOH) of 1.8 USD/kg_{H₂}.

In this report, we cover the progress made during the duration of the project and highlight key technical results for each of the directions presented above. These results demonstrate the completion of the project objectives, despite some delays due to the recent crises (bushfires, hailstorm damage to facilities and COVID-19 lockdowns).

We further provide insights onto the transferability and commercialisation prospects of the systems we have developed so far. This work has led to the production of patents and industry support for the further development of solar-driven water splitting systems.

Project Overview

Project Summary

Owing to their excellent optical and electrical properties, III-V semiconductors are ideal candidates for high-efficiency solar-driven water splitting. However, despite remarkable demonstrations in laboratory, III-V-based PEC systems remain a long way from large-scale fabrication and deployment. The two major bottlenecks to this widespread commercial production are the cost and stability of III-V based systems. III-V structures are indeed typically grown using expensive source materials and demanding, complex, high-maintenance epitaxy techniques such as metal-organic chemical vapour deposition (MOCVD) and molecular beam epitaxy (MBE). Moreover, III-V materials are known to be prone to photocorrosion and III-V-based PEC systems reported in literature have rarely demonstrated operation for more than a couple of hours, making these systems not viable.

This project aimed to address both bottlenecks by targeting increased STH efficiencies, ensuring the reusability of the substrates, investigating earth-abundant co-catalysts and enhancing the resistance of III-V materials to photocorrosion.

The combination of multiple III-V photoabsorbers in multijunction architectures allows an optimal exploitation of the solar spectrum, leading to higher STH efficiencies that could counterbalance the fabrication costs. However, the growth of an ideal structure for water splitting involves significant technical challenges. The project has explored both the metamorphic growth of tandem cells with ideal electronic structure (combination of 1.0 and 1.7 eV bandgaps) but highly mismatched layers and the combination in series of commercial triple-junction cells and custom-made electrolyzers to reach the target STH efficiency.

A further goal of the project involved the development of epitaxial lift-off techniques that would allow the exfoliation of the photoactive region and multiple reuses of the underlying substrate. The spalling technique, in particular, was investigated on GaAs and InP substrates, which are cornerstones of high-efficiency PV and PEC systems. This technique is quite recent and holds promise for cost reduction for III-V systems, not only for solar applications. It is an interesting alternative to the traditional chemical lift-off that often involves toxic and polluting substances for making flexible devices.

Additional cost reduction is expected from the replacement of platinum group metals by earth-abundant co-catalysts. Co-catalysts are essential components of PEC systems as they provide a significant boost of the catalytic activity of the photoabsorber. Additional benefits include the enhancement of the charge carrier separation, as well as a relative passivation of the underlying material by favouring HER and OER over photocorrosion. Co-catalysts are typically made of noble metals, raising system costs. Highly versatile Ni-based catalyst foils were developed in this project as an alternative that provides both high catalytic efficiency and cost-effectiveness.

Last but not least, the development of efficient passivation techniques is an inevitable requirement for practical applications of PEC systems. Both materials and deposition techniques were investigated for this purpose and have proven to provide long-term protection. More systemic approaches like

photoelectrode decoupling and encapsulation were also implemented to enable a simplification of the fabrication process and reduced costs.

As the final goal of this project, the above-mentioned strategies were combined to realise high-efficiency, bias-free water splitting *via* a decoupled, encapsulated, co-catalyst-coated multijunction III-V PEC prototype. Ultimately, this project achieved its target of STH efficiency above 20% and stability over 200 h.

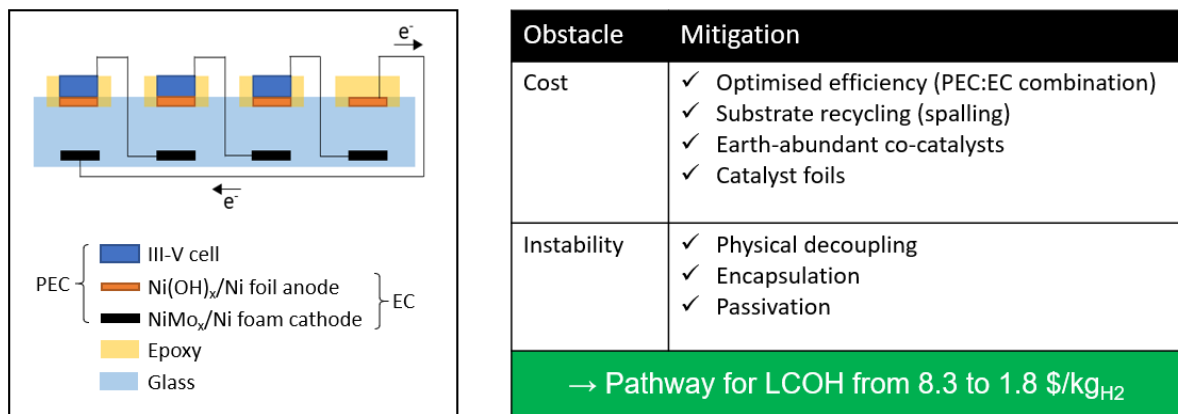


Figure 1. (Left) schematics of the prototype and (right) recapitulative table of the strategies developed in this project to address the cost and instability issues typically associated with III-V-based devices for water splitting.

Project Scope

For the first half of the project, one of the main goals was (1) to design and establish epitaxial growth techniques for double-junction photovoltaic devices with optimal bandgaps for water electrolysis. The major development effort went towards designing a metamorphic buffer that allowed the combination of materials with ideal bandgaps but highly mismatched lattices. Theoretical simulations have shown that a tandem PEC cell combining the 1.7 and 1.0 eV bandgaps was the best candidate to achieve high STH conversion efficiencies, required for commercialisation prospects. We have developed III-V alloys demonstrating these specific bandgaps. We have further designed and fabricated a metamorphic buffer structure to bridge the two lattice parameters.

We have also investigated other techniques to make the proposed PEC system more cost-effective and stable: (2) the spalling of III-V thin films to enable substrate recycling, (3) the integration of earth-abundant co-catalysts with III-V cells and (4) the effective protection of III-V cells by either a passivating film or effective encapsulation in a decoupled-photoelectrode configuration.

In the second half of the project, we have focused on integrating these elementary bricks into a high-efficiency, long-stability, cost-effective III-V water splitting system. Considering the many technical and economic challenges linked with the fabrication of ideal metamorphic tandem cells (1), we have investigated series-connection of more mature triple-junction cells and their combination with the co-catalyst foils developed earlier in the project (3). With the summed excess photovoltages generated by the triple-junction cells, we were able to power additional electrolysis cells, thereby maximising the conversion efficiency of the system and achieving the performance target of the project. By relying on encapsulation and physical decoupling of the photoactive and electrocatalytic regions (4), we were able to achieve the stability target of the project.

Finally, we have conducted a techno-economic analysis of the developed prototype. This analysis included a detailed sensitivity analysis that considered benefits arising from technology advancement developed in this project. These include advancement in:

- (1) design and establish epitaxial growth techniques for double-junction photovoltaic devices with optimal bandgaps for water electrolysis;
- (2) the spalling of III-V thin films to enable substrate recycling;
- (3) the integration of earth-abundant co-catalysts with III-V cells;
- (4) the effective protection of III-V cells by either a passivating film or effective encapsulation in a decoupled-photoelectrode configuration.

Starting with a current LCOH of 8.3 USD/kg_{H₂}, we illustrated a pathway towards 1.8 USD/kg_{H₂}.

Outcomes

Theoretical studies have identified the ideal bandgap combination for water splitting to be 1.7/1.0 eV. We have explored multiple options to achieve this desired structure and studied all candidate materials ($\text{In}_{0.80}\text{Ga}_{0.20}\text{As}_{0.44}\text{P}_{0.56}$, $\text{In}_{0.32}\text{Ga}_{0.68}\text{As}_{0.34}\text{P}_{0.66}$, $\text{In}_{0.27}\text{Ga}_{0.73}\text{As}$, $\text{Al}_{0.44}\text{In}_{0.56}\text{As}$). We have further designed and grown an $\text{In}_{0.32}\text{Ga}_{0.68}\text{As}_{0.34}\text{P}_{0.66}/\text{In}_x\text{Ga}_{1-x}\text{P}/\text{In}_{0.27}\text{Ga}_{0.73}\text{As}$ metamorphic structure, studying various design parameters of the $\text{In}_x\text{Ga}_{1-x}\text{P}$ step-graded buffer such as growth temperature, pause time, misfit grade and overshoot layer composition. We were able to reach a 10^8 cm^{-2} threading dislocation density for a relatively thin Al-free buffer (3 μm) with simple design. We identified thickening the buffer, slowing the growth rate, including additional polishing steps, adding surface preparation and/or post-processing measures as directions to further reduce the threading dislocation density. We were then faced with the compromise of improving material quality, hence STH efficiency, *versus* limiting the fabrication costs (dependent on reactor usage time, materials consumption, pre- and post-processing, all significantly increased by the proposed research directions).

We thus explored an alternative route to make the best use of III-V multijunction cells' outstanding efficiency. Indeed, although double-junction cells are theoretically ideal for solar water splitting, their light-harvesting efficiency is far from optimal. Triple-junction cells, on the other hand, are a mature technology and remain the most efficient photovoltaic devices to date. We have engineered a system that collects the excess photovoltage provided by commercial triple-junction cells and use it to power additional electrolyzers. By adjusting the ratio of series-connected triple-junction cells (photoanodes) to electrolyzers, the combined photovoltage from the photoanodes can be tailored to match the combined potential required by the electrolyzers. We have compared photoanodes:electrolyzers combinations of 1:1, 2:3 and 3:4 and shown that the 3:4 combination allowed to operate the closest to the maximum power point of the triple-junction cells, maximising STH efficiency above 20%. [1]

We have further explored exfoliation techniques to enable substrate recycling and fabrication cost reduction. Among the various techniques available to produce high-quality III-V thin films, we have identified spalling as one of the most promising. This technique makes use of mechanical stress to detach a crystalline layer from a substrate. We have investigated the spalling of large-area InP films and demonstrated the potential of this technique for reduced-cost III-V systems. The obtained InP thin (< 20 μm) films proved of high quality, even after multiple spallings from the same substrate. We have further demonstrated that the fractured surface could be tailored to introduce texture, which is beneficial for anti-reflection properties, as shown in Figure 2. We have also studied the influence of induced strain on the electronic properties of the spalled film. Although the thickness of the spalled films should be slightly reduced for application to metamorphic multijunction solar cells, these results show excellent promise for this cost-effective substrate recycling technique. Moreover, they constitute highly promising results for any other type of flexible electronics application. [2]

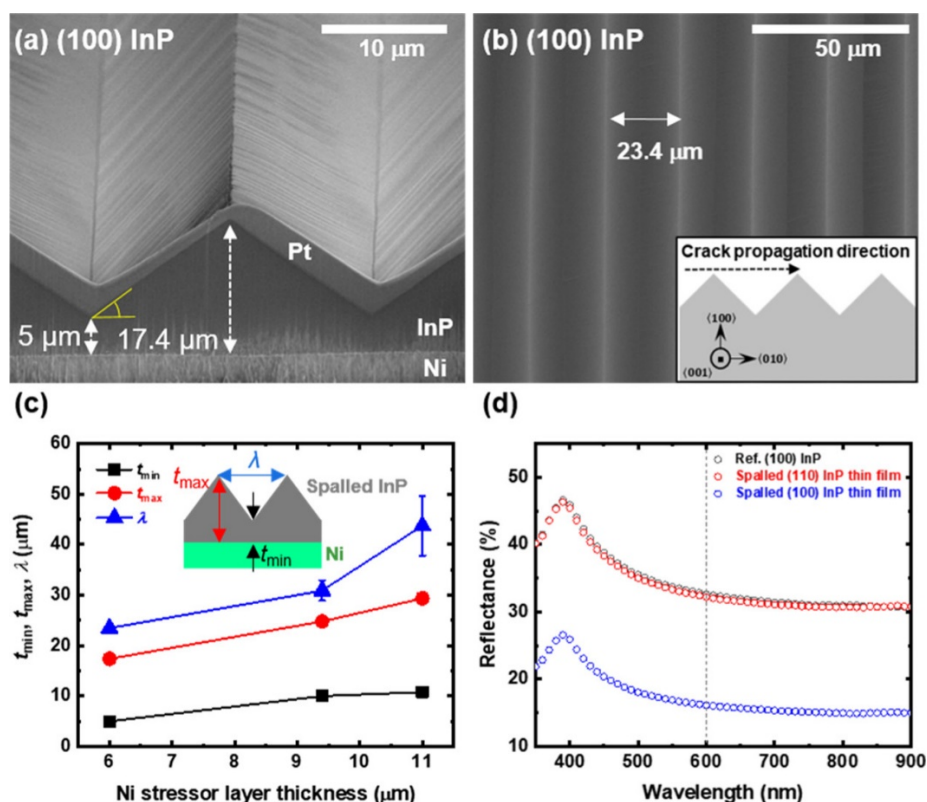


Figure 2. Spalled InP film with a textured surface. (a) Tilted cross-sectional and (b) top view SEM images of the spalled (100) InP film. The thin Platinum (Pt) layer in (a) was deposited to protect the surface during the focused ion beam milling process. The inset in (b) shows the crack propagation direction and crystal orientation of the spalled (100) InP thin film. (c) The period of grating (λ), maximum (t_{\max}), and minimum (t_{\min}) thickness of the spalled film as a function of Ni stressor layer thickness. (d) Optical reflectance of a mirror-like (100) InP substrate, spalled (110) film with planar surface, and spalled (100) film with a grating structure, which was fabricated with 6 μm -thick Ni stressor layer. The optical reflectances of ref. InP (black dots) and the spalled (110) film (red dot) are nearly identical. [2]

In terms of co-catalysts, we have developed NiFe(OH)_x and NiMo_x alloys to drive OER and HER, respectively, at high catalytic efficiencies. We have integrated these earth-abundant co-catalysts onto Ni foil with commercial III-V solar cells and demonstrated an enhanced water-splitting performance for a GaAs photoanode. The photoelectrode demonstrated record performance, not only for GaAs photoanodes but for any single-junction photoanode. More importantly, we have fabricated an unassisted water splitting PEC system made of two commercial GaAs solar cells in series with the Ni foil-supported earth abundant co-catalysts. This system achieved the highest STH efficiency reported for a single-junction PEC device with earth-abundant electrocatalysts and the second-highest for any single-junction PEC device. The long-term stability of the artificial leaf was also maintained for over 9 days, which is the second-longest duration reported in the literature for a PEC water splitting device. [3]

Concerning the improvement of III-V cells stability, we have investigated two approaches. For the first one, we have developed an efficient sulfide layer for passivation of InP and demonstrated its efficiency in protecting InP nanostructures. The passivated photocathodes proved to be highly stable for over 24 h of testing, compared to a few minutes only in the absence of passivation. Moreover, the photocathode performance was improved both in terms of light absorption (the applied bias photon-

to-current efficiency improved by 89%) and catalytic efficiency (approaching 100% Faradaic efficiency). [4] The other approach we have studied consisted in the decoupling of the photoactive and catalytic components of a PEC system. We have thus integrated commercial III-V solar cells with catalysts. This decoupled configuration allowed us to encapsulate the solar cells, providing them extended protection, while maximising the catalytic efficiency and offering more flexibility in the choice of catalysts. [1]

Building on all the techniques presented above, we have fabricated a prototype combining PEC and electrolysis cells to reach the target 20% STH efficiency, shown in Figure 3. The cells are based on III-V triple-junction InGaP/InGaAs/Ge cells provided by our partner Microlink Devices and the earth-abundant NiFe(OH)_x/Ni and NiMo_x/Ni electrocatalyst foils conceived earlier. To mitigate light absorption, stability and thermal integration, the photoanodes were encapsulated in glass and immersed only on the back side (the one covered with electrocatalyst foils). The developed prototype, combining 3 photoanodes and 4 electrolyzers, achieved a record 20.7% efficiency under 1-sun illumination and demonstrated stability for 40 hours. The proposed design is flexible and can be optimised for any capacity (by adjusting the photoanode-electrolyser ratio), allowing for further improvement in STH efficiency. We have further identified and modelled improvements in encapsulation, shading and catalysts, which would lead to STH efficiencies around 28% under 1-sun illumination. [1]

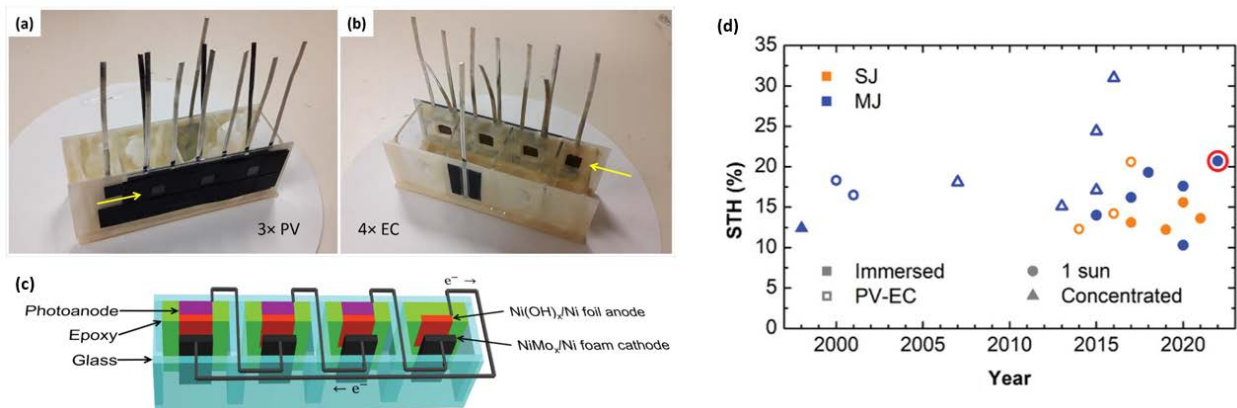


Figure 3. a) Front and b) back images and c) schematic of the triple-junction solar water splitting device. d) Comparison of this work (circled) with previously reported solar water splitting systems.

Finally, we have conducted a techno-economic assessment of the technology, summarised in Figure 4. We have estimated a LCOH of 8.3 USD/kg_{H2} with current component prices and production levels. Additionally, we forecast potential reduction toward 1.8 USD/kg_{H2}. Such long-term target will be made achievable by further progress in STH efficiencies, lift-off techniques, passivation techniques and cost-effective catalyst films, such as the ones investigated in this project. This project thus illustrates a strategy to make direct water electrolysis competitive with production streams such as low-carbon-intensity-powered proton-exchange-membrane electrolysis (IEA 2060 global average LCOH estimation: 1.3-3.3 USD/kg_{H2}) or steam methane reforming with carbon capture and storage (IEA 2060 global average LCOH estimation: 1.2-2.1 USD/kg_{H2}). [1]

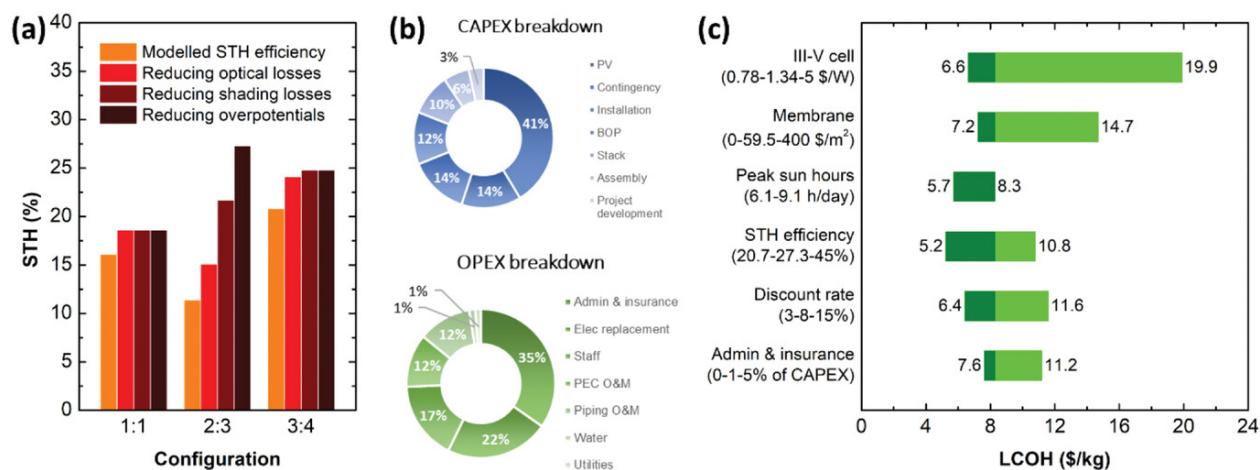


Figure 4. a) Modelled STH efficiency of each photoanodes:electrolyzers configuration with sequential improvements. b) capital expenditure (CAPEX) and operational expenditure (OPEX) cost repartitions for the proposed system. c) Sensitivity analysis of the proposed system.

Transferability

The innovative material/device designs and techniques with the highest commercial potential have been identified and patented. The IP developed during the project has led to a new research partnership with a key industry player seeking to further improving the technology readiness level by developing the technology from lab-scale to pilot-scale demonstration. The innovations made and challenges addressed in this project are also broadly applicable to electrolysers. For example, the earth-abundant catalyst foils can find use in alkaline electrolysers. Similarly, the developed passivation layers can be transferred to other photoelectrodes. Beyond electrolysis, the spalling technique is of interest for any field involving III-V thin films (flexible electronics). Subsequent commercial agreements will dictate their wider use.

Knowledge sharing within the project occurred through regular meetings, seminars, as well as internally produced documents that detail specific processes. The chief investigators and other researchers involved in the project regularly attended conferences, visited research institutions, and gave talks at a variety of forums for both specialist and non-specialist audiences.

Finally, in addition to the experimental articles that resulted from the work presented above, we have conveyed the knowledge gathered during this project in two review articles illustrating promising directions for PEC systems. The first one, focused on III-V materials, has been published in ACS Energy Letters (Tournet, J., Lee, Y., Karuturi, S.K., Tan, H.H. and Jagadish, C., 2020. III–V Semiconductor Materials for Solar Hydrogen Production: Status and Prospects. ACS Energy Letters, 5(2), pp.611-622). The second one, focused on the spalling technique, has been published in ACS Applied Electronic Materials (Lee, Y., Tan, H.H., Jagadish, C. and Karuturi, S.K., 2021. Controlled Cracking for Large-Area Thin Film Exfoliation: Working Principles, Status, and Prospects).

Conclusion and Next Steps

The project has been successful in advancing cost-effective III-V PEC systems by tackling various challenges met by III-V semiconductors in this context. Building on work in PEC design, fabrication, catalyst loading and passivation, the project culminated in the demonstration of a robust integrated III-V-based solar-driven water splitting system with STH efficiency over 20% under 1-sun illumination. To better inform future work on this technology, we have conducted a techno-economic assessment of the developed solar water splitting system providing a detailed analysis of the LCOH produced *via* direct water electrolysis in comparison to that from the conventional streams. There are only a few commercial direct water electrolysis production systems in development at this stage. While this project demonstrated remarkable STH performance at lab-scale and considerable potential for cost reduction, there remains several technological challenges towards commercial adoption, including scaling-up the technology, balance of plant design and pilot-scale demonstration. Ultimately, the outcomes of the project will benefit the development of commercial technologies for direct water electrolysis, providing widespread potential for renewable hydrogen exports from Australia.

Addendum

News Articles:

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